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# ***2008 DOE Hydrogen Program Review***

## **Hydrogen Storage Research**

Presenters: Lee Stefanakos/Sesha Srinivasan  
University of South Florida

June 9, 2008  
Arlington, Virginia

*Project ID#*  
**STP 31**

# Participants and Projects

## Participants

- **PI/Co-PI:** Lee Stefanakos, Yogi Goswami
- S. Srinivasan (CERC), V. Bhethanabotla (ChE), A. Kumar (ME)
- **Ph.D. Graduate students:** M. Jurczyk, P. Choudhury

## Projects

### **Hydrogen Storage (STP 31)**

- Advanced material-based technologies for on-board vehicular storage
- Density Functional Theory calculations for complex borohydrides
- **Hydrogen Production and Fuel Cell Research (Please see Project # PDP 13)**

# Overview

## Timeline

Start: May 2004

End: August 2009

Percent Completed: 80%

## Technical Targets

- Volumetric H<sub>2</sub> density, > 45g H<sub>2</sub>/L
- Gravimetric H<sub>2</sub> density, > 6.0 wt.%
- Operating temperature, -30/50 °C
- Delivery T of H<sub>2</sub>, -40/80 °C
- Cycle life, 1000 cycles
- Fast absorption/desorption rates

## 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 H<sub>2</sub> physisorption and chemisorption
  - Reproducibility of performance

# Overall Objectives

# Milestones

- Synthesis and characterization of materials with high H<sub>2</sub> storage potential.
- New materials and processes discovery
- Catalytic doping, destabilization and substitution strategies to improve the kinetics and reversibility of hydrides at low temperature.
- Employ ab initio calculations to validate the experimental observations.

Year	Materials
<b>June'05- May'07</b>  <b>Completed</b>	<ul style="list-style-type: none"> <li>• Zn(BH<sub>4</sub>)<sub>2</sub>; Nanocatalyst Doped</li> <li>• LiBH<sub>4</sub> + ½ MgH<sub>2</sub> + Xmol% catalyst</li> <li>• LiNH<sub>2</sub>/LiH; Ti doped and Mg ad-mixed</li> <li>• New quaternary complex hydrides Li-B-N-H</li> <li>• Nano TM loaded MgH<sub>2</sub></li> <li>• Catalytic doping and substitution</li> </ul>
<b>October'06- June'08</b>  <b>On-going</b>	<ul style="list-style-type: none"> <li>• Li-Mg-B-N-H (Multinary Complex Hydrides)</li> <li>• USF processed Li-Mg-B-N-H</li> <li>• Mn(BH<sub>4</sub>)<sub>2</sub>, LiMn(BH<sub>4</sub>)<sub>3</sub>, LiSc(BH<sub>4</sub>)<sub>2</sub></li> <li>• Ca(BH<sub>4</sub>)<sub>2</sub> and catalytic effects</li> <li>• PANI Nanostructures (specially processed)</li> </ul>
<b>Jan'06 – June'08</b>  <b>On-going</b>	<ul style="list-style-type: none"> <li>• Electronic structure (DFT) calculations</li> <li>• Crystal structure identification</li> <li>• Stability analysis of modified complex borohydrides</li> </ul>



# Critical Assumptions (No Go)

Critical Assumptions	Zn(BH <sub>4</sub> ) <sub>2</sub>	LiBH <sub>4</sub> /MgH <sub>2</sub>	Li-Mg-N-H
<b>Reversibility</b>	No	Reversible at high temperatures (> 300 °C)	Reversible at high T (280 °C)
<b>Volumetric Capacity</b>	>100 kg m <sup>-3</sup>	>100 kg m <sup>-3</sup>	>100 kg m <sup>-3</sup>
<b>Gravimetric Capacity</b>	8.4 wt. %	> 6.0 wt. %	>7.0 wt. %
<b>Gas Analysis</b>	B-H gases with H <sub>2</sub>	H <sub>2</sub>	N-H with H <sub>2</sub>
<b>Kinetics</b>	Slow	moderate	Slow

## Possible Solutions & Approach carried out by CERC, USF

- Nanocatalysts doping for advancing the melting and decomposition temperatures of borohydrides
- Nano-engineering of catalyzed LiBH<sub>4</sub>/ MgH<sub>2</sub> to improve the reversibility at low temperatures
- Nanocatalysts co-doping and MgH<sub>2</sub> ad-mixing to enhance the reversibility of Li-B-N-H
- Theoretical simulation using DFT gives the predictive capability of stability of a structure for H<sub>2</sub> storage
- New materials and processes discovery and optimization of reaction pathways

# Critical Assumptions (Go)

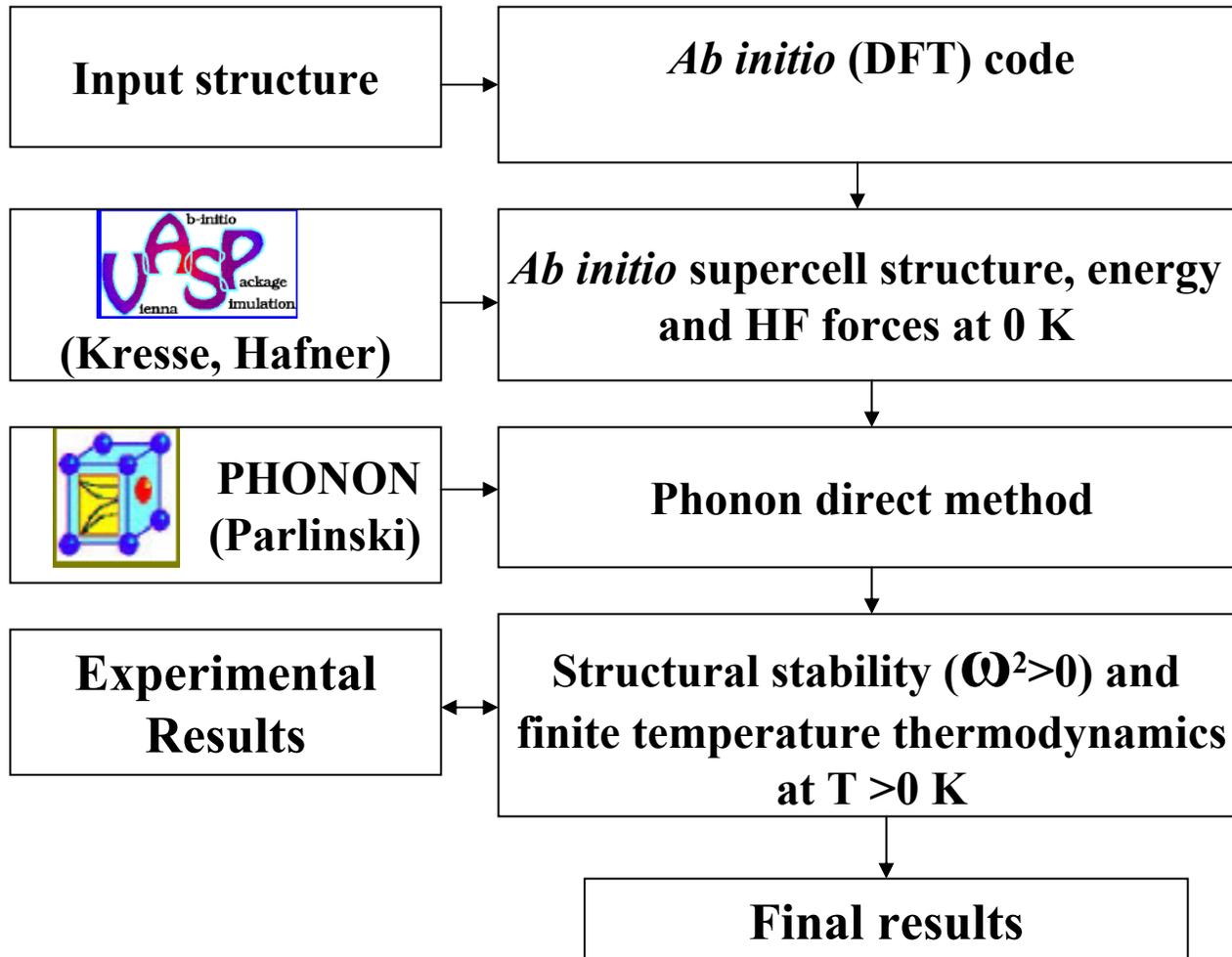
Critical Assumptions	Li-Mg-B-N-H	$X(\text{BH}_4)_2$ (X=Mn, Zr, Ca)	PANI Nanostructures
<b>Reversibility</b>	Good at lower T, specially processed materials	Reversible at moderate and high temperatures	Good at Room Temperature, specially processed materials
<b>Volumetric Capacity</b>	$>100 \text{ kg m}^{-3}$	$>100 \text{ kg m}^{-3}$	$>100 \text{ kg m}^{-3}$
<b>Gravimetric Capacity</b>	$>7.0 \text{ wt.}\%$	$> 8.0 \text{ wt.}\%$	$\sim 3\text{-}10 \text{ wt.}\%$ uptake
<b>Gas Analysis</b>	$\text{H}_2$	B-H with $\text{H}_2$	$\text{H}_2$
<b>Kinetics</b>	Fast	medium	Fast

**Density Functional Theory Calculations to predict, validate and optimize the hydrogen storage properties of complex hydrides and nanostructures**

# Approach (Experiment)

- Selection and synthesis of complex hydrides
  - Mechano-chemical milling methodology (optimization of milling parameters and precursor concentrations)
  - Catalytic doping and lattice modification
  - Employ ab initio calculations to understand/validate experimental work
- Structural/microstructural/chemical characterization
  - Phase analysis, grain size analysis, surface morphology
- Volumetric, gravimetric and thermal analysis
  - Dehydrogenation kinetics, PCT, life cycle kinetics, heat of reaction
- Gas quantification analysis
  - Gas chromatography of evolving gas using thermal conductivity or mass spec detection, thermal programmed desorption

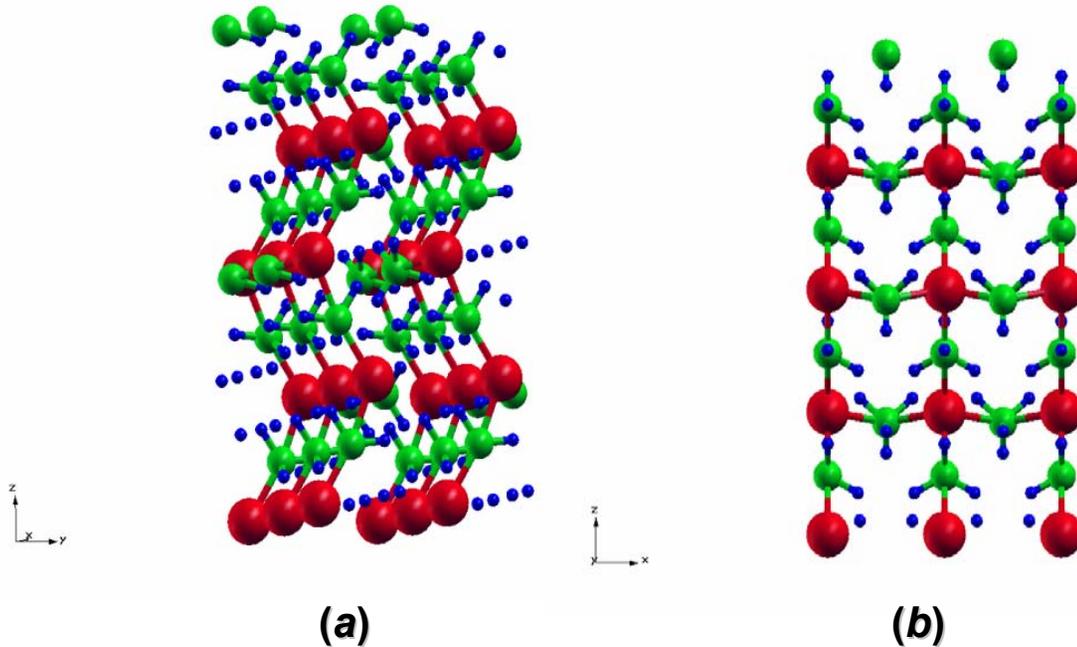
# Approach (Theory)



# Accomplishments

- Successfully synthesized, purified, nanocatalyst doped and characterized  $\text{Zn}(\text{BH}_4)_2$  by a mechano-chemical process with different precursors ( $\text{NaBH}_4/\text{LiBH}_4$ ) +  $\frac{1}{2} \text{ZnCl}_2$  *(Reported in Merit Review Meeting'07 & Articles Published in JALCOM and IJHE 2008)*
- Investigated the electronic structure of  $\text{Zn}(\text{BH}_4)_2$  including estimation of lattice parameters. Studied effect of substitution of Ni in the  $\text{Zn}(\text{BH}_4)_2$  matrix *(New Results & Articles published in PRB and APL 2008)*
- Synthesized complex borohydrides  $\text{Mn}(\text{BH}_4)_2$  from different precursors ( $\text{NaBH}_4/\text{LiBH}_4$ ). Established Thermal Desorption and gravimetric weight loss due to hydrogen decomposition *(New Results)*
- Synthesized quaternary structure of Li-B-N-H by  $\text{LiNH}_2/\text{LiBH}_4$  (2:1) mechano-chemically milling for 5h; and found that incorporation of *nanocatalyst* reduces the desorption temperature; nano Ni seems better catalyst option *(Reported in Merit Review Meeting'07)*
- Prepared Li-Mg-B-N-H complex multinary hydrides by specially designed process; this allows for the greater reversibility of hydrogen sorption at moderate temperatures (150-250 °C) and rapid kinetics (5-10 minutes) *(New and Exiting Results)*
- Synthesized Polymer samples (special chemical and electrospun processes) and accomplished hydrogen uptake of 10 wt.% in initial cycle and reversibility of 3.0 wt.% at room temperature *(New Results and Manuscript under preparation)*

