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

This presentation does not contain any proprietary or confidential information

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)

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Overview

Timeline

Start: May 2004

End: August 2009

Percent Completed: 80%

Technical Targets

- Volumetric H_2 density, > 45g H_2/L
- Gravimetric H_2 density, > 6.0 wt.%
- Operating temperature, -30/50 °C
- Delivery T of H_2, -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_2 physisorption and chemisorption
  - Reproducibility of performance

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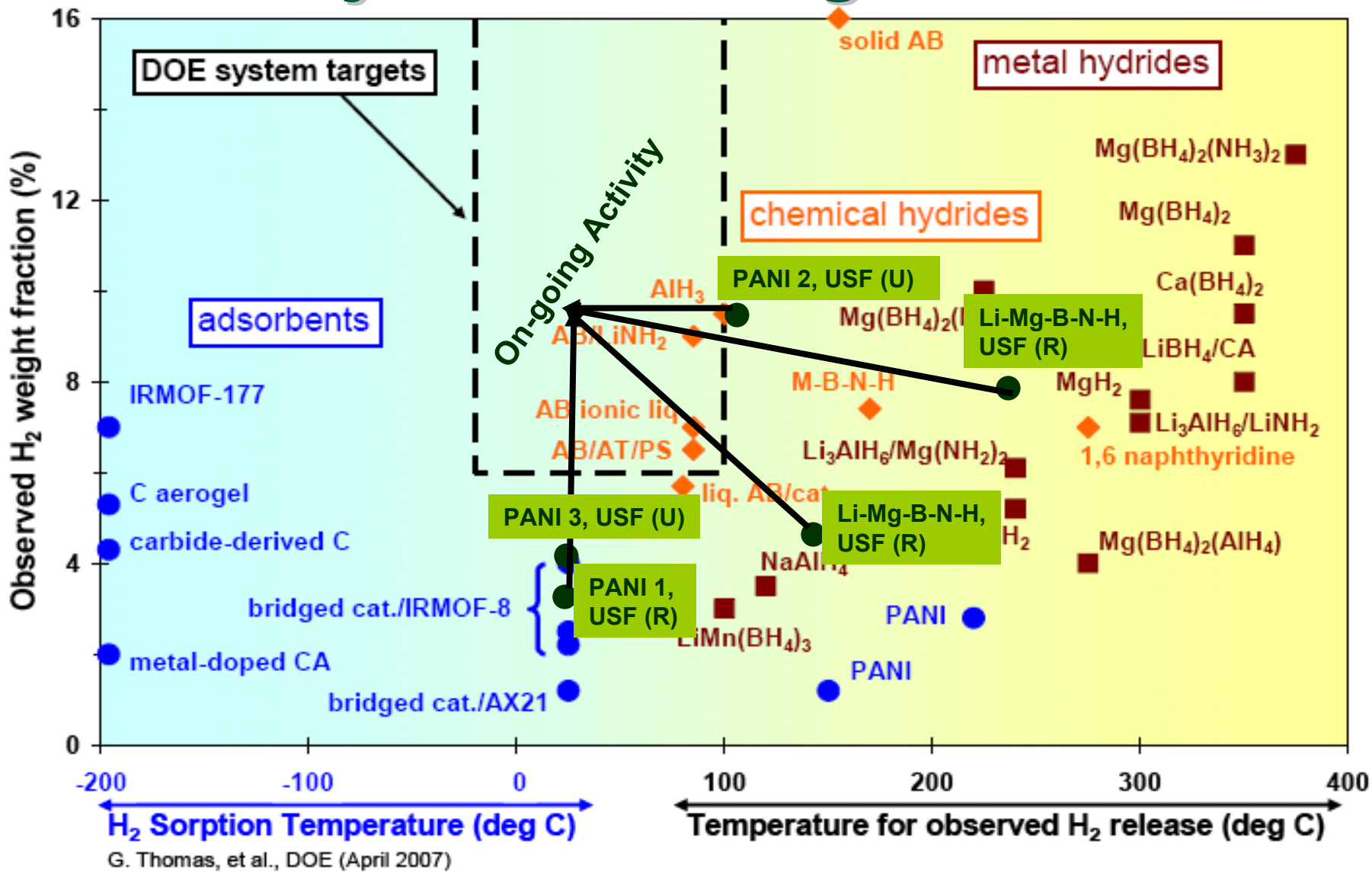
Overall Objectives

- Synthesis and characterization of materials with high H_2 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.

Milestones

Year	Materials
June'05-May'07 **Completed**	• $Zn(BH_4)_2$; Nanocatalyst Doped • $LiBH_4$ + ½ MgH_2 + Xmol% catalyst • $LiNH_2$/LiH; Ti doped and Mg ad-mixed • New quaternary complex hydrides Li-B-N-H • Nano TM loaded MgH_2 • Catalytic doping and substitution
October'06-June'08 **On-going**	• Li-Mg-B-N-H (Multinary Complex Hydrides) • USF processed Li-Mg-B-N-H • $Mn(BH_4)_2$, $LiMn(BH_4)_3$, $LiSc(BH_4)_2$ • $Ca(BH_4)_2$ and catalytic effects • PANI Nanostructures (specially processed)
Jan'06 – June'08 **On-going**	Electronic structure (DFT) calculations • Crystal structure identification • Stability analysis of modified complex borohydrides

USF Hydride Storage Research



G. Thomas, et al., DOE (April 2007)

R = Reversible Hydride
U = Hydrogen Uptake

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Critical Assumptions (No Go)

Critical Assumptions	$Zn(BH_4)_2$	$LiBH_4/MgH_2$	Li-Mg-N-H
Reversibility	No	Reversible at high temperatures (> 300 °C)	Reversible at high T (280 °C)
Volumetric Capacity	>100 kg m^{-3}	>100 kg m^{-3}	>100 kg m^{-3}
Gravimetric Capacity	8.4 wt.%	> 6.0 wt.%	>7.0 wt,%
Gas Analysis	B-H gases with H_2	H_2	N-H with H_2
Kinetics	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 $LiBH_4$/ MgH_2 to improve the reversibilty at low temperatures
- Nanocatalysts co-doping and MgH_2 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_2 storage
- New materials and processes discovery and optimization of reaction pathways

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Critical Assumptions (Go)

Critical Assumptions	Li-Mg-B-N-H	$X(BH_4)_2$ (X=Mn, Zr, Ca)	PANI Nanostructures
Reversibility	Good at lower T, specially processed materials	Reversible at moderate and high temperatures	Good at Room Temperature, specially processed materials
Volumetric Capacity	>100 kg m^{-3}	>100 kg m^{-3}	>100 kg m^{-3}
Gravimetric Capacity	>7.0 wt.%	> 8.0 wt.%	~3-10 wt,% uptake
Gas Analysis	H_2	B-H with H_2	H_2
Kinetics	Fast	medium	Fast

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

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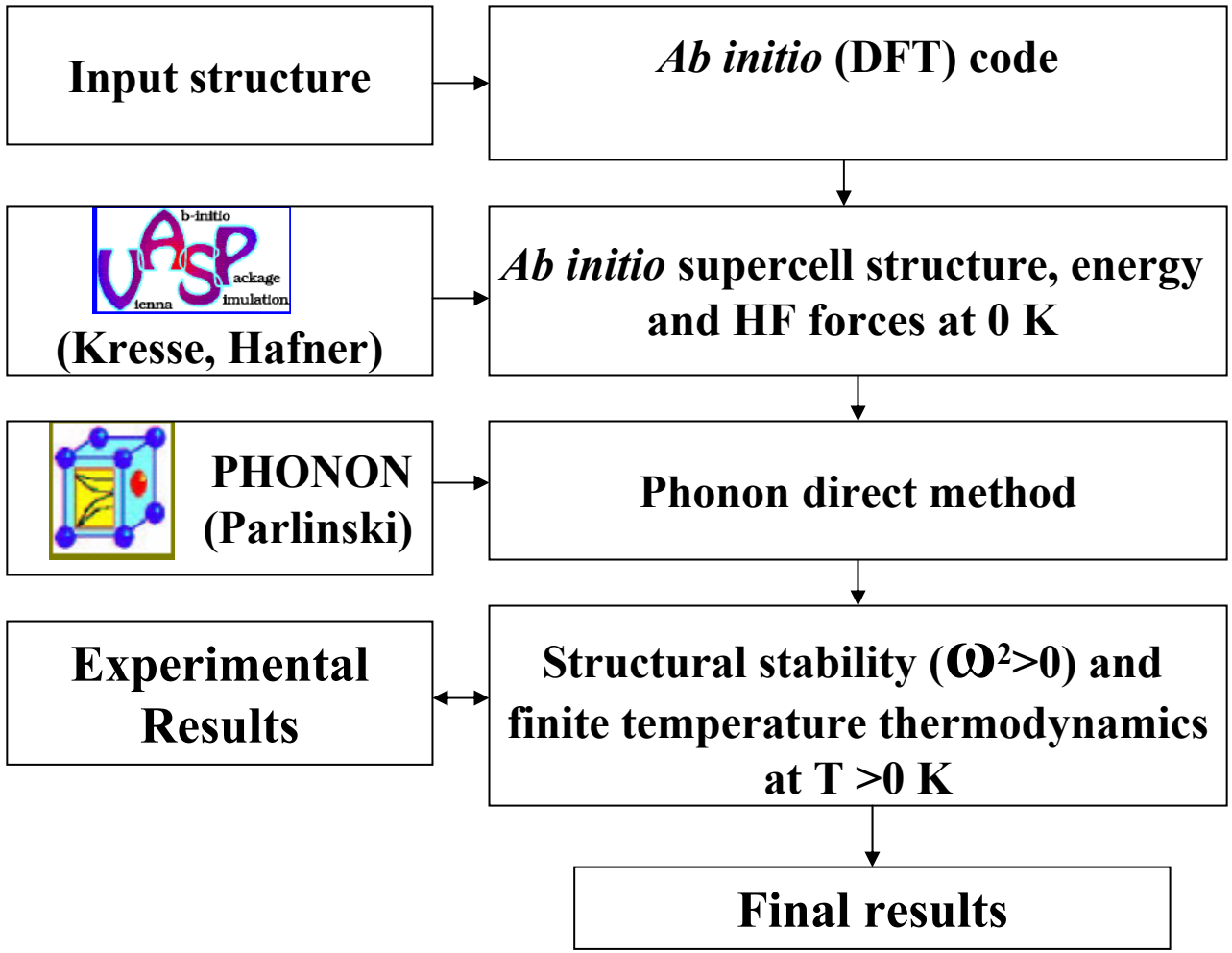
Approach (Experiment)

- 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

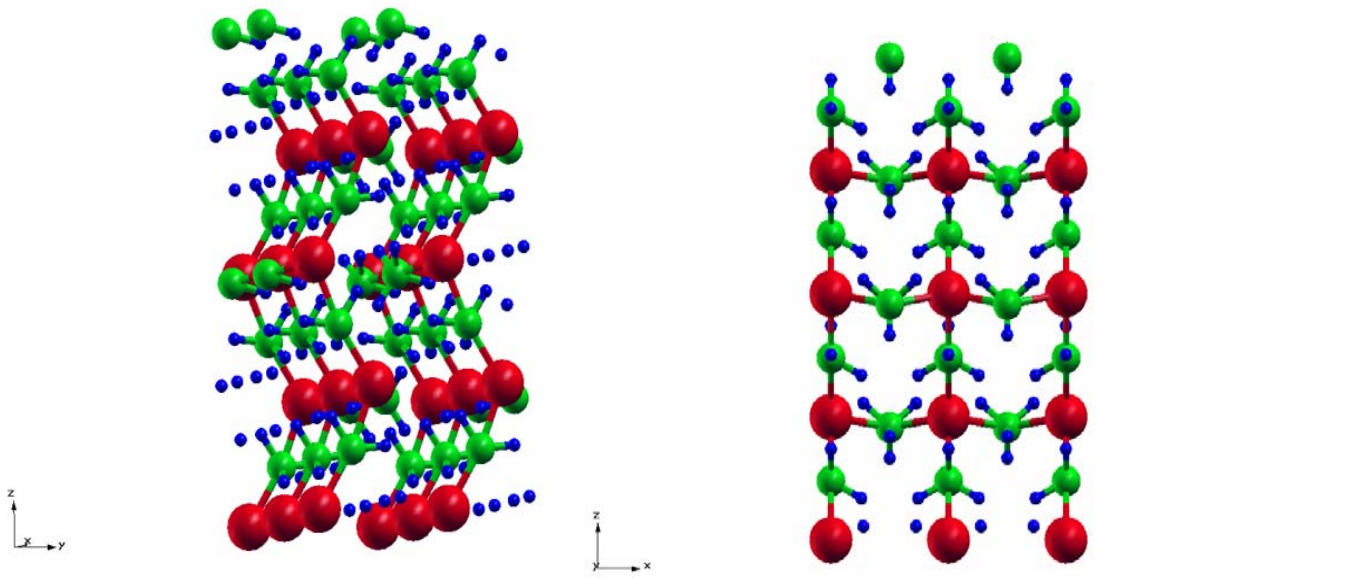
Approach (Theory)