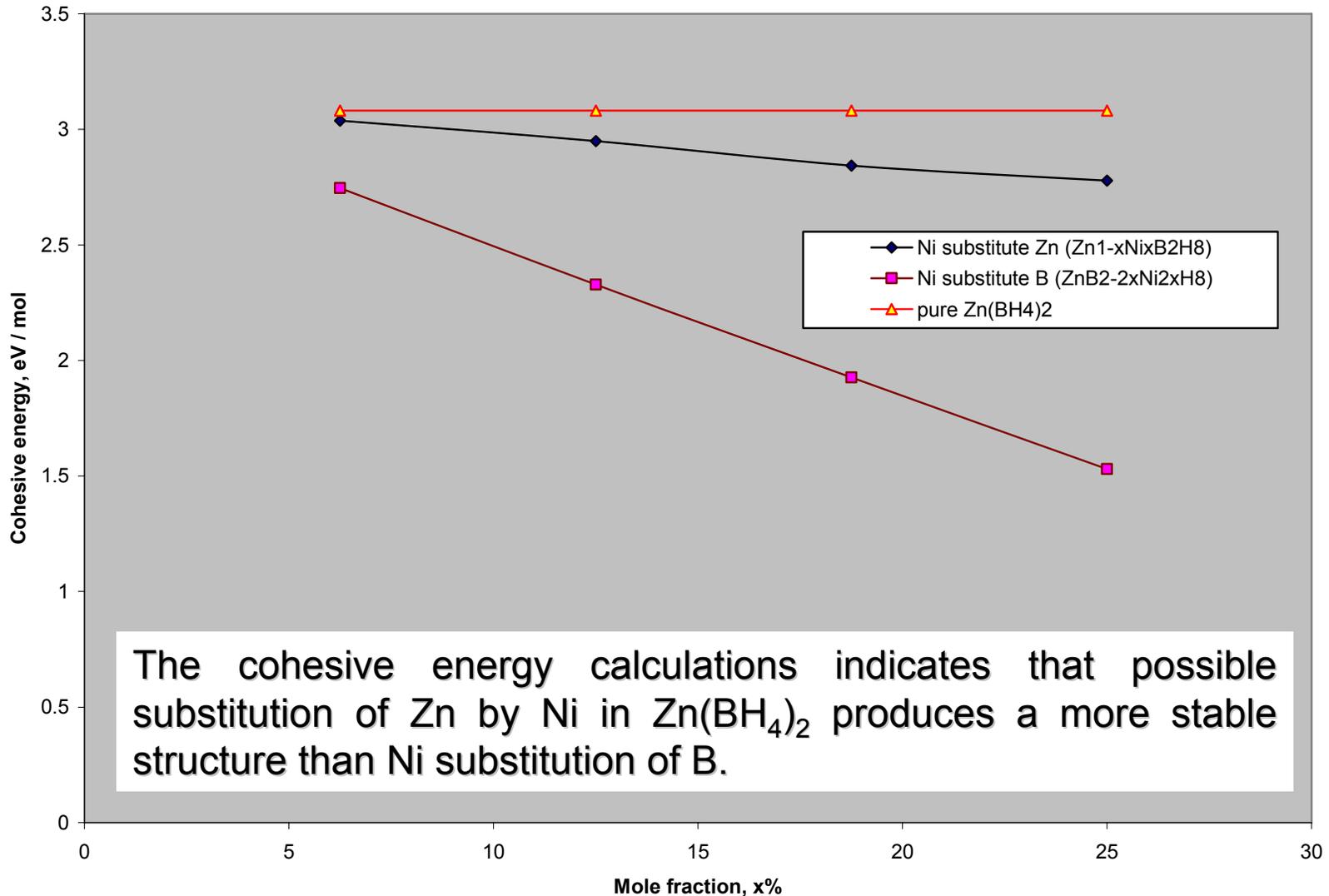
# Crystal Structure of $Zn(BH_4)_2$



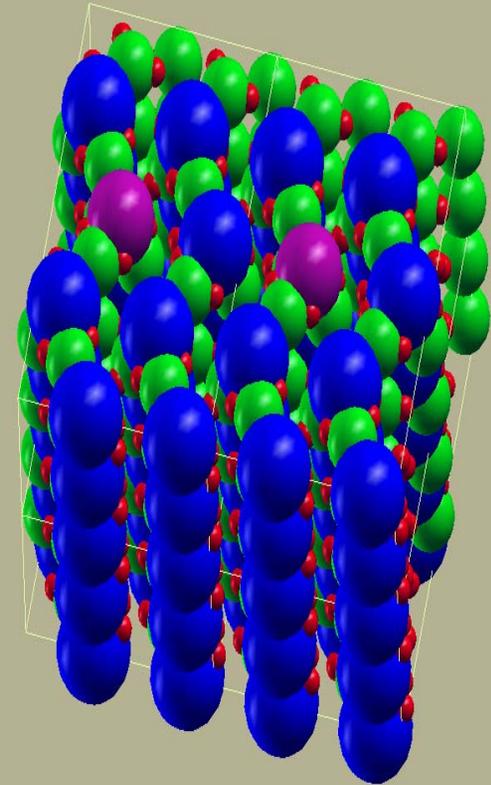
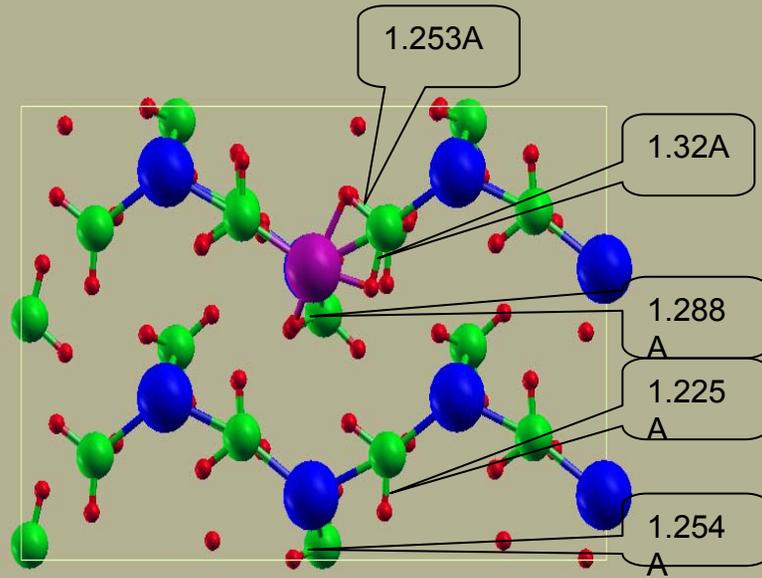
Orthorhombic structure of space group  $Pmc2_1$  (#26) of  $Zn(BH_4)_2$  (a) Proposed three-dimensional crystal structure and (b) Projected structure along [010] plane. (Red: Zn, Blue: H and Green: B atom).

Our calculations showed nearly tetrahedral shape of the  $BH_4$  complex with B-H bond lengths  $d_{B-H} = 1.20-1.25 \text{ \AA}$  and H-B-H bond angles  $\theta_{H-B-H} = 104.16-120^\circ$ .

# Ni doping to $Zn(BH_4)_2$

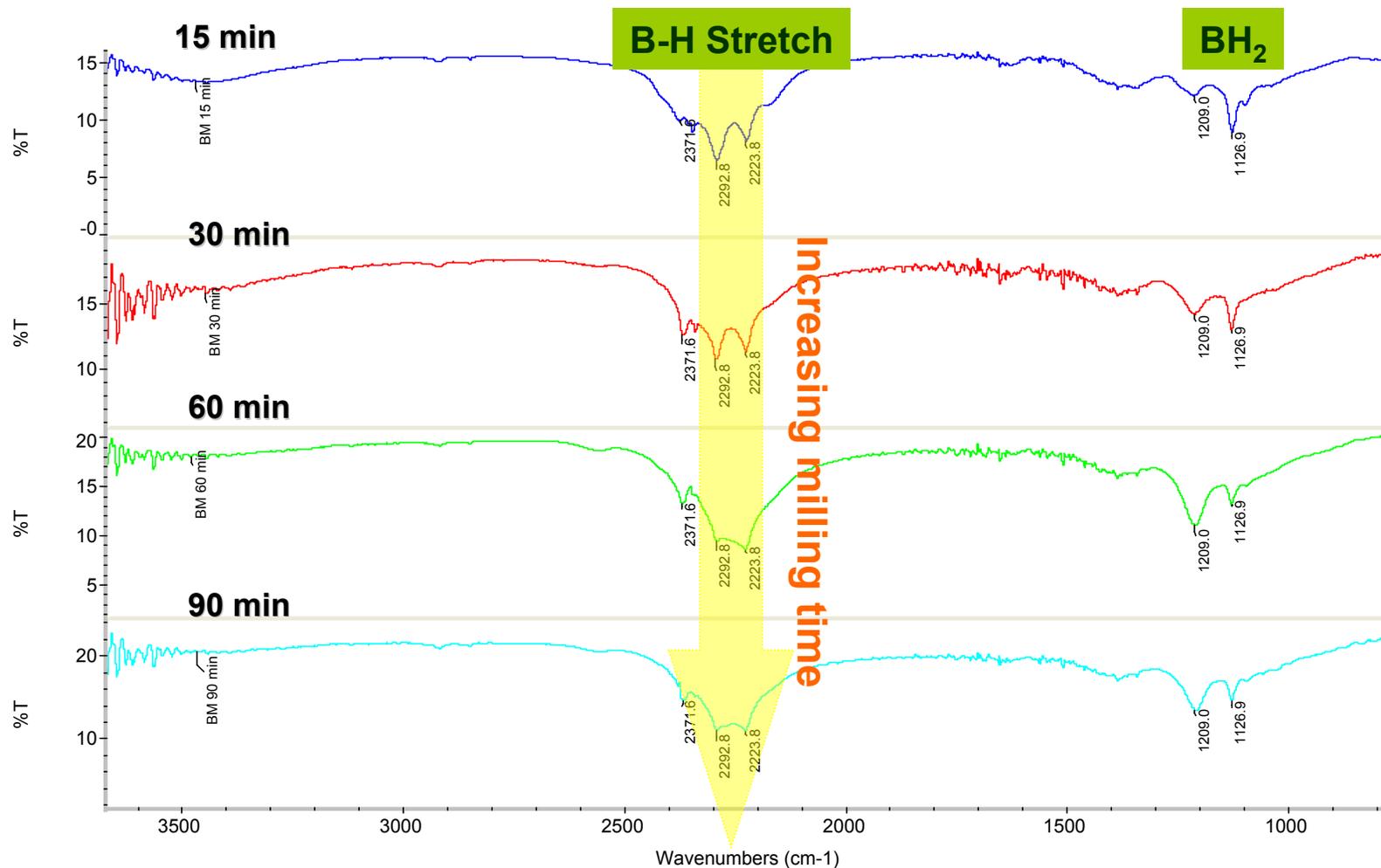
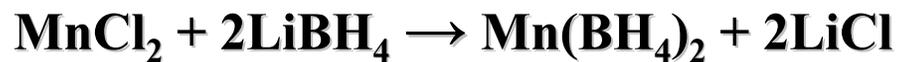


# Ni doping to $Zn(BH_4)_2$



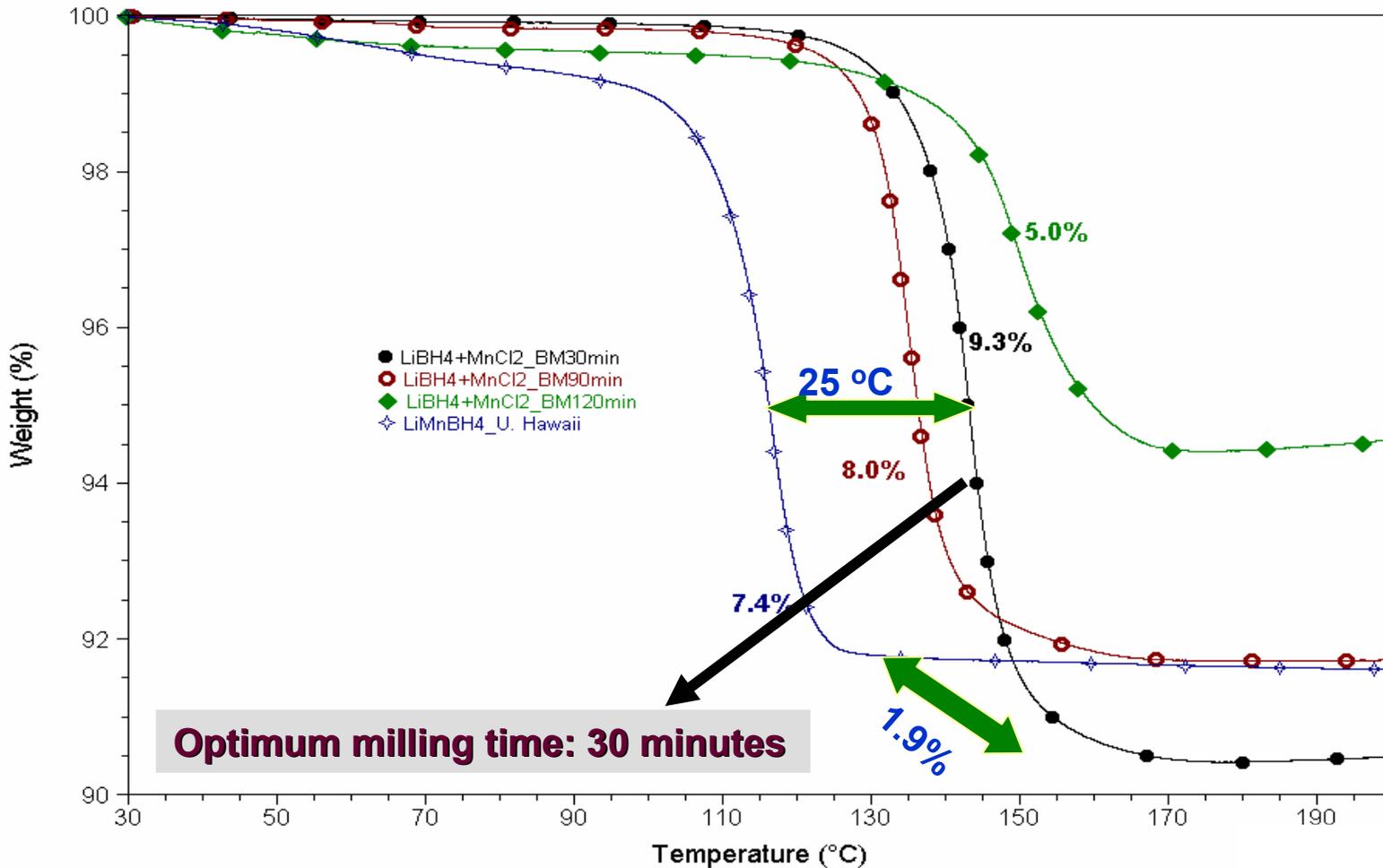
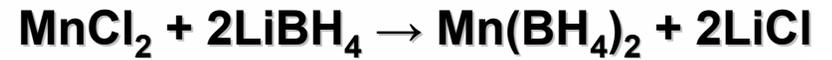
Ni-H bond distance: 1.80 Å, 1.62 Å and 1.69 Å vs. pure Zn-H bond distance: 1.86 Å, 2.0 Å and 1.84 Å.

# Mn(BH<sub>4</sub>)<sub>2</sub> - FTIR



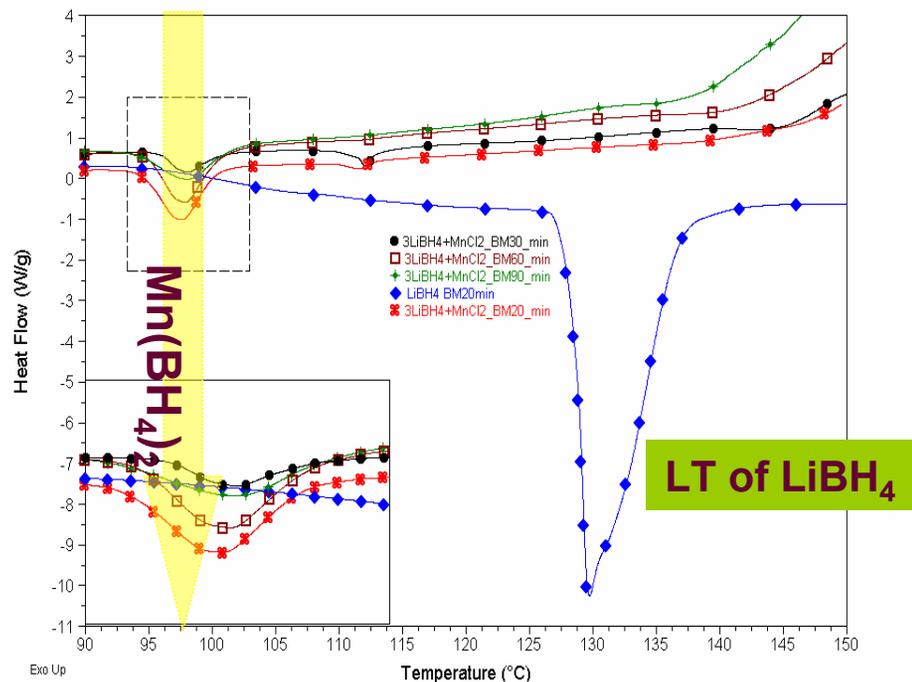
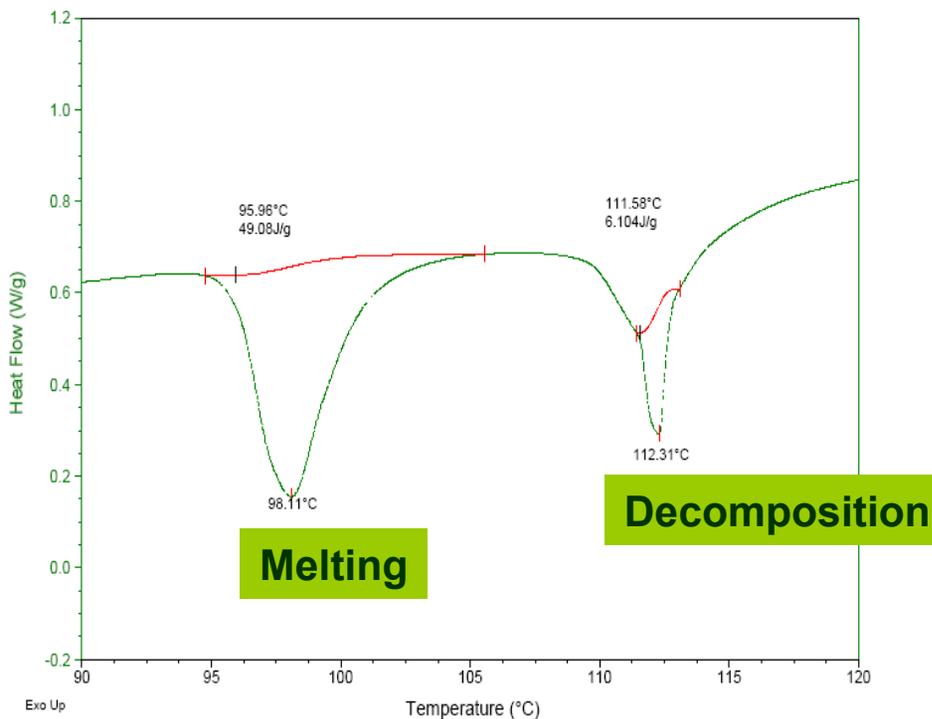
Increasing ball milling time creates well defined B-H stretches at around 2300 cm<sup>-1</sup>