Accomplishments

- Successfully synthesized, purified, nanocatalyst doped and characterized $Zn(BH_4)_2$ by a mechano-chemical process with different precursors ($NaBH_4$/$LiBH_4$) + ½ $ZnCl_2$ *(Reported in Merit Review Meeting'07 & Articles Published in JALCOM and IJHE 2008)*
- Investigated the electronic structure of $Zn(BH_4)_2$ including estimation of lattice parameters. Studied effect of substitution of Ni in the $Zn(BH_4)_2$ matrix *(New Results & Articles published in PRB and APL 2008)*
- Synthesized complex borohydrides $Mn(BH_4)_2$ from different precursors ($NaBH_4$/$LiBH_4$). Established Thermal Desorption and gravimetric weight loss due to hydrogen decomposition *(New Results)*
- Synthesized quaternary structure of Li-B-N-H by $LiNH_2$/$LiBH_4$ (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 ^oC) 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 $Zn(BH_4)_2$

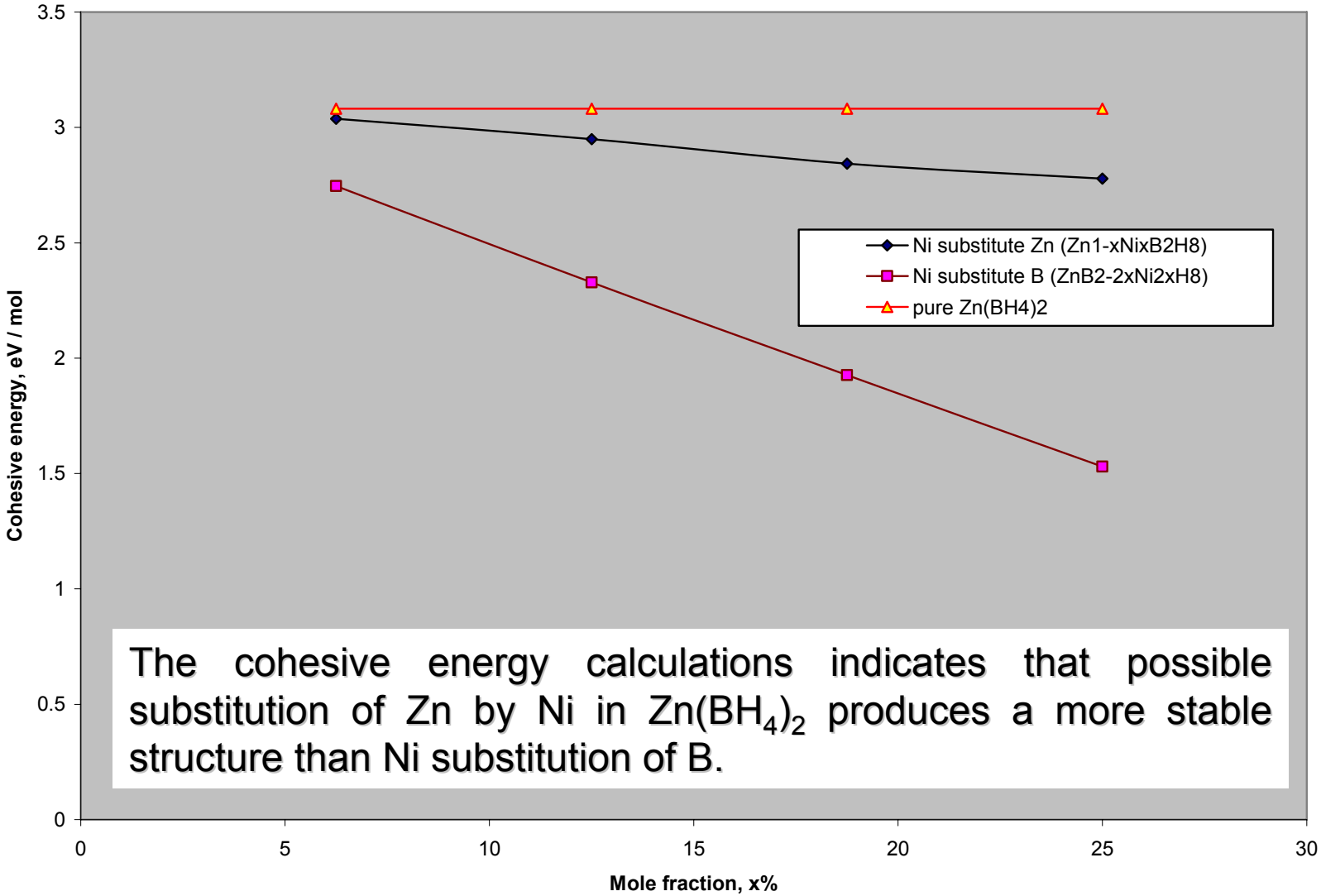


(*a*) (*b*)

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).

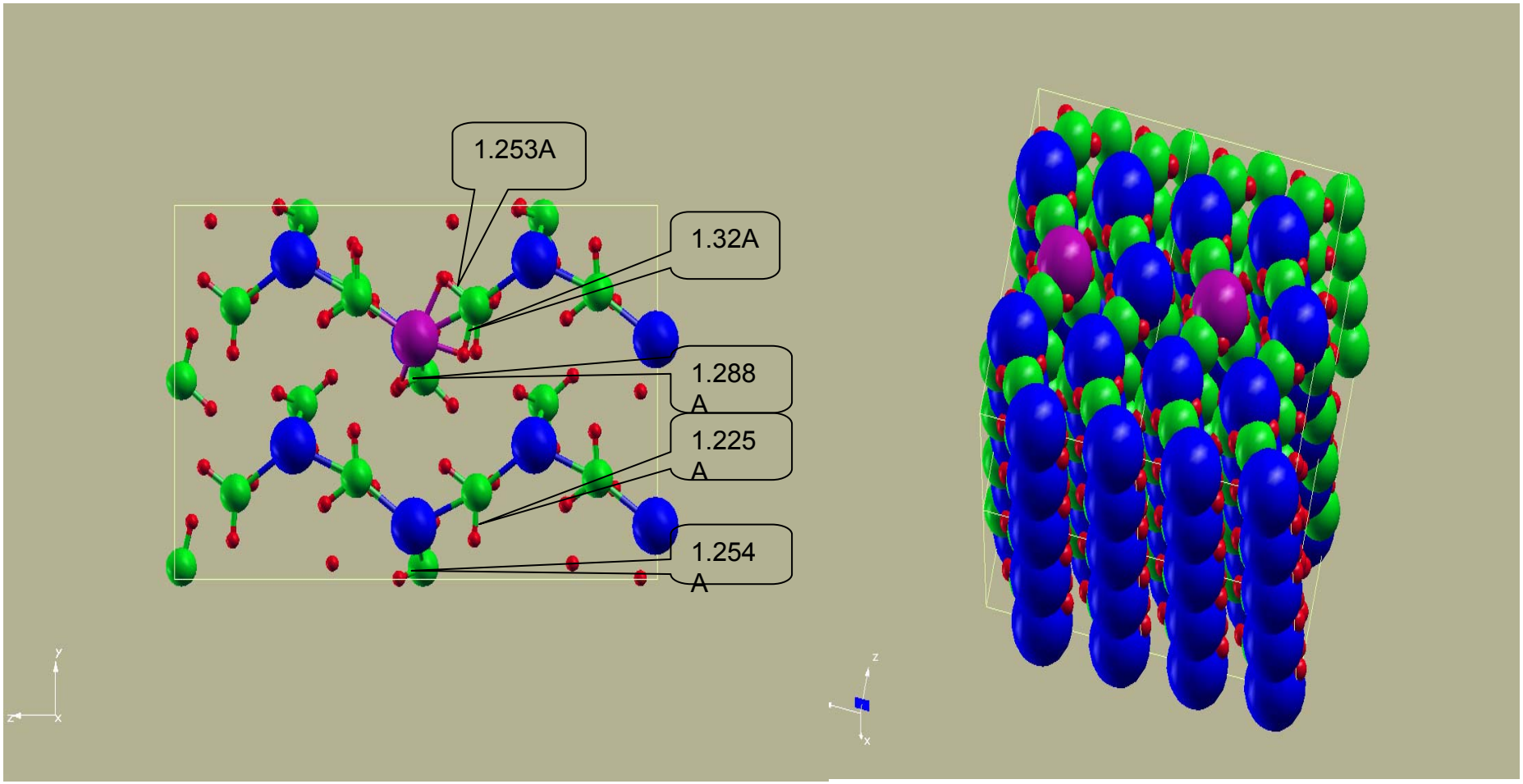
Our calculations showed nearly tetrahedral shape of the BH_4 complex with B-H bond lengths $d_{B\text{-}H}$ = 1.20-1.25 Å and H-B-H bond angles $\theta_{H\text{-}B\text{-}H}$ = 104.16-120°.