# $Mn(BH_4)_2$ - SDT



For Li based  $Mn(BH_4)_2$ , milling time of 30 minutes will release 9.3% hydrogen at around 150 °C

# Mn(BH<sub>4</sub>)<sub>3</sub> - DSC

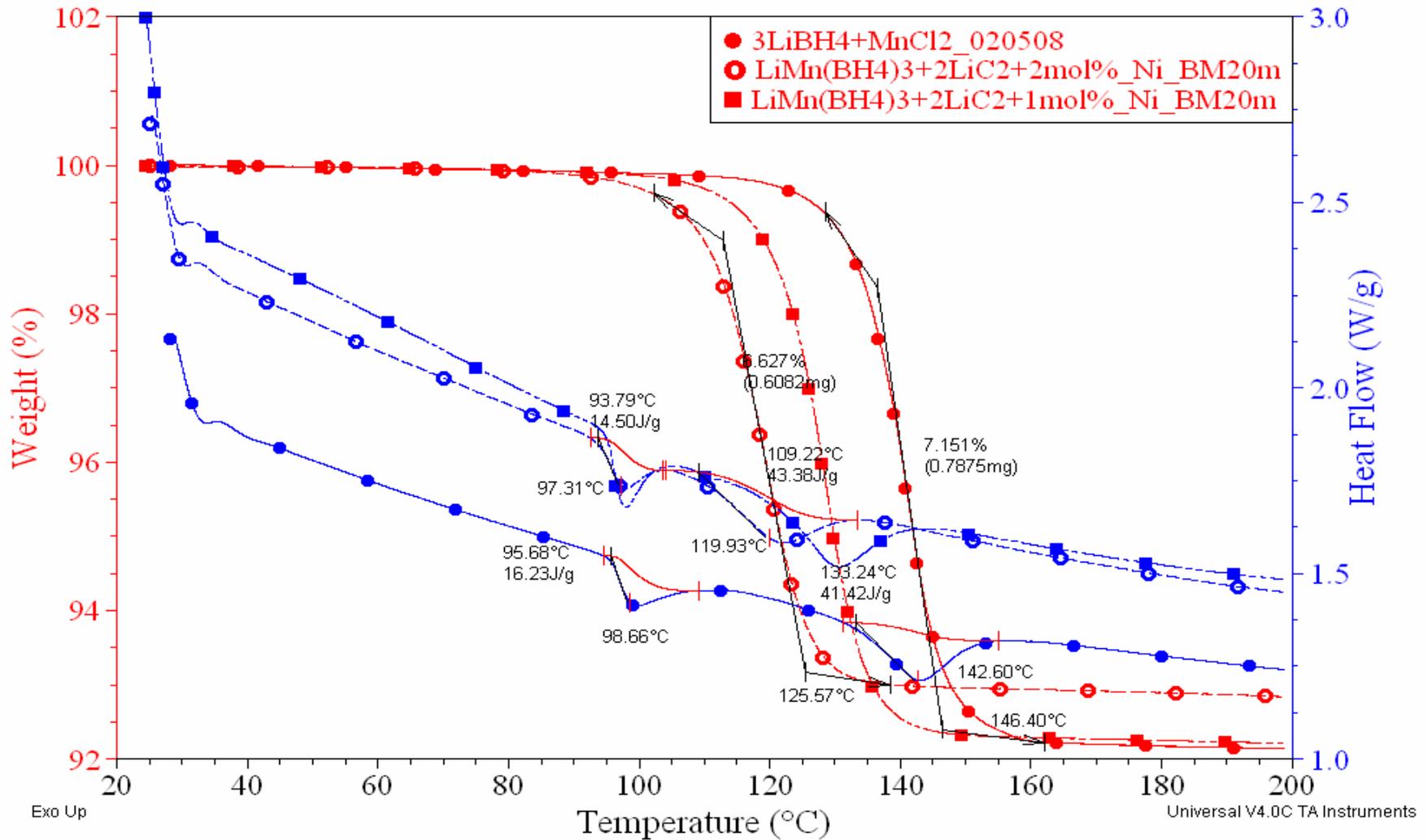


An endothermic melting and decomposition transition occurs at temperatures lower than 150 °C

When compared to LiBH<sub>4</sub>, Mn(BH<sub>4</sub>)<sub>3</sub> exhibit low temperature hydrogen decomposition with >8 wt%

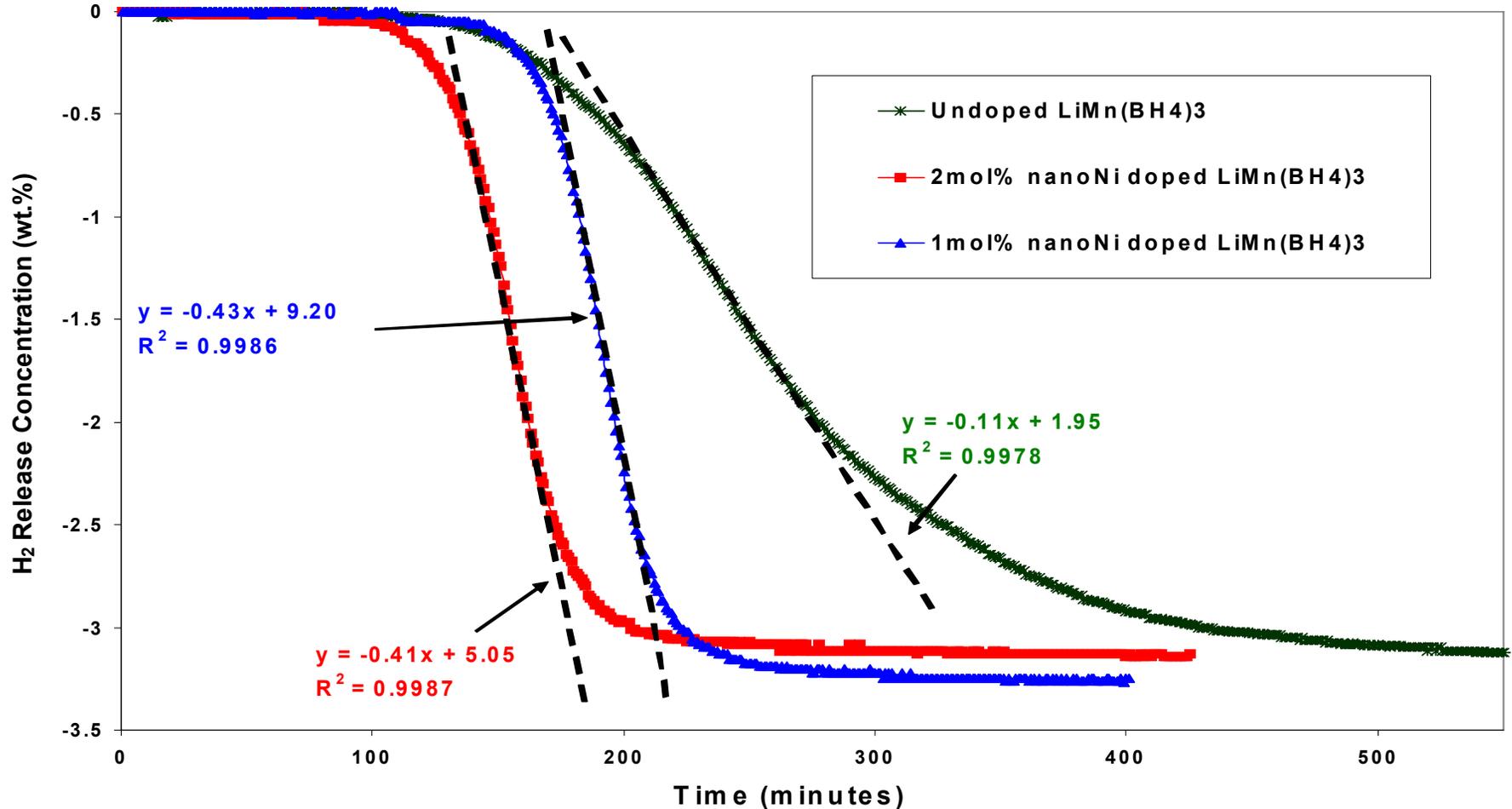


# Ni doped $Mn(BH_4)_3$ - SDT



Ni doping of 1-2 mol% destabilizes the structure with at least 10-20 °C reduction in hydrogen T<sub>dec</sub>

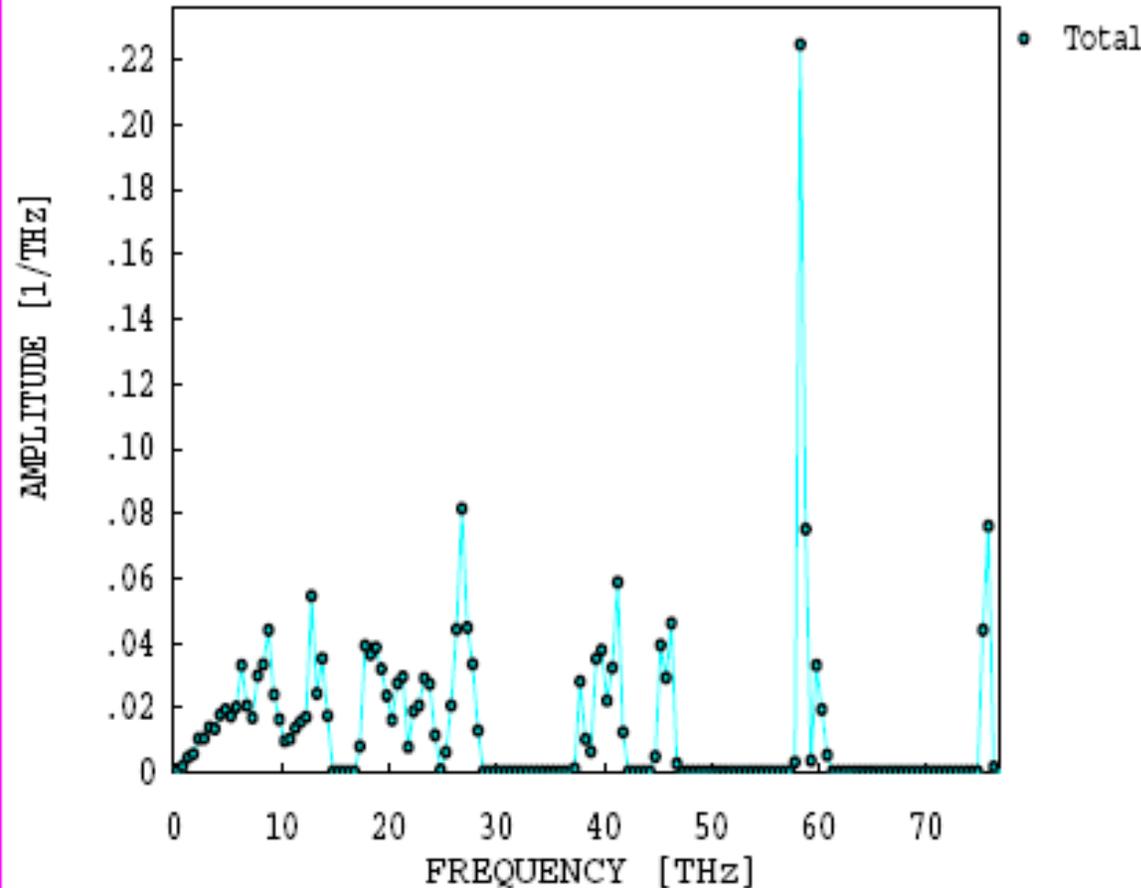
# Ni doped $Mn(BH_4)_3$ – Desorption Kinetics



2mol% Ni doping on the  $LiMn(BH_4)_3$  shows rapid release of hydrogen in comparison to the undoped materials

# Crystal Structure of $Mn(BH_4)_2$

Project: sg164

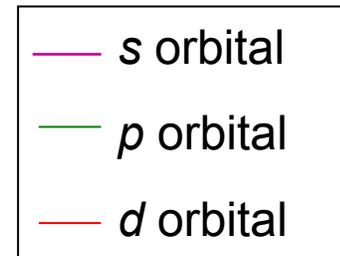
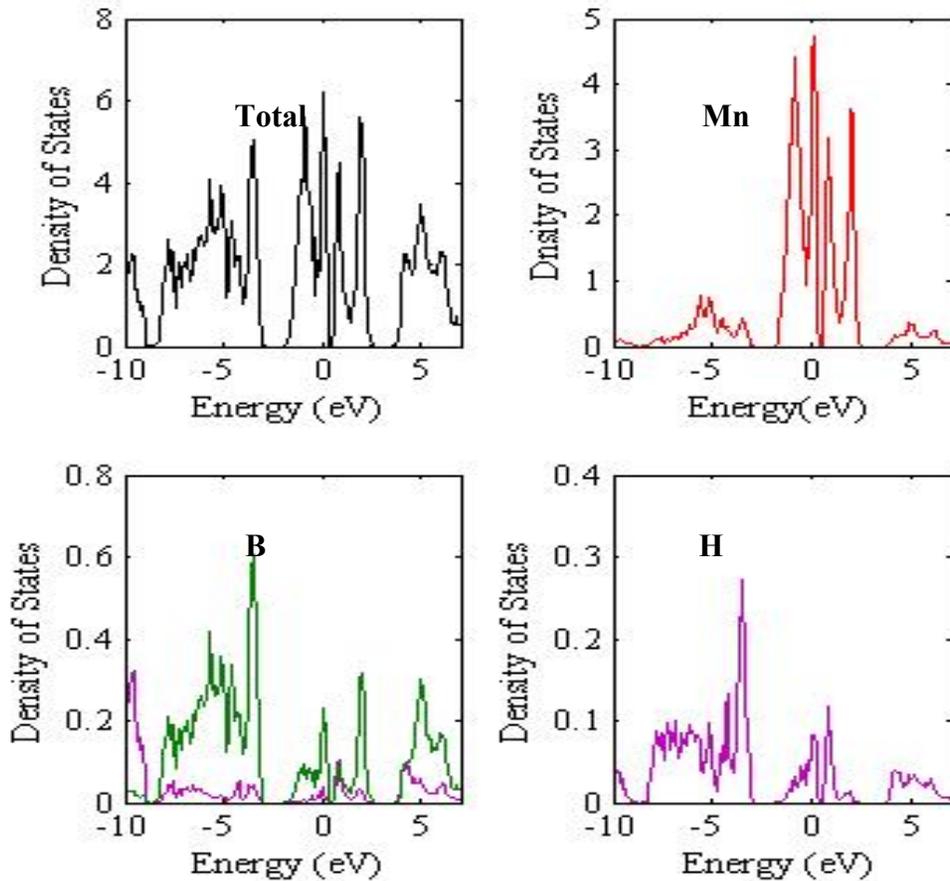


Phonon density of states confirms the stability of  $Mn(BH_4)_2$  exists at finite temperature.