Ni doping to $Zn(BH_4)_2$



The cohesive energy calculations indicates that possible substitution of Zn by Ni in $Zn(BH_4)_2$ produces a more stable structure than Ni substitution of B.

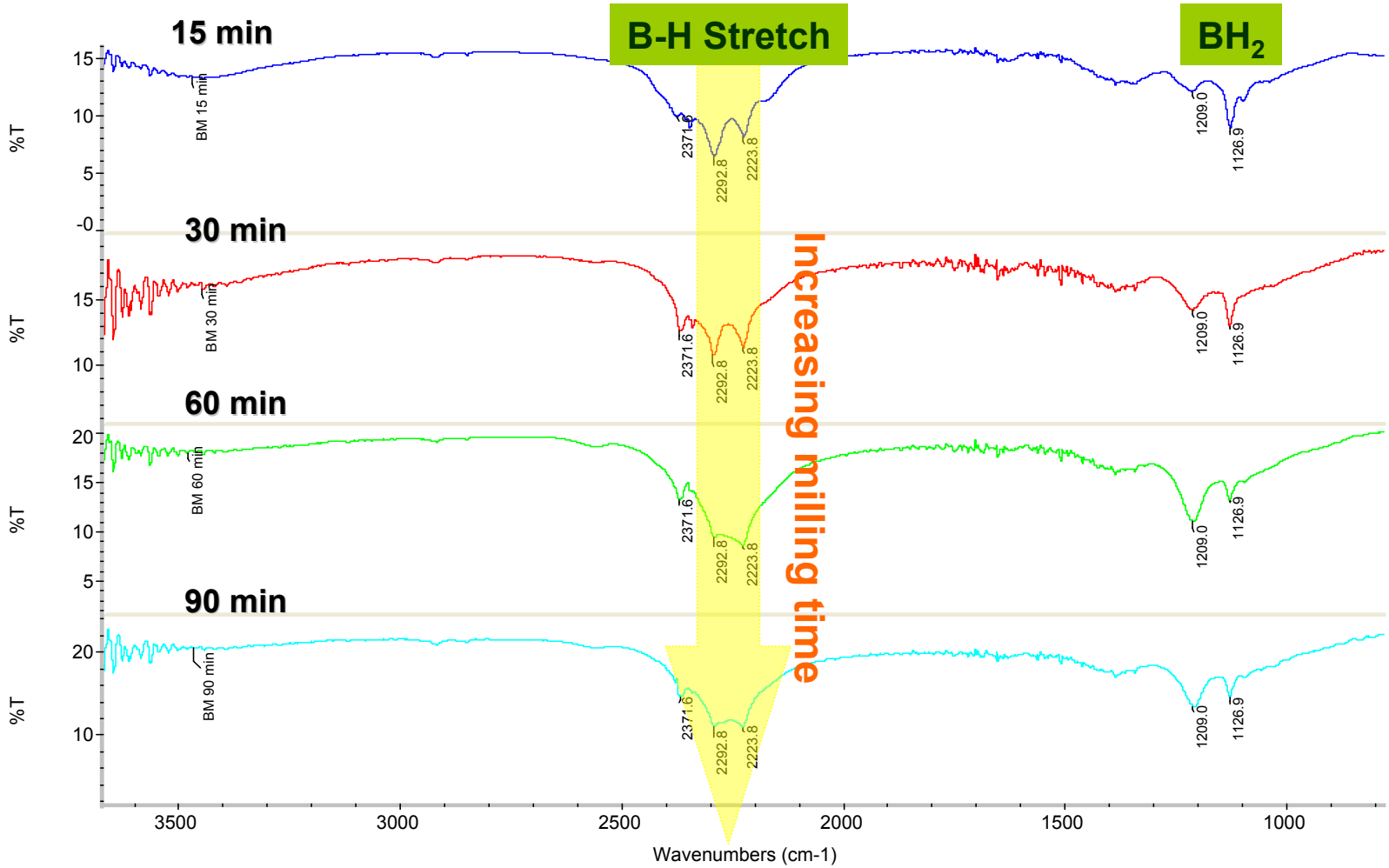
Ni doping to $Zn(BH_4)_2$



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

$Mn(BH_4)_2$ - FTIR

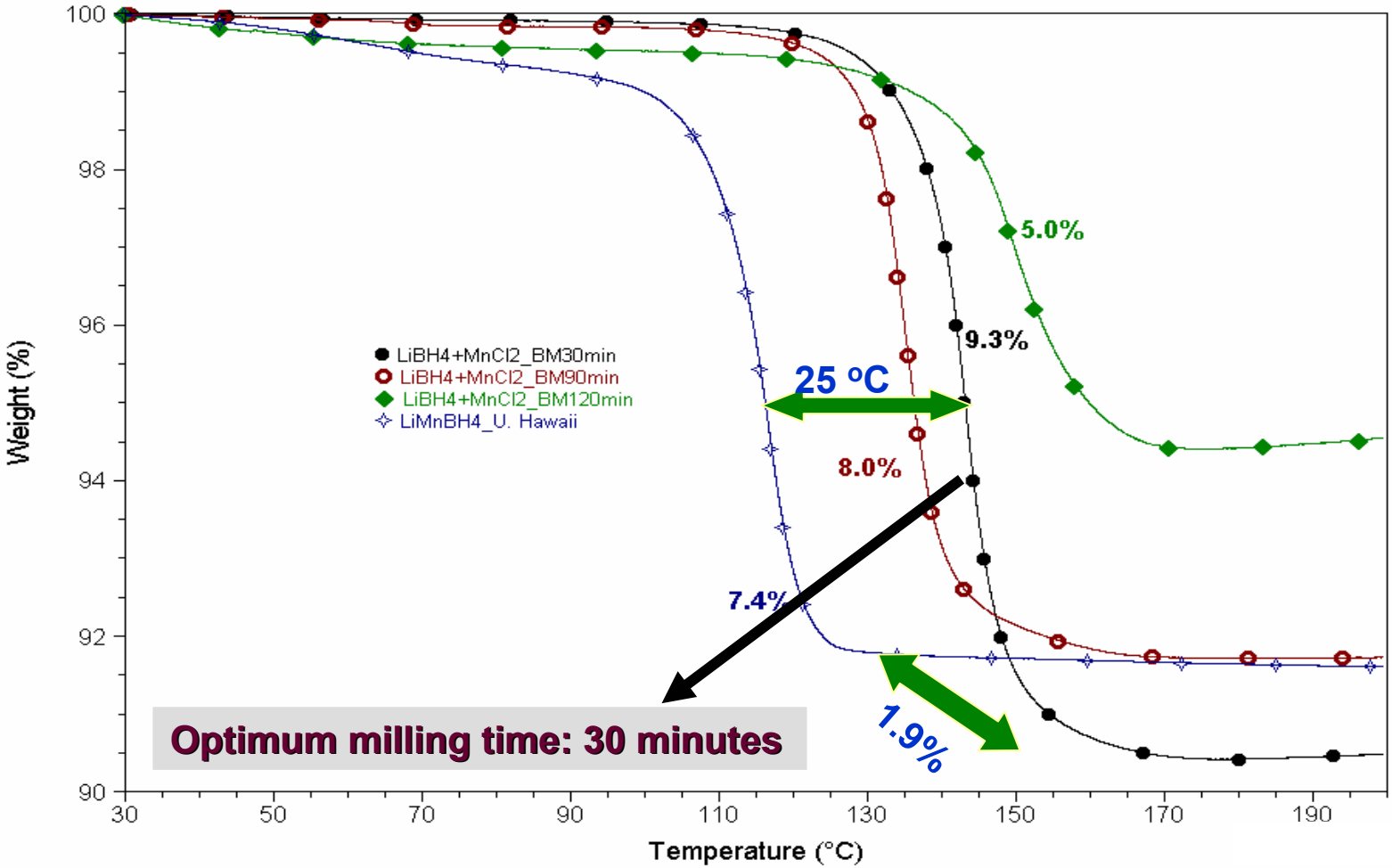
$$MnCl_2 + 2LiBH_4 \rightarrow Mn(BH_4)_2 + 2LiCl$$



Increasing ball milling time creates well defined B-H stretches at around 2300 cm^{-1}