Total density of phonon states  $g(\omega)$  of  $Mn(BH_4)_2$  in  $P-3m1$  symmetry. Total phonon density of states is normalized as

$$\int g(\omega) d\omega = 1$$

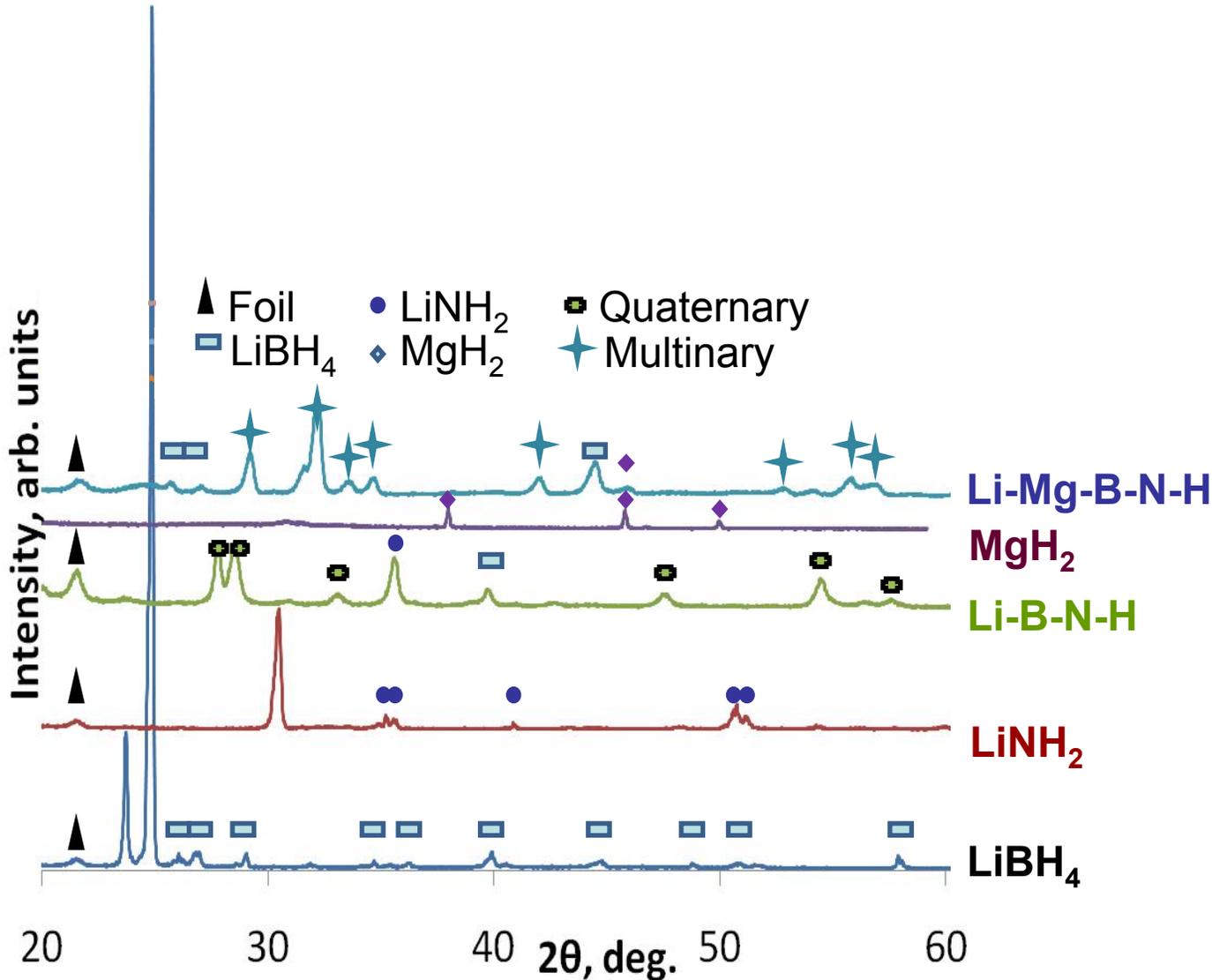
# Electronic Structure of $Mn(BH_4)_2$



It was found that  $Mn(BH_4)_2$  possesses a metallic character as this does not have any band gap.

Total and partial DOS of  $Mn(BH_4)_2$ : zero energy is considered as Fermi energy level.

# Li-Mg-B-N-H - XRD

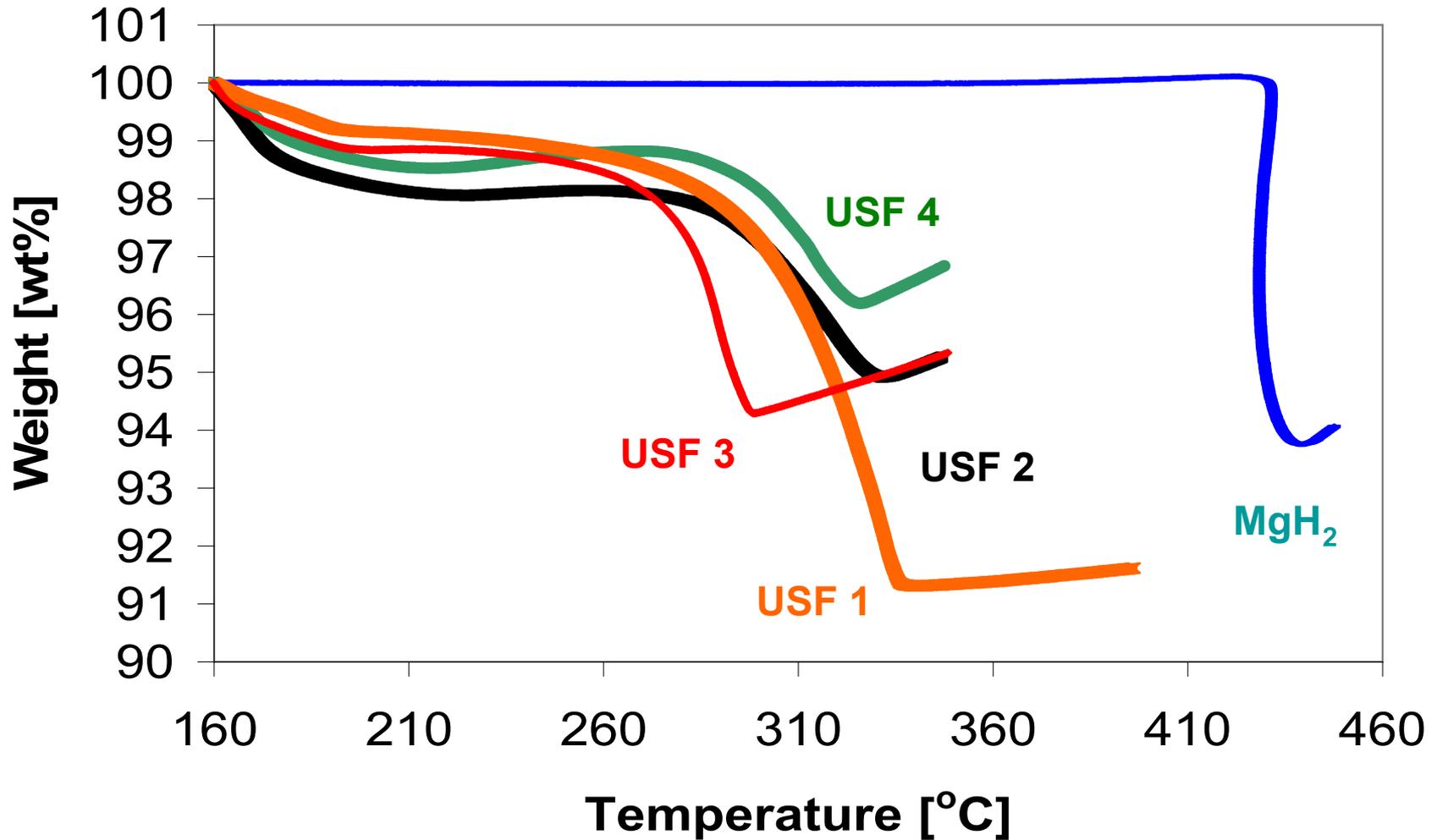


➤ Parent compounds eliminated in all processed materials

➤ Quaternary phase formed with Li-B-N-H

➤ New multinary phase formed with Li-Mg-B-N-H

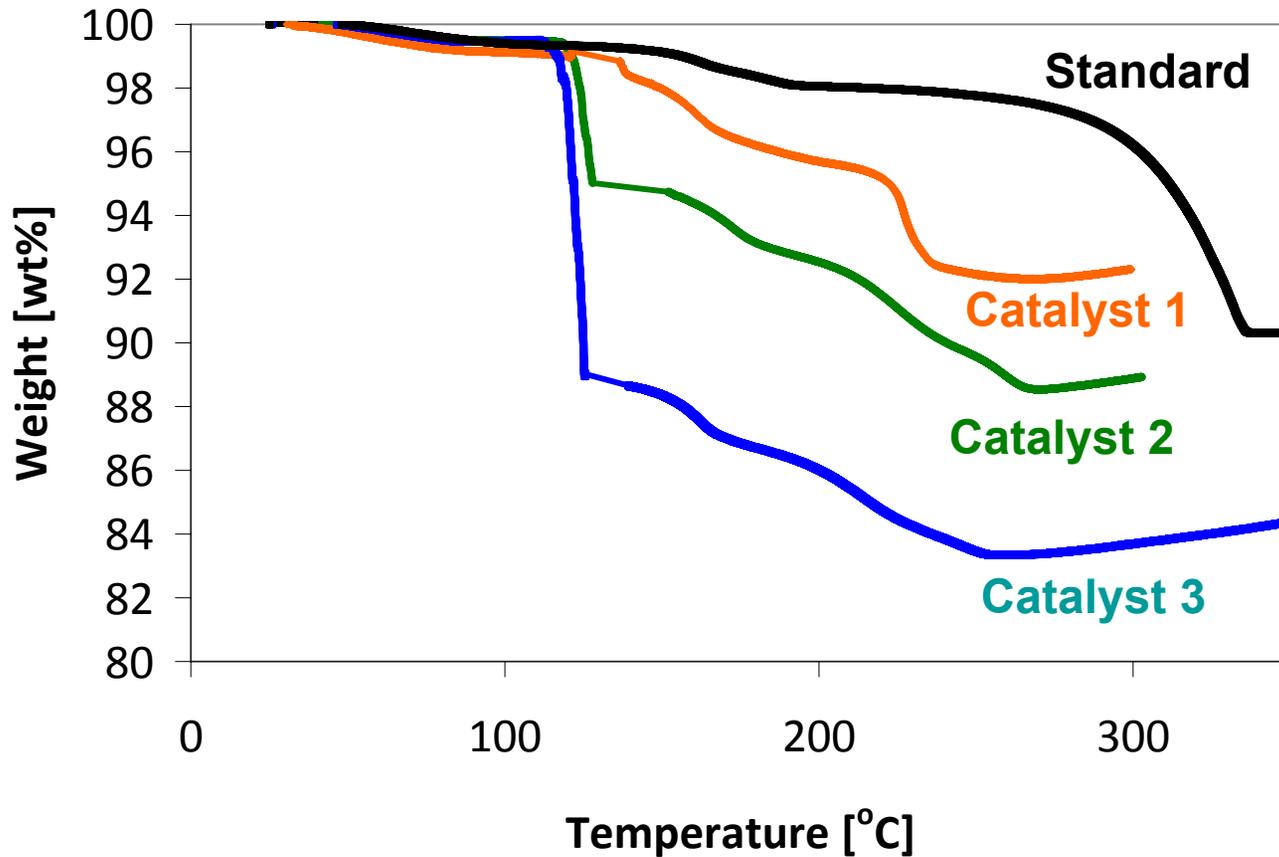
# Li-Mg-B-N-H-TGA



New multinary complex hydrides show promising weight loss due to hydrogen decomposition (~8-10 wt%) at 250-300 °C

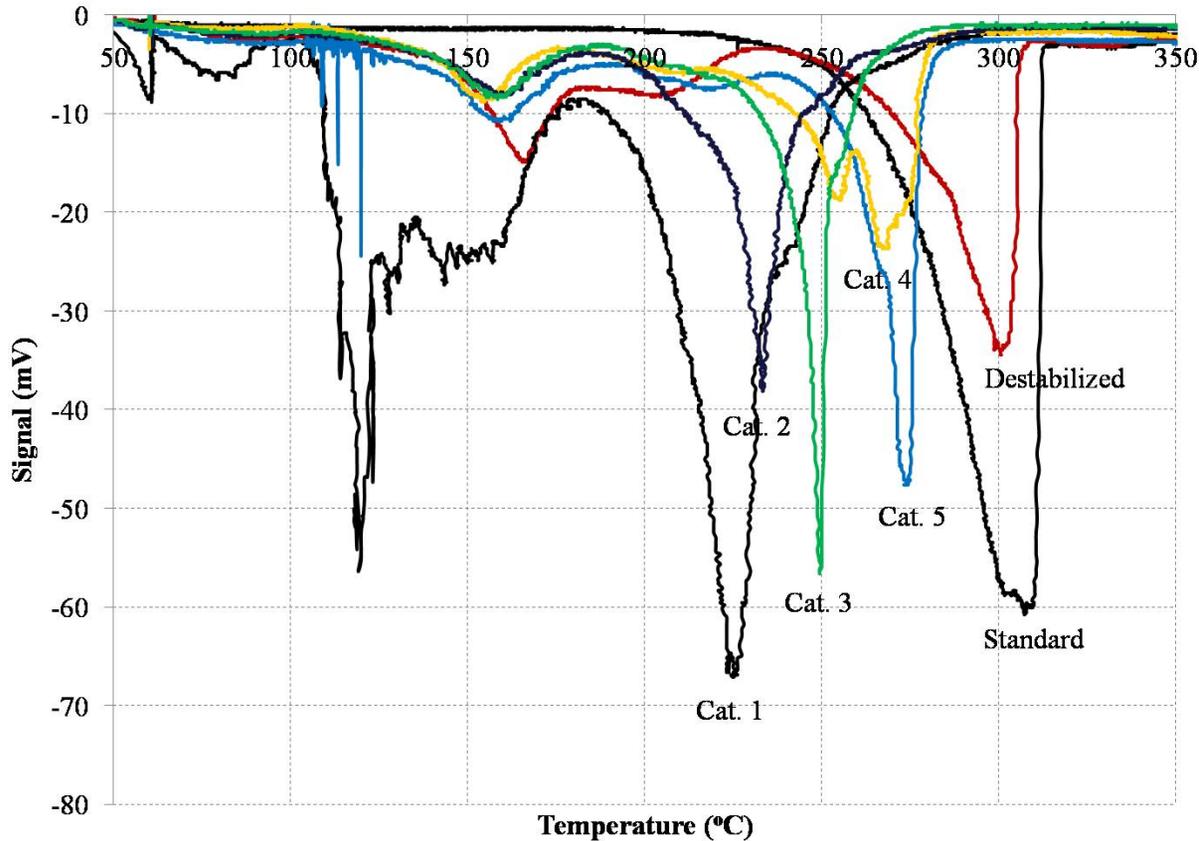
*Accomplishments*

# Li-Mg-B-N-H / Catalysts - TGA



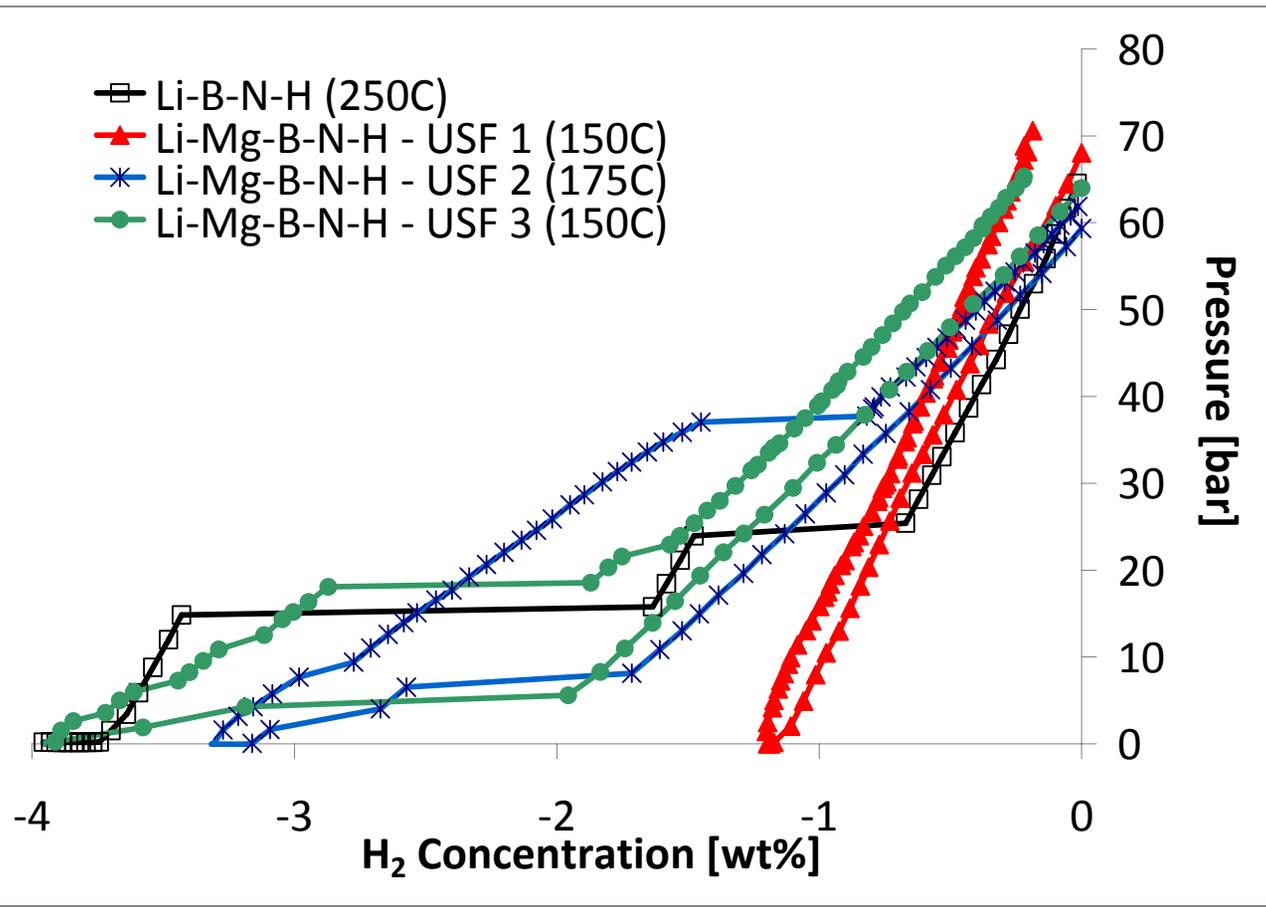
- Decomposition temperature reduced
- Gravimetric weight loss increased significantly
- Hydrogen performance testing underway

# Li-Mg-B-N-H / Catalysts - TPD



- Standard destabilized with  $\text{MgH}_2$  – emergence of peak at 175°C
- Catalyst addition lowers main desorption peak
- Cat.5 - DT 25°C
- Cat.4 - DT 30°C
- Cat.3 - DT 50°C
- Cat.2 - DT 70°C
- Cat.1 – DT 80°C

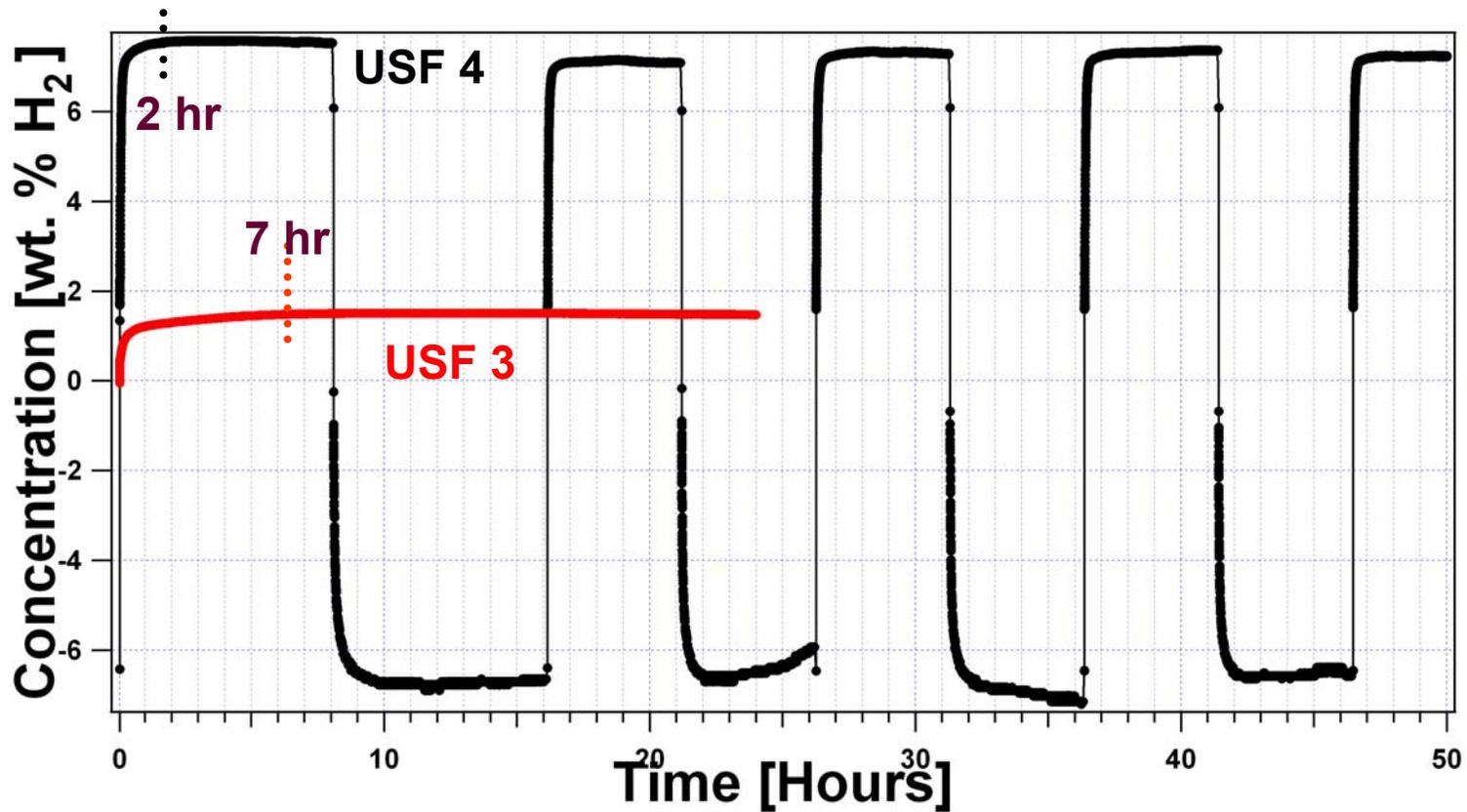
# Li-Mg-B-N-H - PCT Cycle Life



- Li-B-N-H
  - No reversibility at 250 °C
  - 4 wt%
  - 10 hr for 4 wt%
- Li-Mg-B-N-H (USF 1)
  - reversibility at 150 °C
  - 1.2 wt%
  - 4 hr for 1.2 wt%
- Li-Mg-B-N-H (USF 2)
  - reversibility at 175 °C
  - 3.2 wt%
  - 3 hr for 3.2 wt%
- Li-Mg-B-N-H (USF 3)
  - reversibility at 150 °C
  - 4wt%
  - 5 hr for 4 wt%

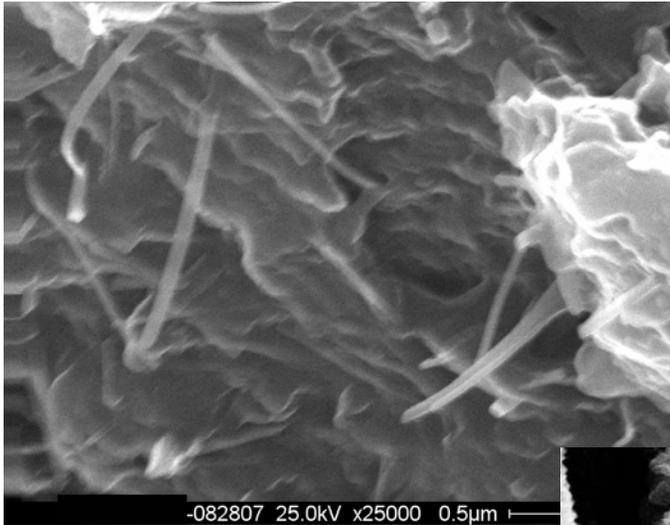
Temperature decreased from 250 °C to 150 °C; Reversibility increased from non-reversible to reversible

# *Li-Mg-B-N-H - Cycle Life Kinetics (250 °C)*

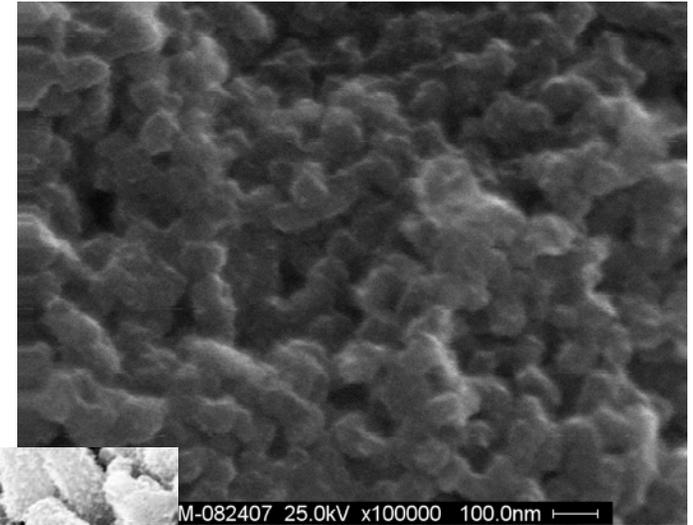


- Significant increase in capacity
- Full sorption reached after less than 2 hr compared to 7 hr for USF 1-3
- >80% capacity reached within 5 minutes