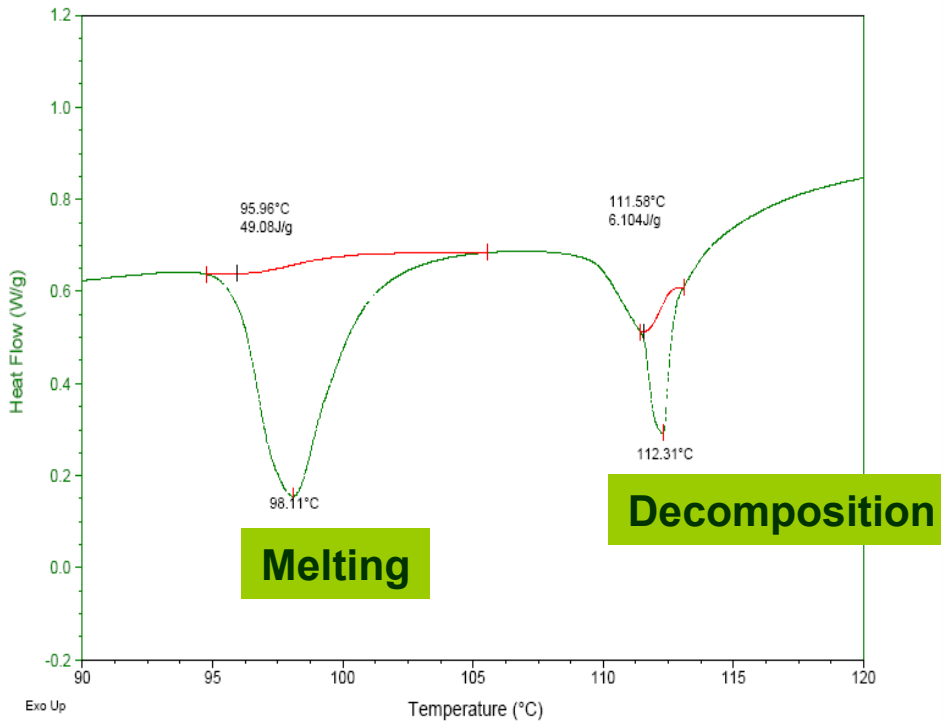
$Mn(BH_4)_2$ - SDT

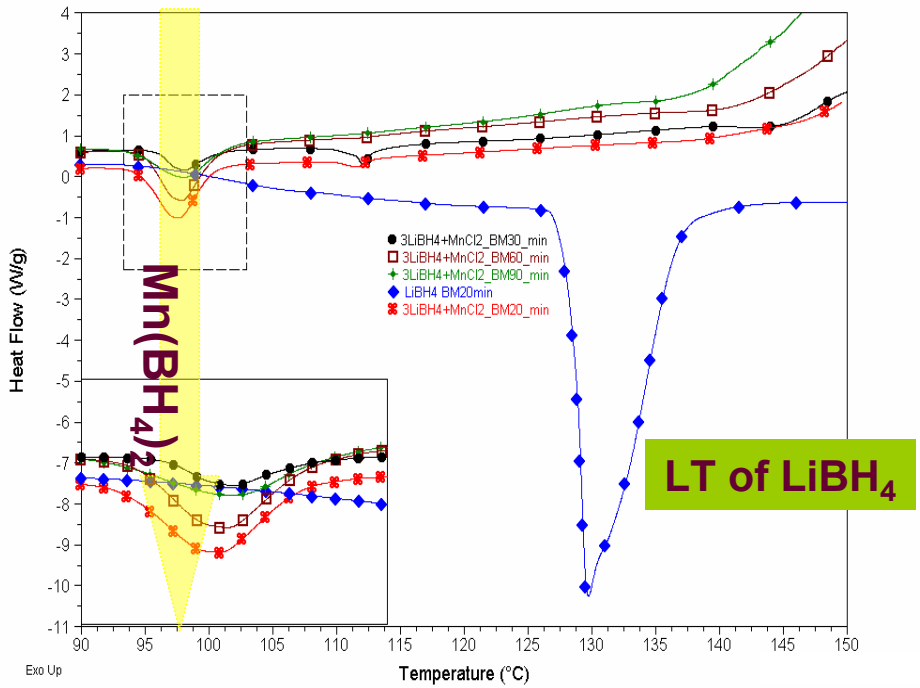
$MnCl_2 + 2LiBH_4 \rightarrow Mn(BH_4)_2 + 2LiCl$



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

$Mn(BH_4)_3$ - DSC



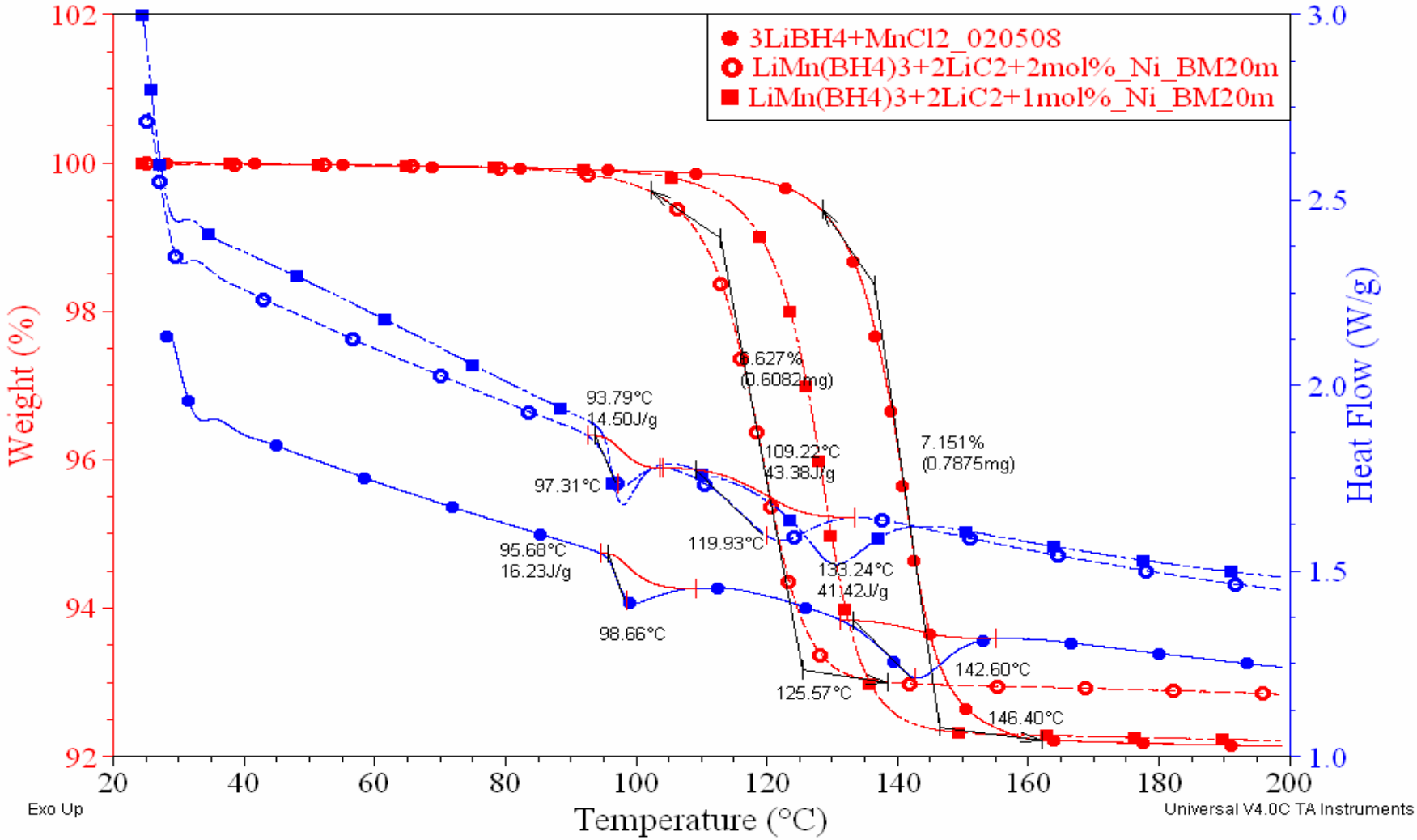


An endothermic melting and decomposition transition occurs at temperatures lower than 150 °C

When compared to $LiBH_4$, $Mn(BH_4)_3$ exhibit low temperature hydrogen decomposition with >8 wt%