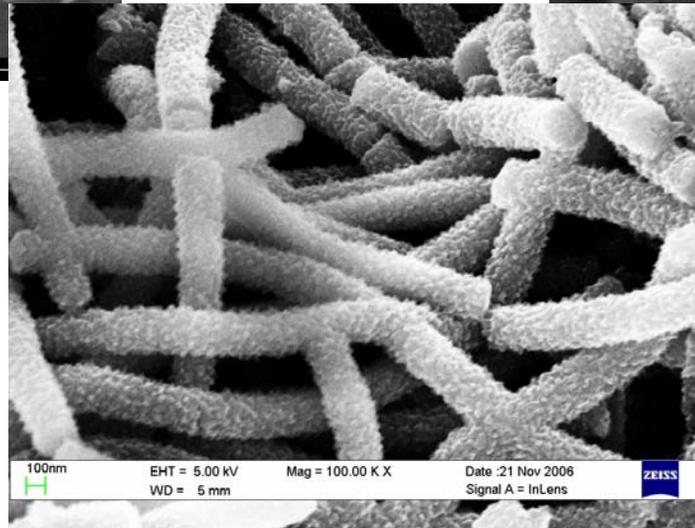
# PANI Nanostructures



PANI 1

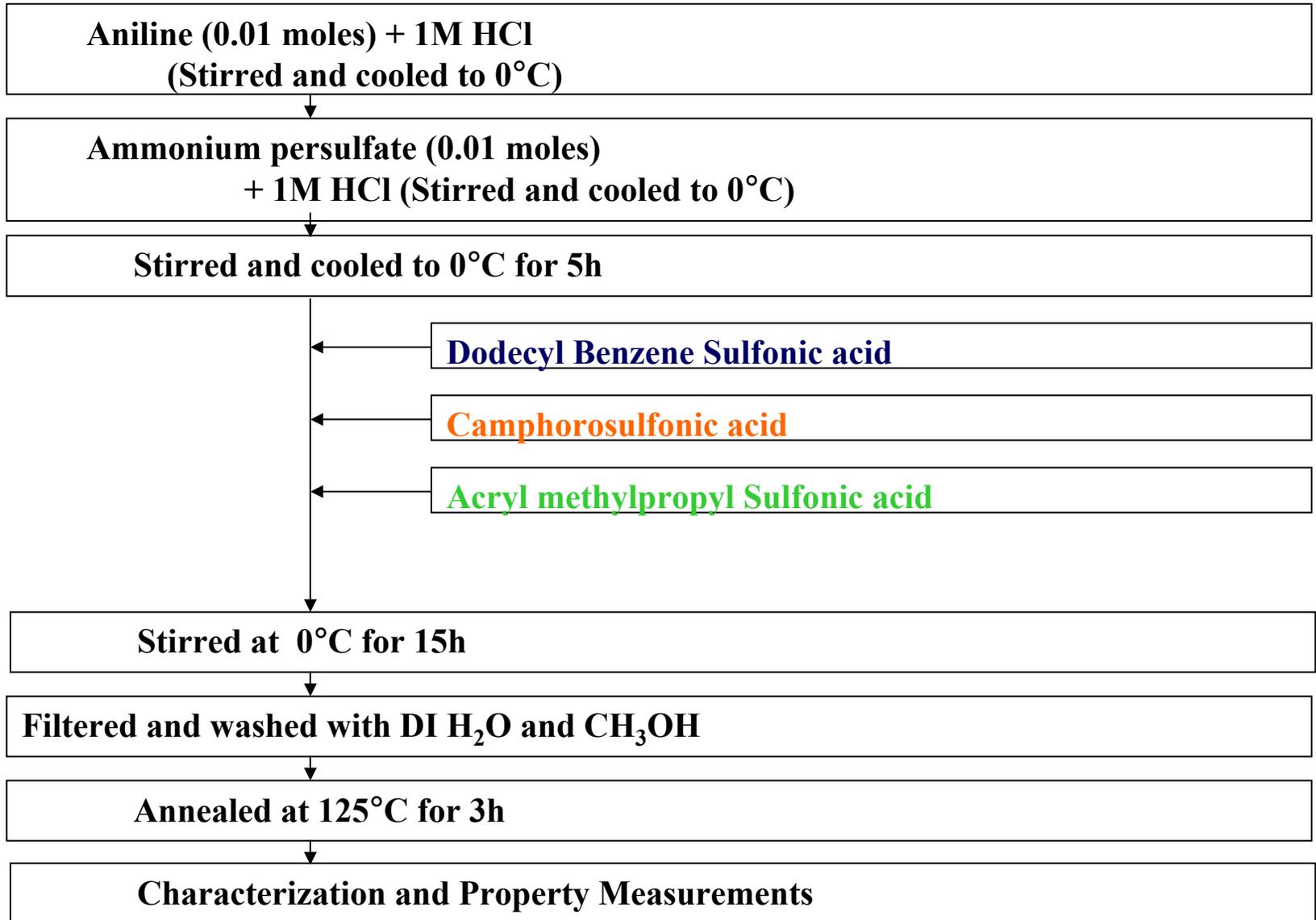


PANI 3

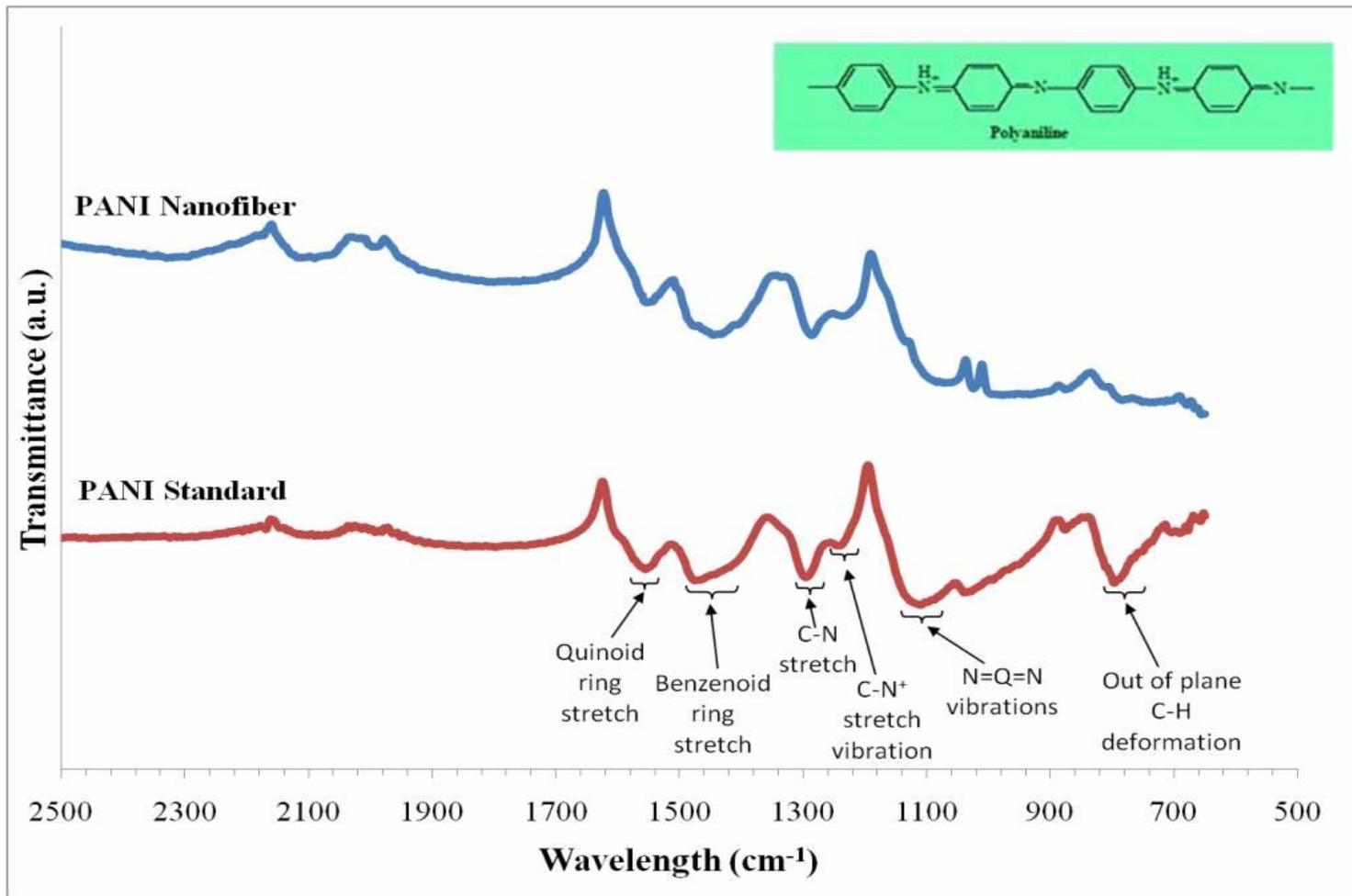


PANI 2

# PANI1 Synthesis

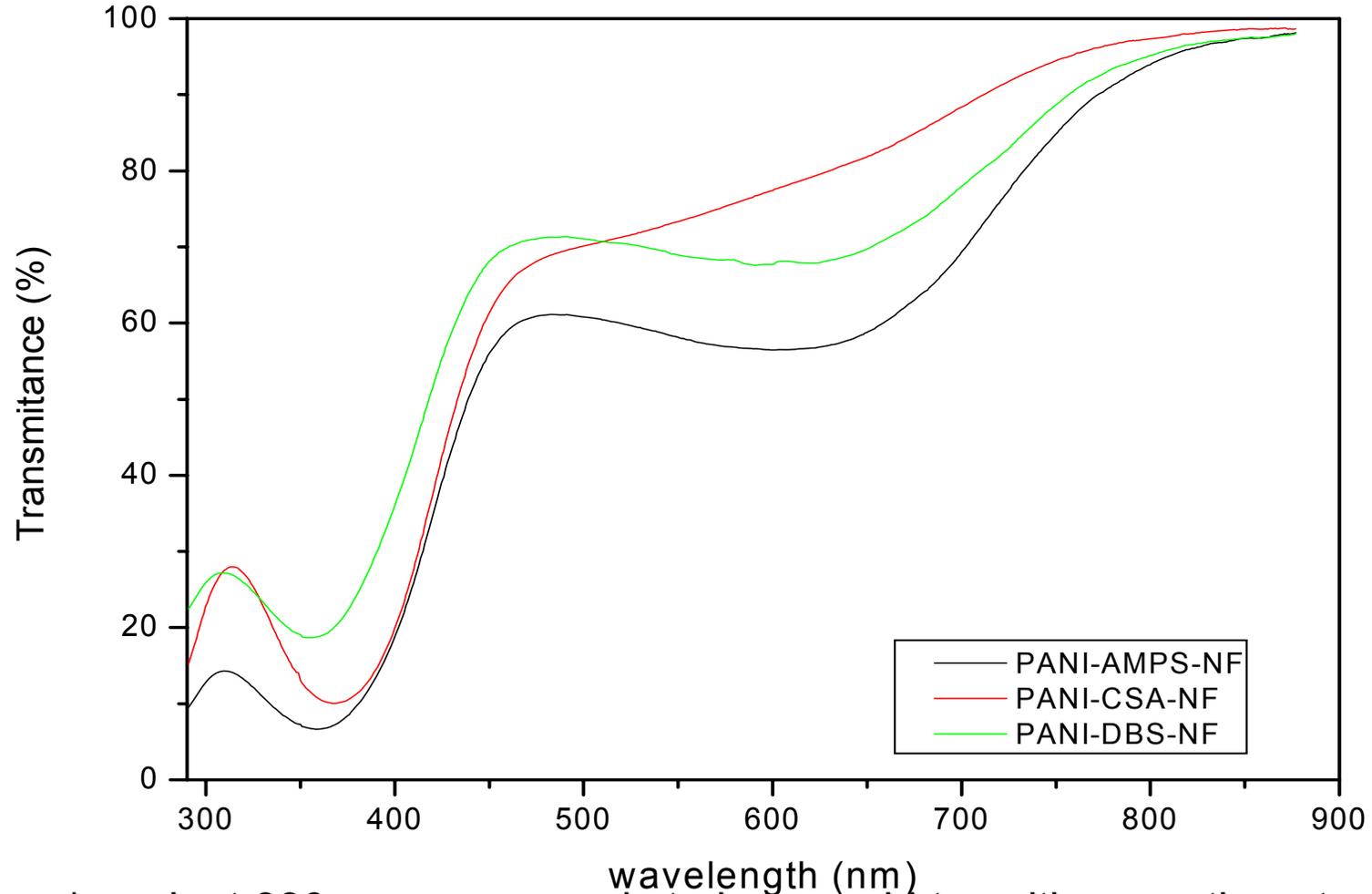


# PANI1 - FTIR



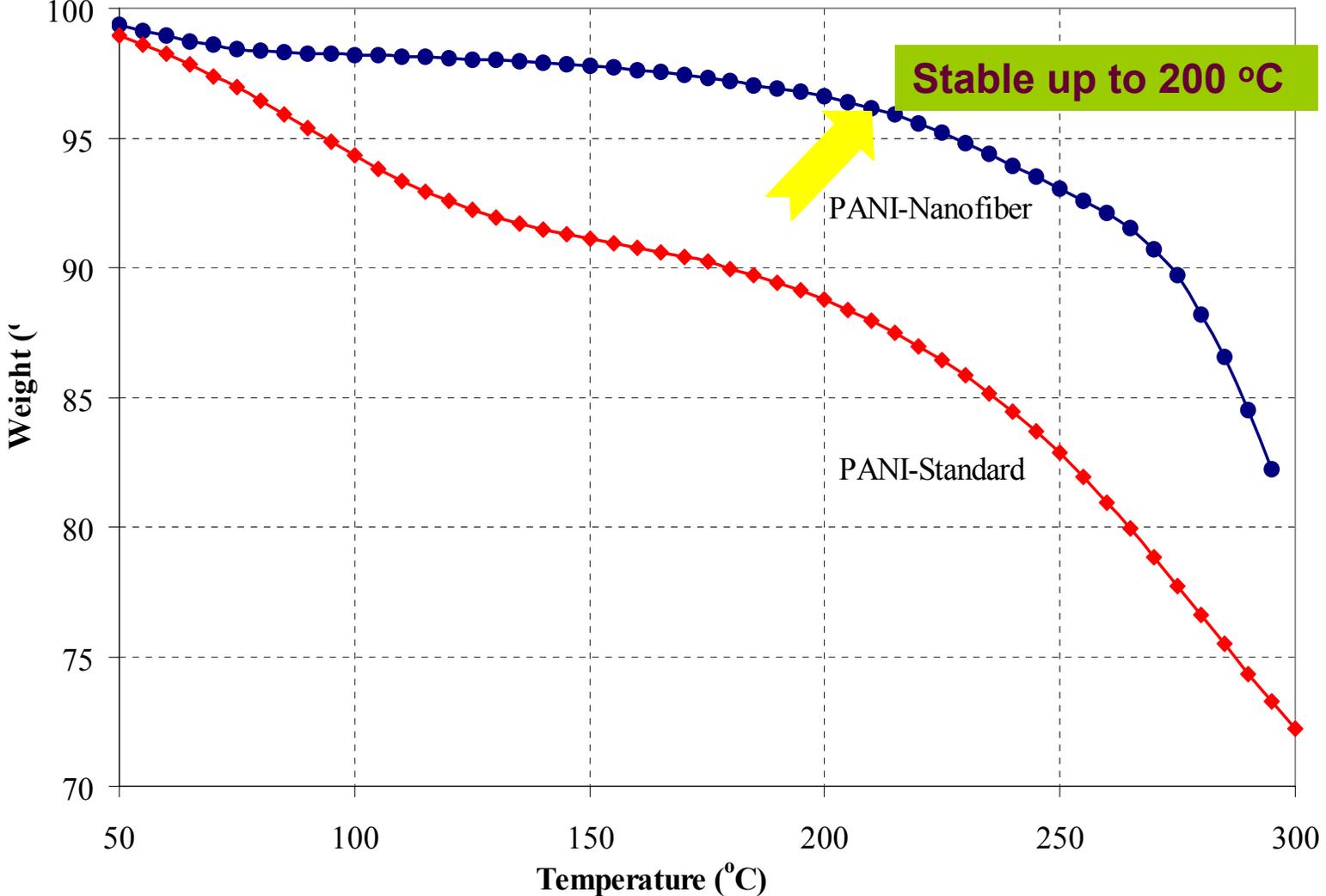
The signature bands of benzenoid and quinoid transitions in the vicinities of 1500 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>, respectively, as evidenced from FTIR confirms the formation of polyaniline structure irrespective of the surfactants used in the precursor preparation.

# PANI1 – UV-Vis



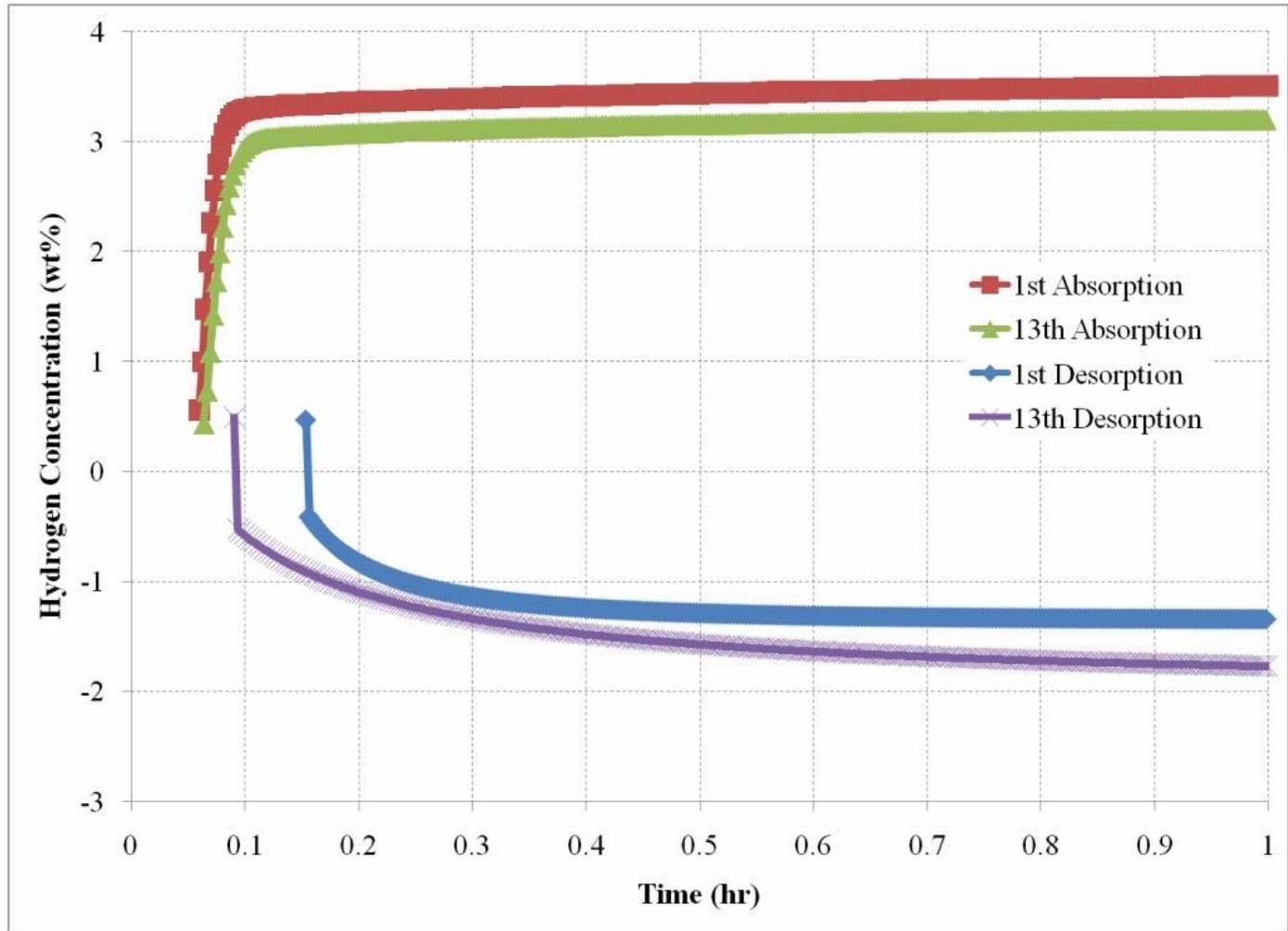
Strong  $\pi-\pi^*$  peak at 330 nm corresponds to benzenoid transition, another strong  $\pi-\pi^*$  peak at 630 nm corresponds to benzenoid to quinoid transition indicating the synthesized polymer was polyaniline in oxidized form.

# PANI 1- TGA



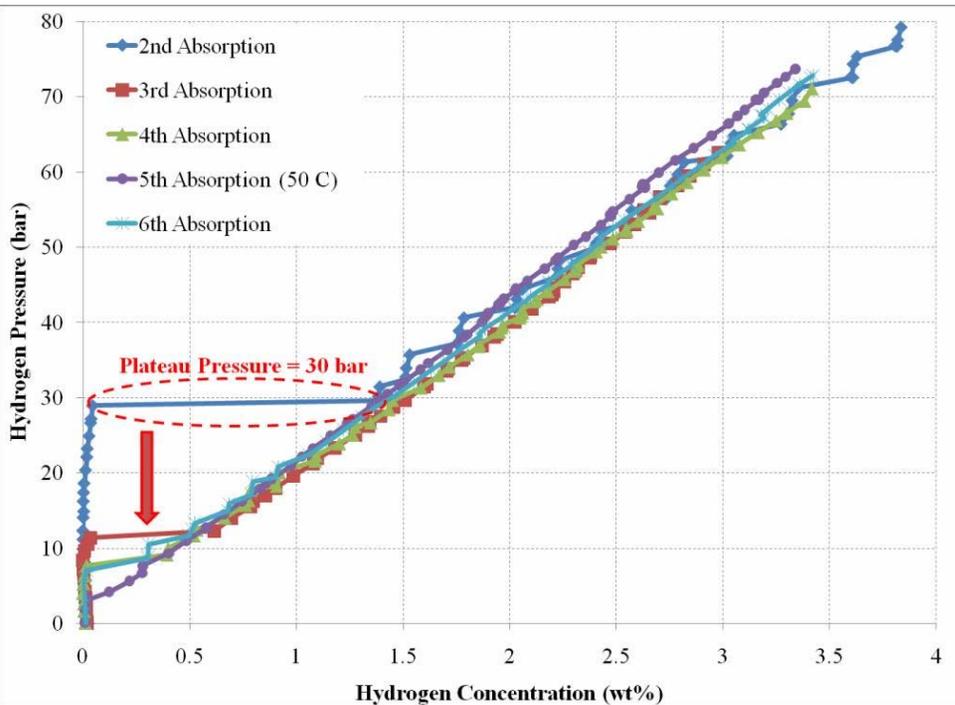
The thermogravimetric analysis reveals that these PANI nanofibers are stable up to 200 oC due to their high density nanofibrous matrix.

# PANI 1 – KINETICS at Room Temperature



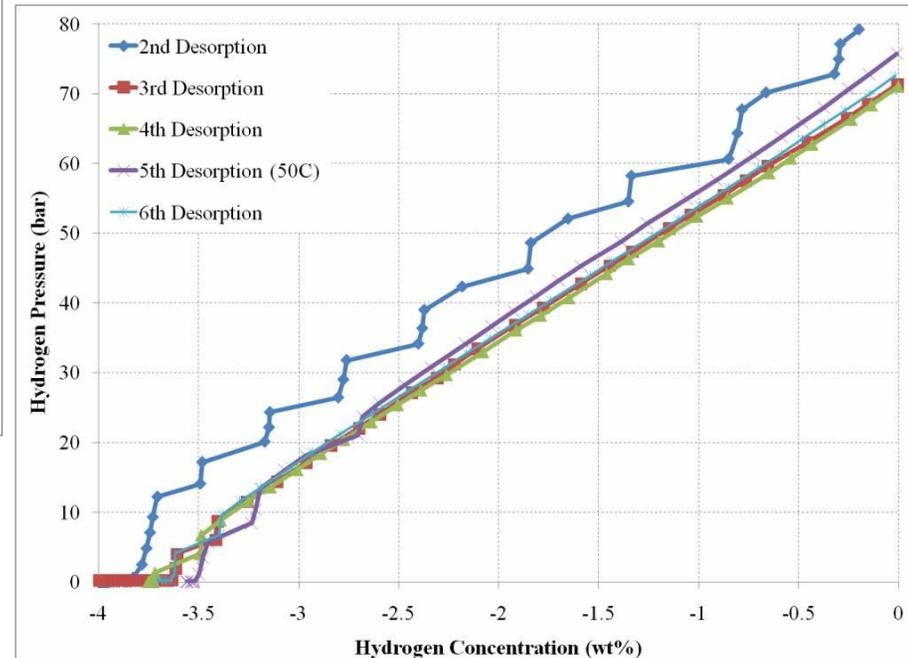
Hydrogen absorption and desorption kinetics of PANI-NF in initial (1<sup>st</sup>) and 13<sup>th</sup> cycle: 3 wt/% of hydrogen absorbed by the sample at room temperature.

# PANI 1 – PCT at Room Temperature



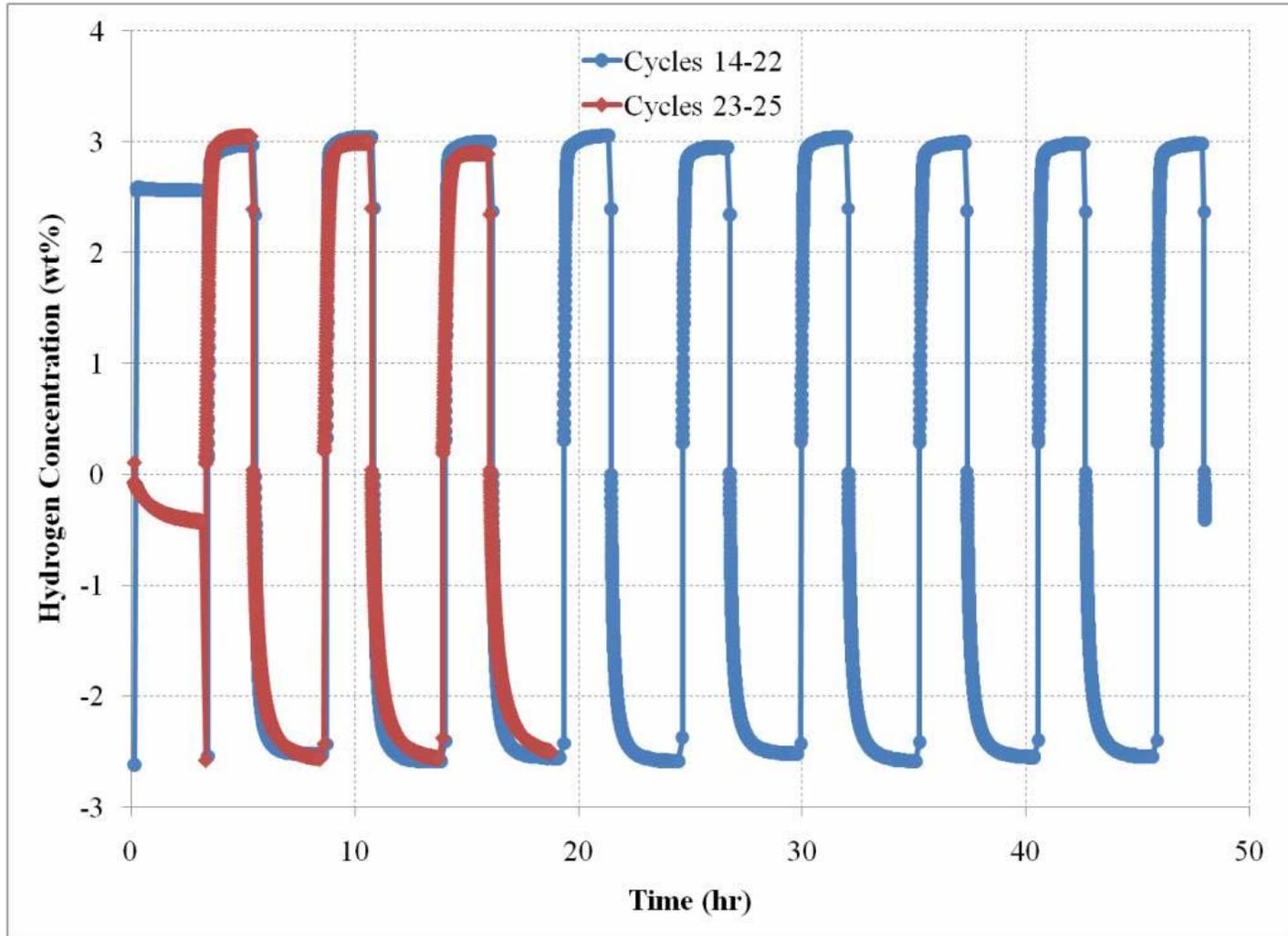
## ABSORPTION

## DESORPTION



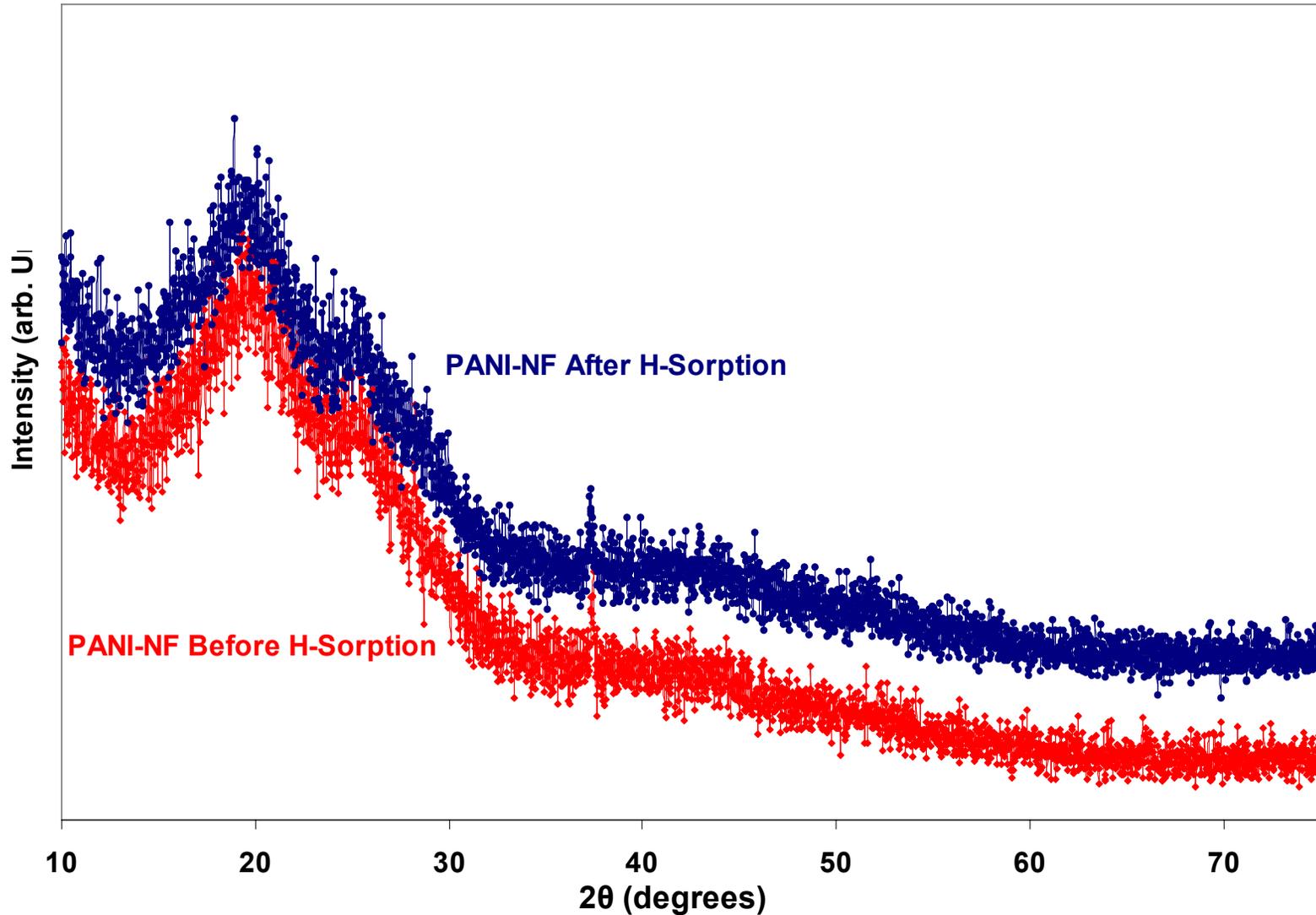
Pressure-Composition Isotherms of PANI-NF at room temperature from 2<sup>nd</sup> to 6<sup>th</sup> (a) absorption (b) desorption cycles; Hydrogen absorption plateau pressure of 30 bars was clearly seen in the 2<sup>nd</sup> absorption PCT and it reduces in the subsequent sorption cycles

# PANI 1 - LIFE CYCLE KINETICS at Room Temperature



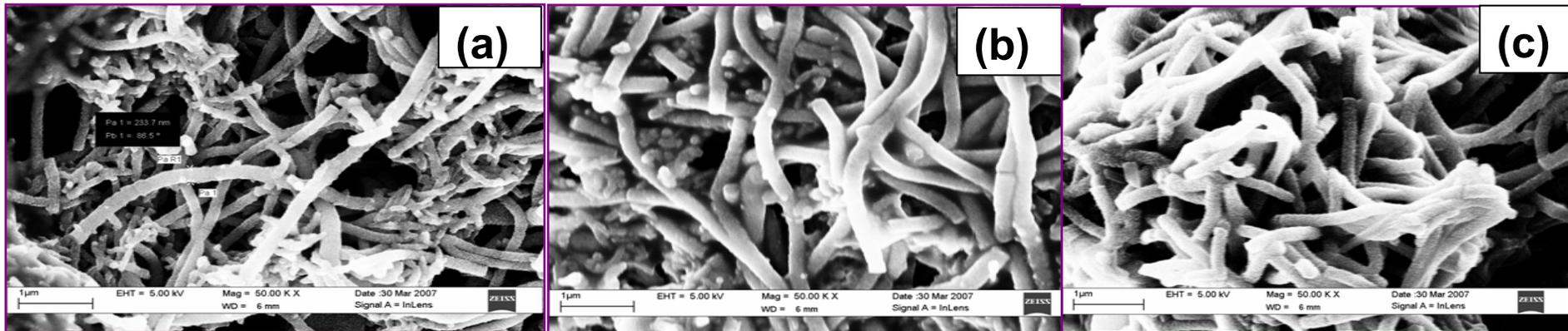
Hydrogen sorption kinetics at room temperature from 14<sup>th</sup> cycle to 25<sup>th</sup> cycle. No degradation in the hydrogen sorption kinetics and storage capacity was observed.

# PANI 1 - XRD



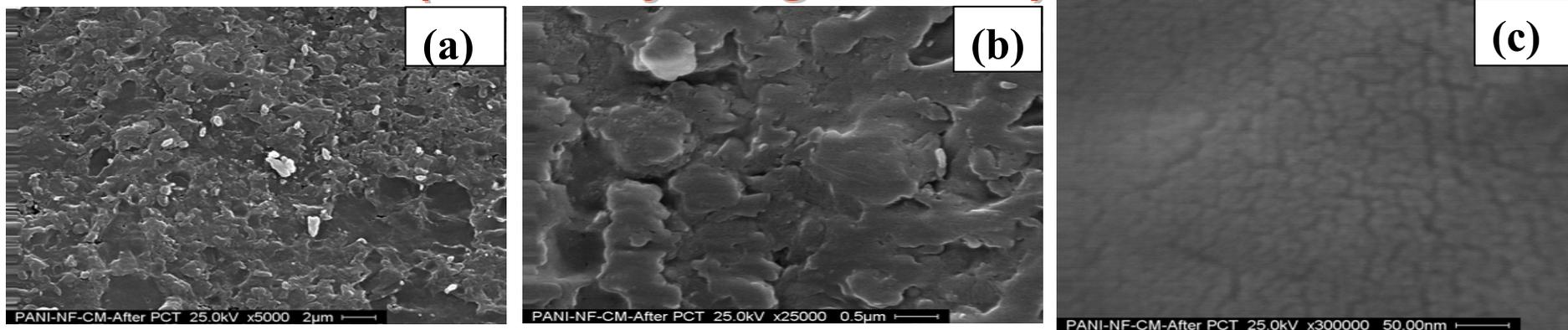
XRD profiles of PANI 1 before and after hydrogen sorption cycles; No structural changes observed

# PANI 1- SEM (Before Hydrogenation)



Scanning electron micrographs of polyaniline nanofibers grown at room temperature in aqueous medium with different surfactants (a) Dodecylbenzenesulfonic acid (b) Acrylmethylpropyl sulfonic acid (c) camphorosulfonic acid using ammonium persulfate as oxidizing agent

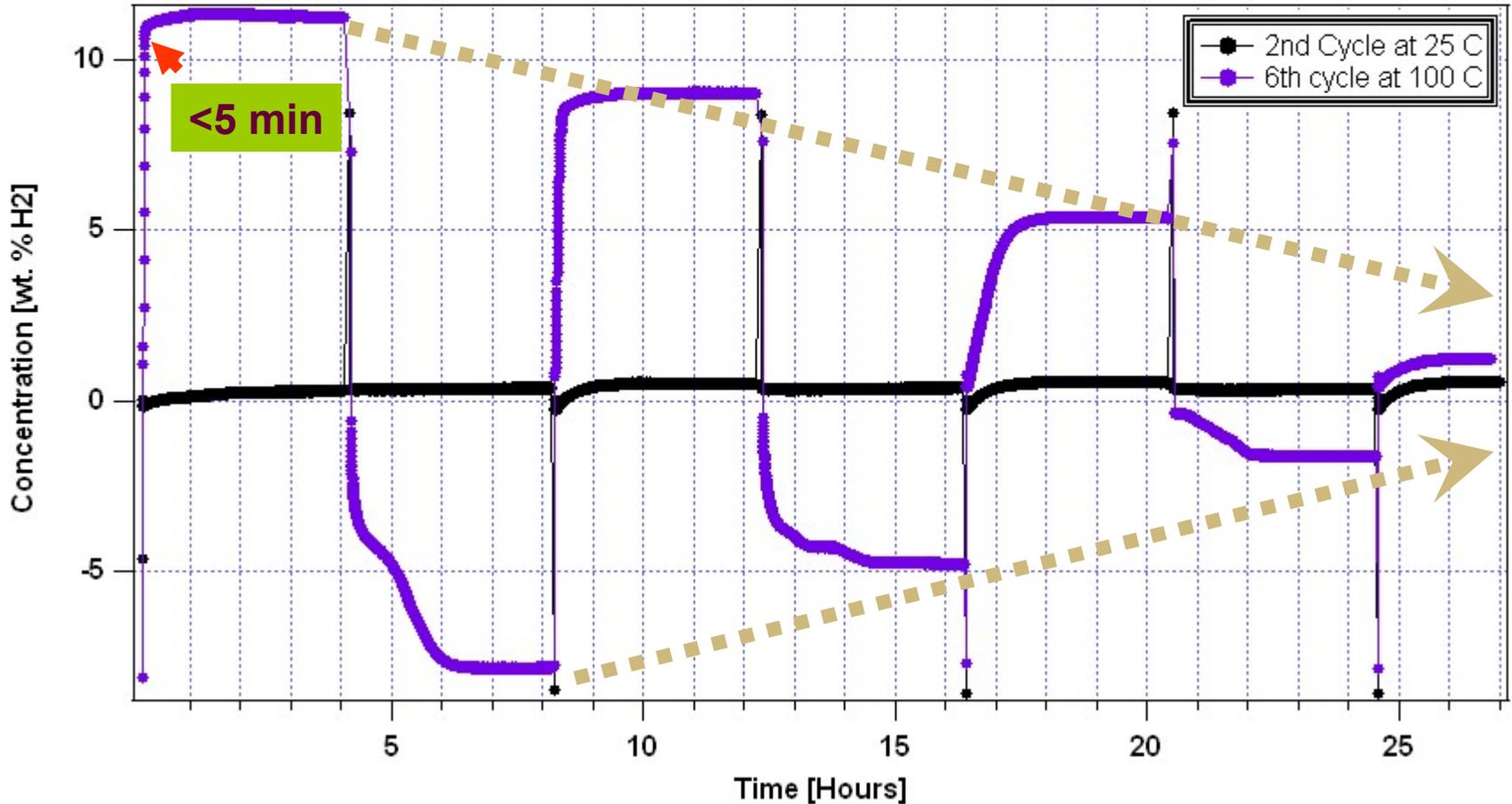
# PANI 1- SEM (After Hydrogenation)



SEM Microstructure of PANI-NF after hydrogen sorption cycles at different magnifications (a) 5000X (b) 25000X and (c) 300000X