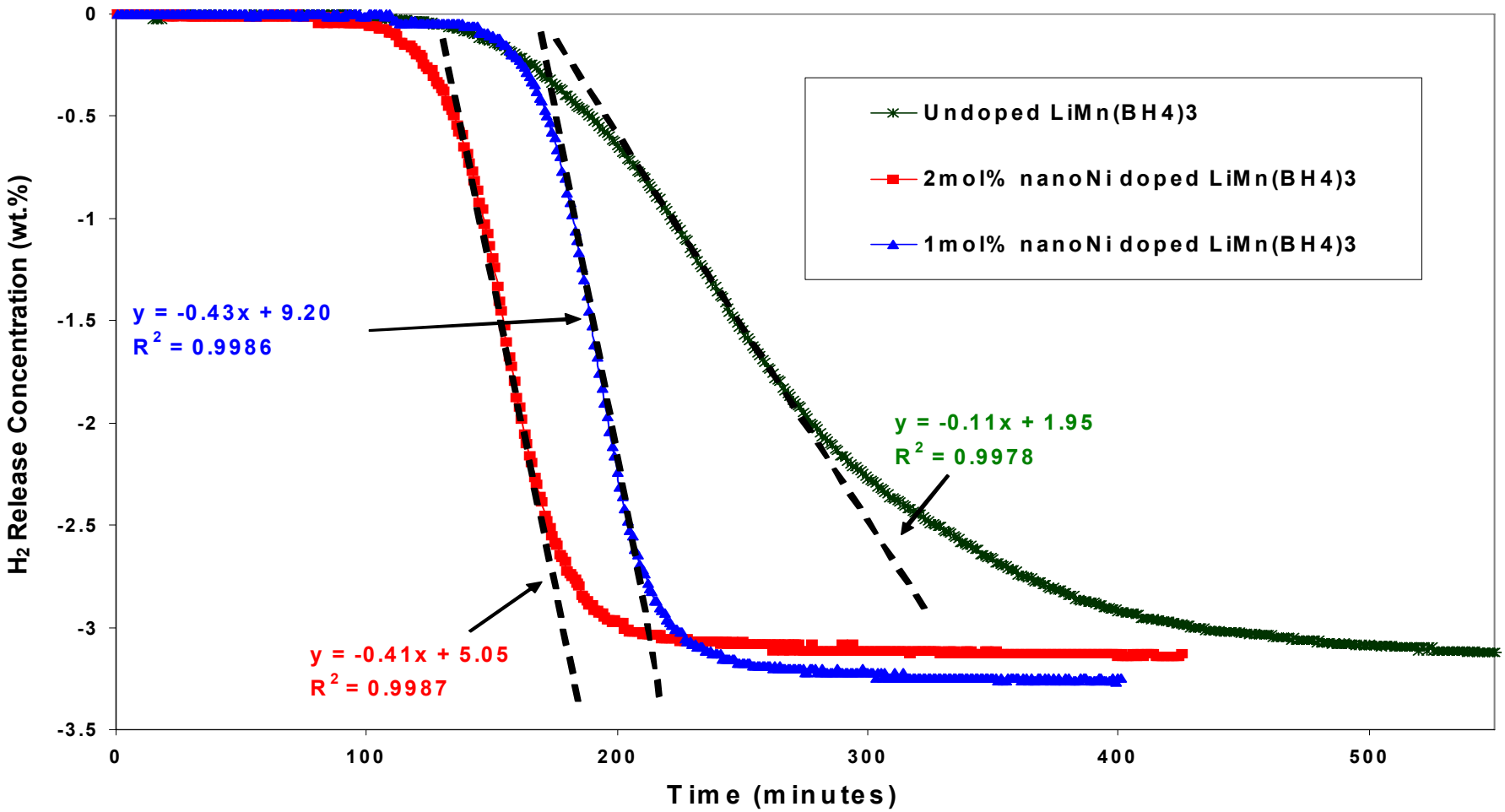
$$MnCl_3 + 3LiBH_4 \rightarrow Mn(BH_4)_3 + 3LiCl$$

Ni doped $Mn(BH_4)_3$ - SDT



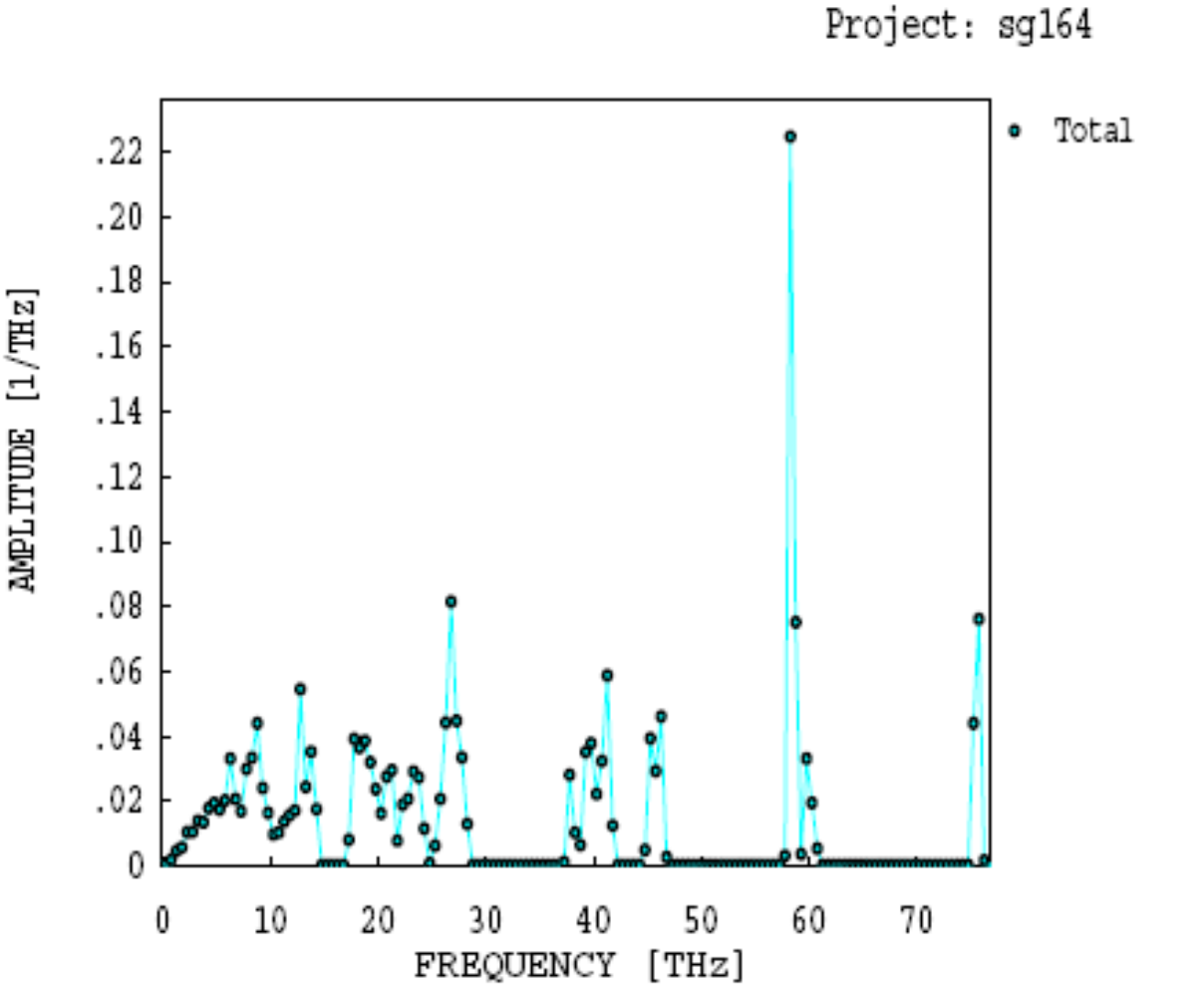
Ni doping of 1-2 mol% destabilizes the structure with at least 10-20 °C reduction in hydrogen T_{dec}