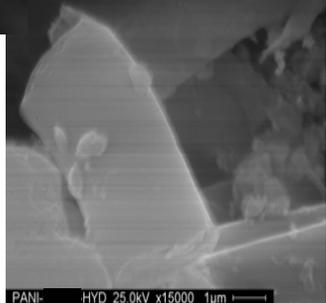
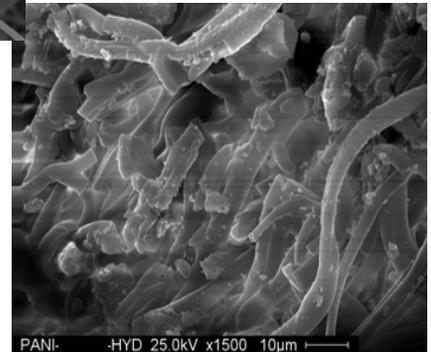
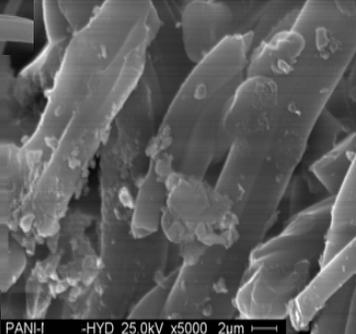
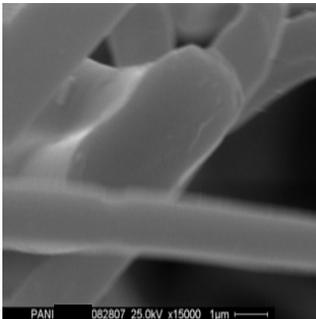
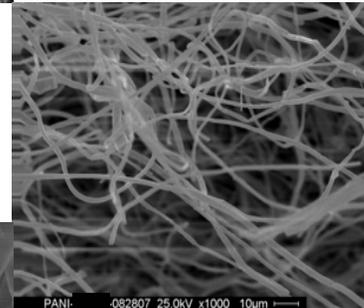
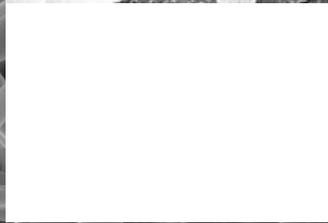
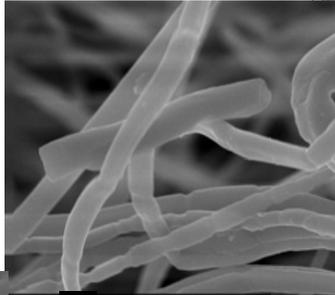
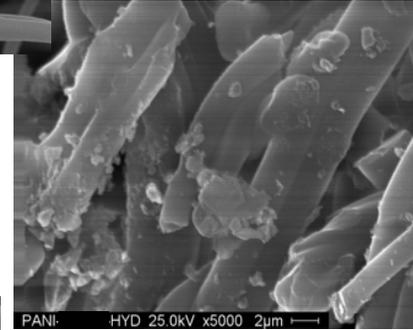
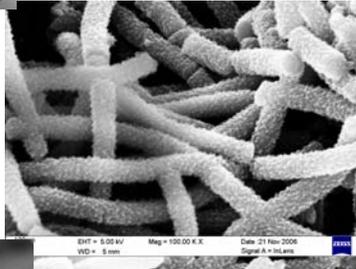
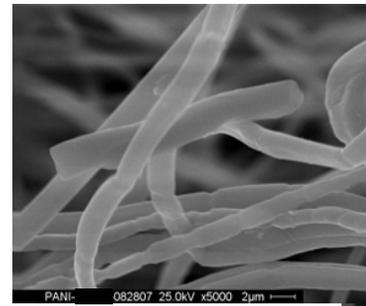
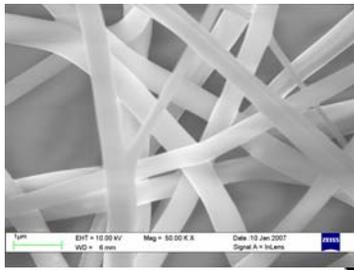
# PANI 2 - CYCLE LIFE KINETICS AT DIFFERENT TEMP.

Life Cycle Kinetics at different T for PANI 3



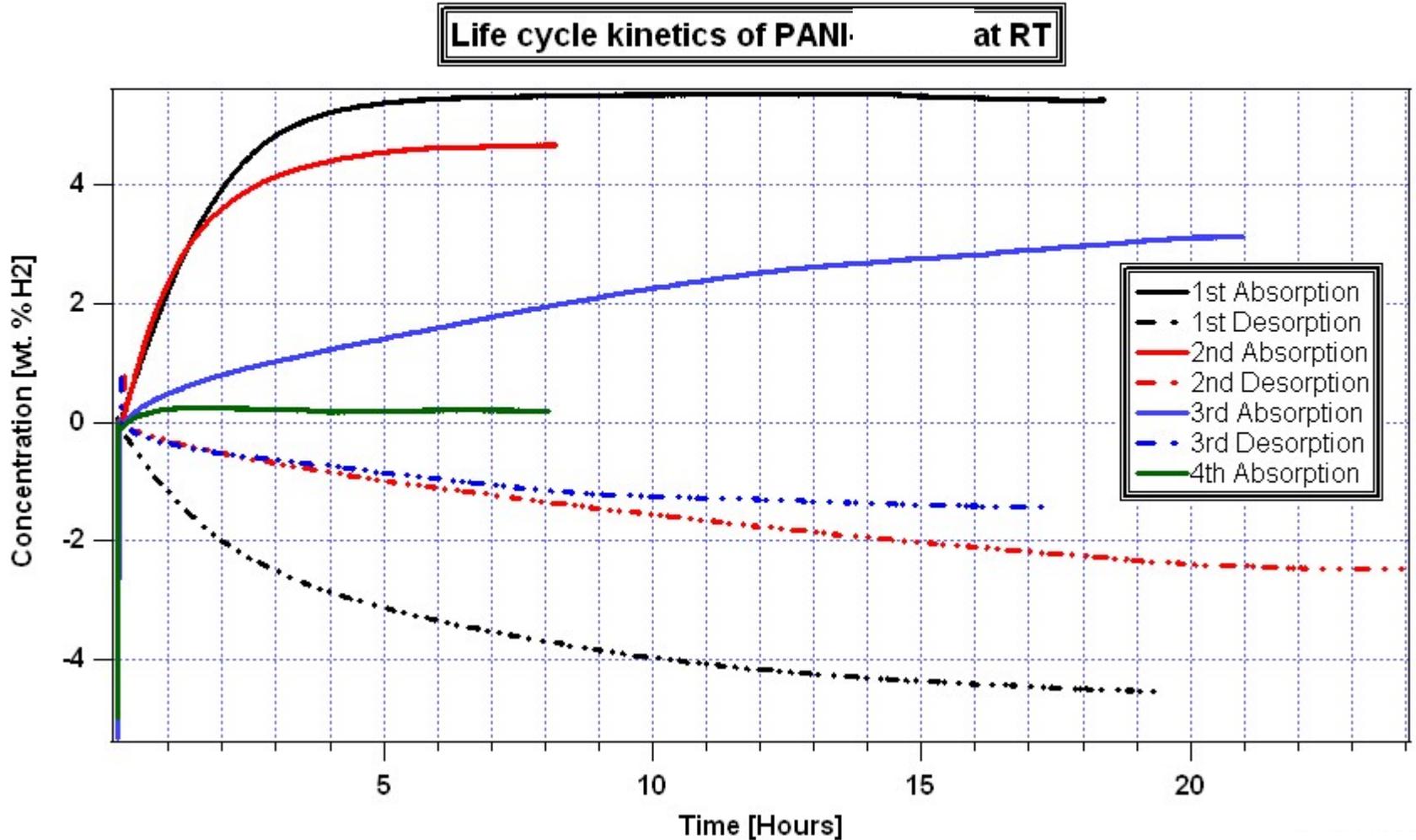
Fast kinetics with high capacity of ~10 wt% at 100 °C;  
Capacity decreases with number of Abs. and Des. cycles

# PANI 2 SEM



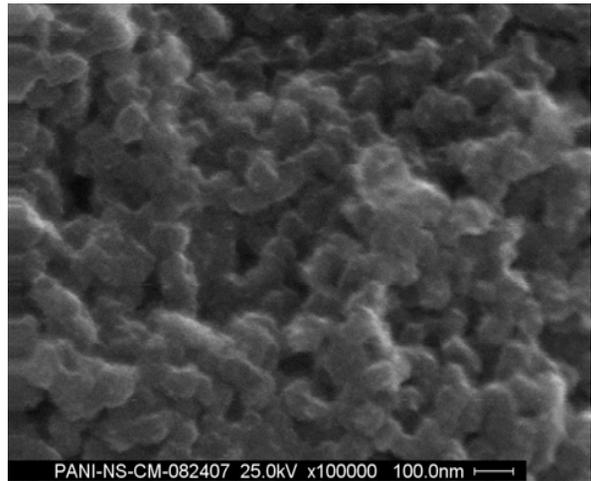
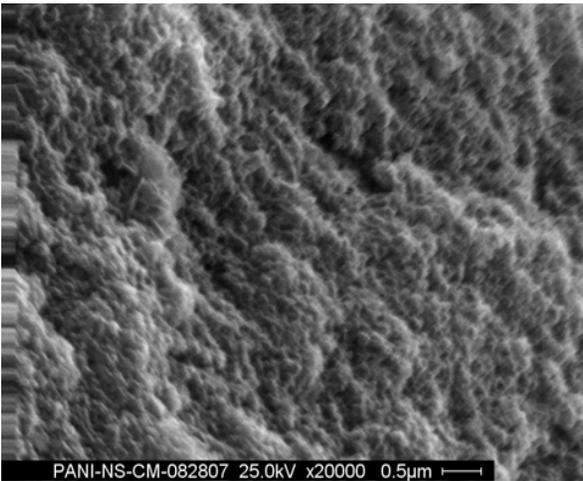
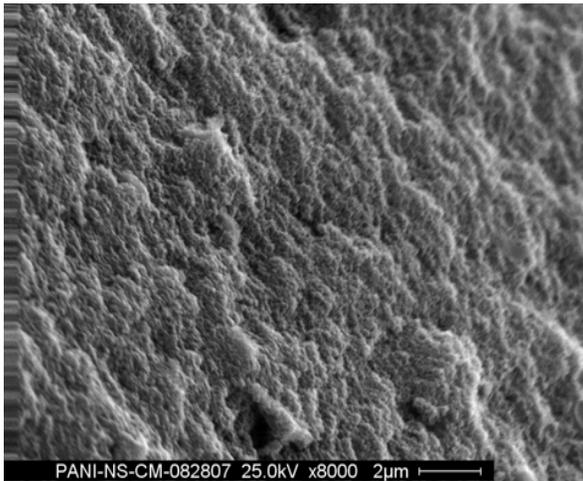
**Accomplishments**

# PANI 3 - CYCLE LIFE KINETICS at Room Temp.

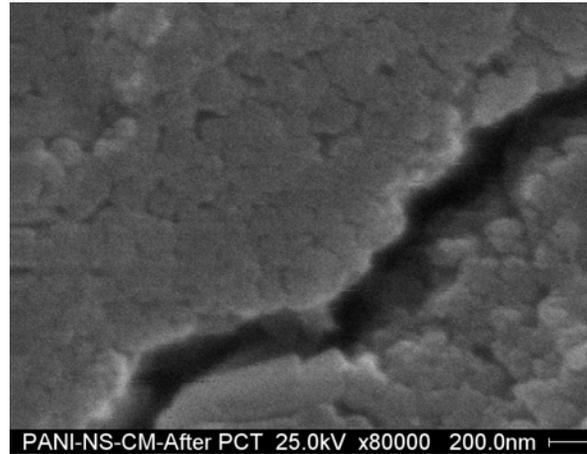
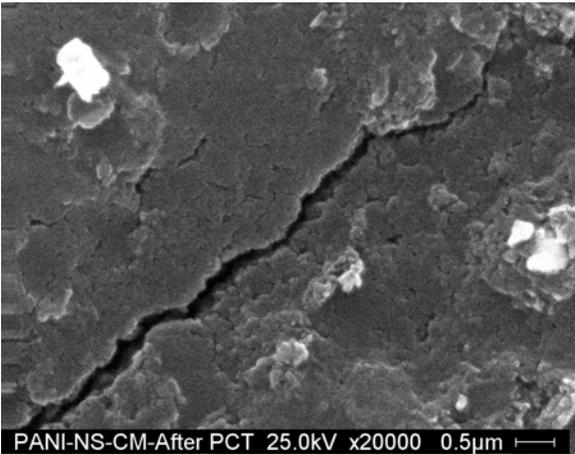
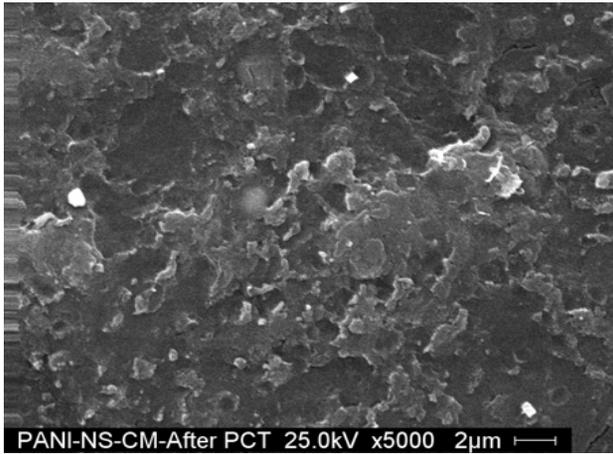


Hydrogen sorption capacity of ~4.5 wt% at 1<sup>st</sup> cycle and it decreases with cycling

# PANI 3- SEM (Before Hydrogenation)



# PANI 3- SEM (After Hydrogenation)



Micro-cracks observed after hydrogen sorption indicated effective hydrogen reaction

# Summary

## Subtask 1 & 2: $\text{Mn}(\text{BH}_4)_2$ (Experiment and Theory)

- An optimum milling duration of 30 minutes was sufficient to complete the reaction  $2\text{NaBH}_4 + \text{MnCl}_2 \rightarrow \text{Mn}(\text{BH}_4)_2 + 2\text{NaCl}$
- An optimum milling duration of 90 minutes was sufficient to complete the reaction  $2\text{LiBH}_4 + \text{MnCl}_2 \rightarrow \text{Mn}(\text{BH}_4)_2 + 2\text{LiCl}$
- For the  $3\text{LiBH}_4 + \text{MnCl}_3$  samples, the melting and decomposition temperatures lowers down to 98 and 112 °C
- We have executed the borohydride complexes from Univ. Hawaii and found our approach is comparable for hydrogen storage
- We have established the crystal structure and electronic band structure of complex hydrides such as  $\text{Zn}(\text{BH}_4)_2$  based on Density functional theory calculations.

## Subtask 3: Li-Mg-B-N-H

- USF Specially prepared and processed Li-Mg-B-N-H materials exhibited new multinary structure having hydrogen storage reversibility of 4-8 wt.% at temperature range of 150-250 °C
- The Life cycle kinetics from 10 minutes upwards to 5hrs was reproducibly observed in these Li-Mg-B-N-H systems.
- Initial catalysts studies indicate significant temperature reduction for hydrogen decomposition

# Summary (cont'd.)

## Subtask 4: PANI

- Hydrogen Absorption is feasible in PANI nanonetworks
- PANI 1 exhibit reversible hydrogen sorption behavior at room temp (3wt%) for at least 25 cycles
- PANI 2 prepared through special process shows up to 10 wt.% (RT) in the initial cycle and it decreases with cycling
- Though PANI 3 possesses high hydrogen capacity (4.0 wt%), they do lack the reversible sorption behavior due to agglomeration or hydrogen saturation effects

# Future Work

## Subtask 1: $\text{Mn}(\text{BH}_4)_2$

- Analysis of the residual gas after thermal decomposition of  $\text{Mn}(\text{BH}_4)_2$  by GC/MS
- Kinetic and thermodynamic characteristics optimization of  $\text{Mn}(\text{BH}_4)_2$  by catalytic doping and lattice substitution

## Subtask 2

- Finite temperature reaction enthalpy of complex pure Manganese boro-hydride with combination of DFT and lattice dynamics methods
- Effect of additives on decomposition reaction equilibria for these systems from DFT, lattice dynamics and thermodynamics

## Subtask 3: Li-Mg-B-N-H

- Hydrogen measurements of catalysts doped Li-Mg-B-N-H
- GC/MS of the desorbed gases
- Thermodynamic characterization of the USF developed complex materials
- Kinetics and full cycle life measurements for the new materials

## Subtask 4: PANI

- Future works to decorate PANI nanonetworks with CNT and transition metals such as Ni and Ti
- Future works also to prepare nanocomposite PANI nanonetworks for efficient hydrogen storage