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 $Mn(BH_4)_2$

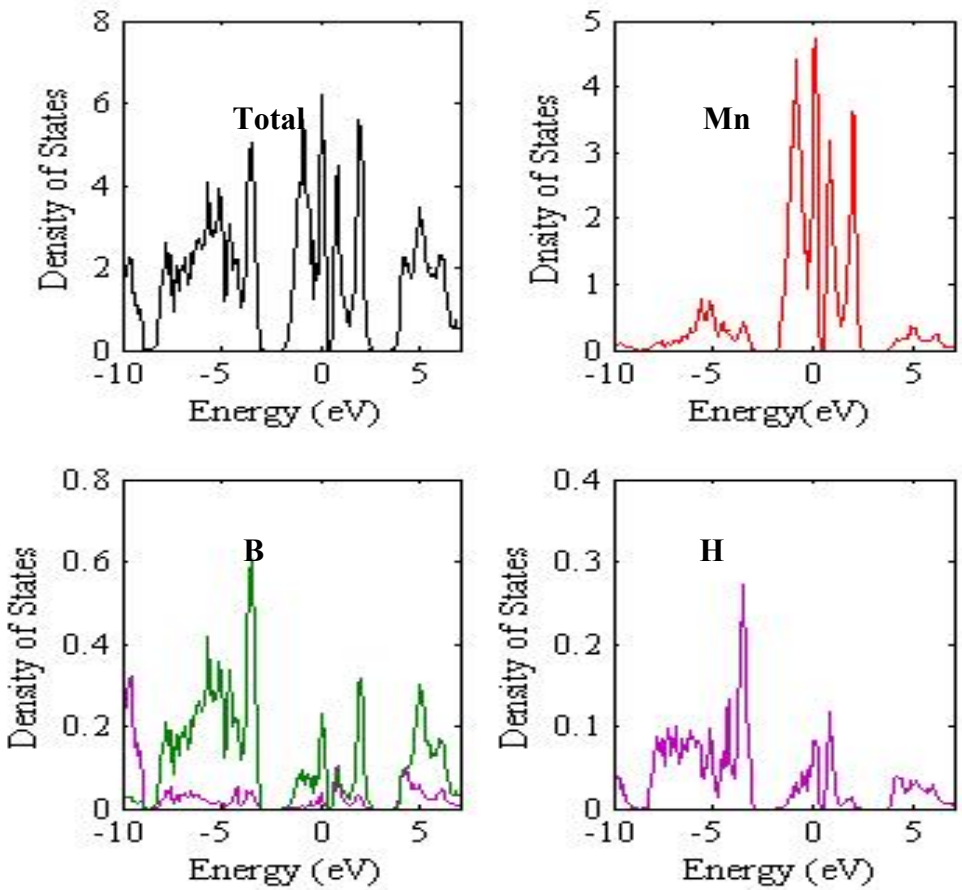


Phonon density of states confirms the stability of $Mn(BH_4)_2$ exists at finite temperature.

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

$$\int g(w)dw = 1$$

Electronic Structure of $Mn(BH_4)_2$

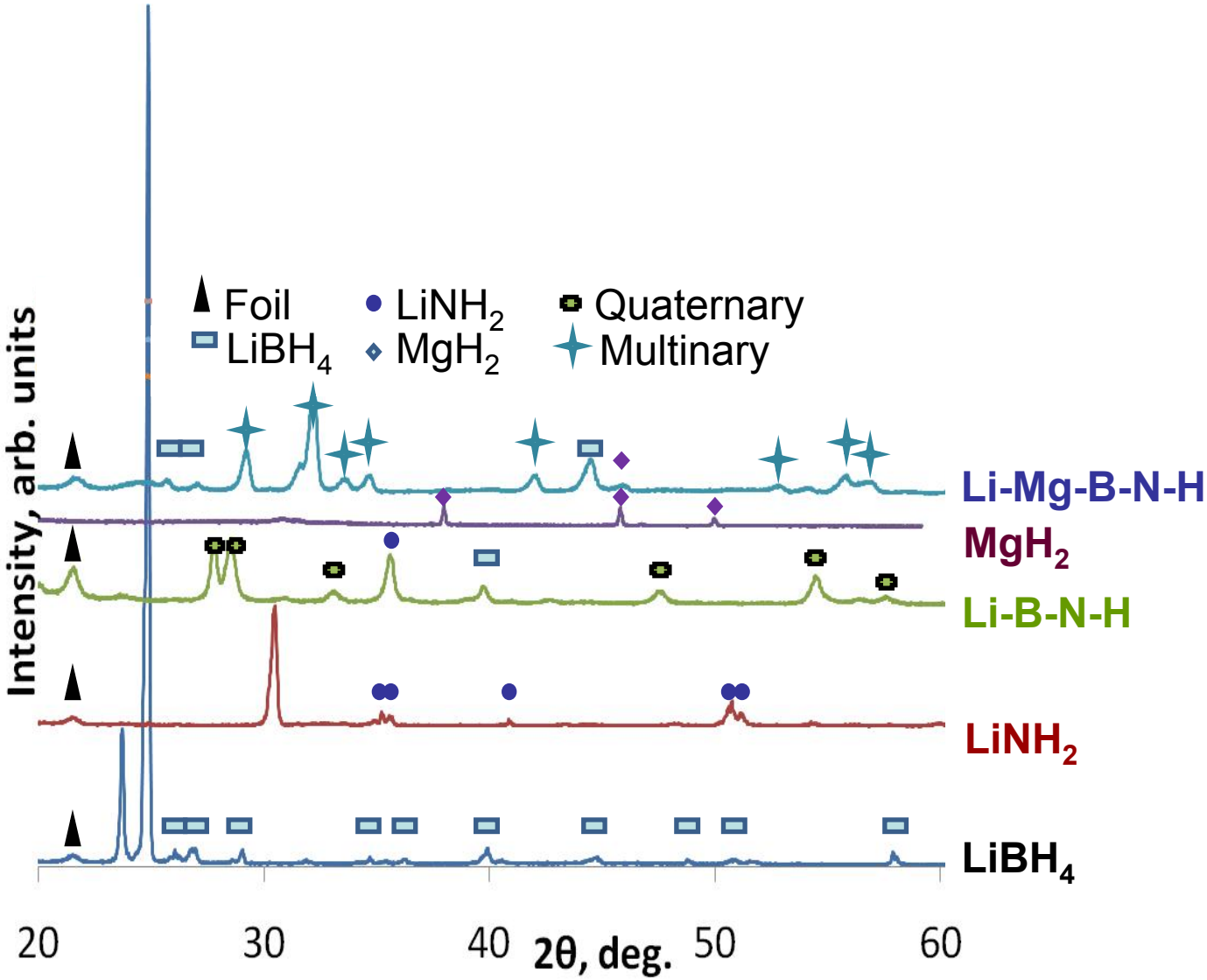


s orbital
p orbital
d orbital

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

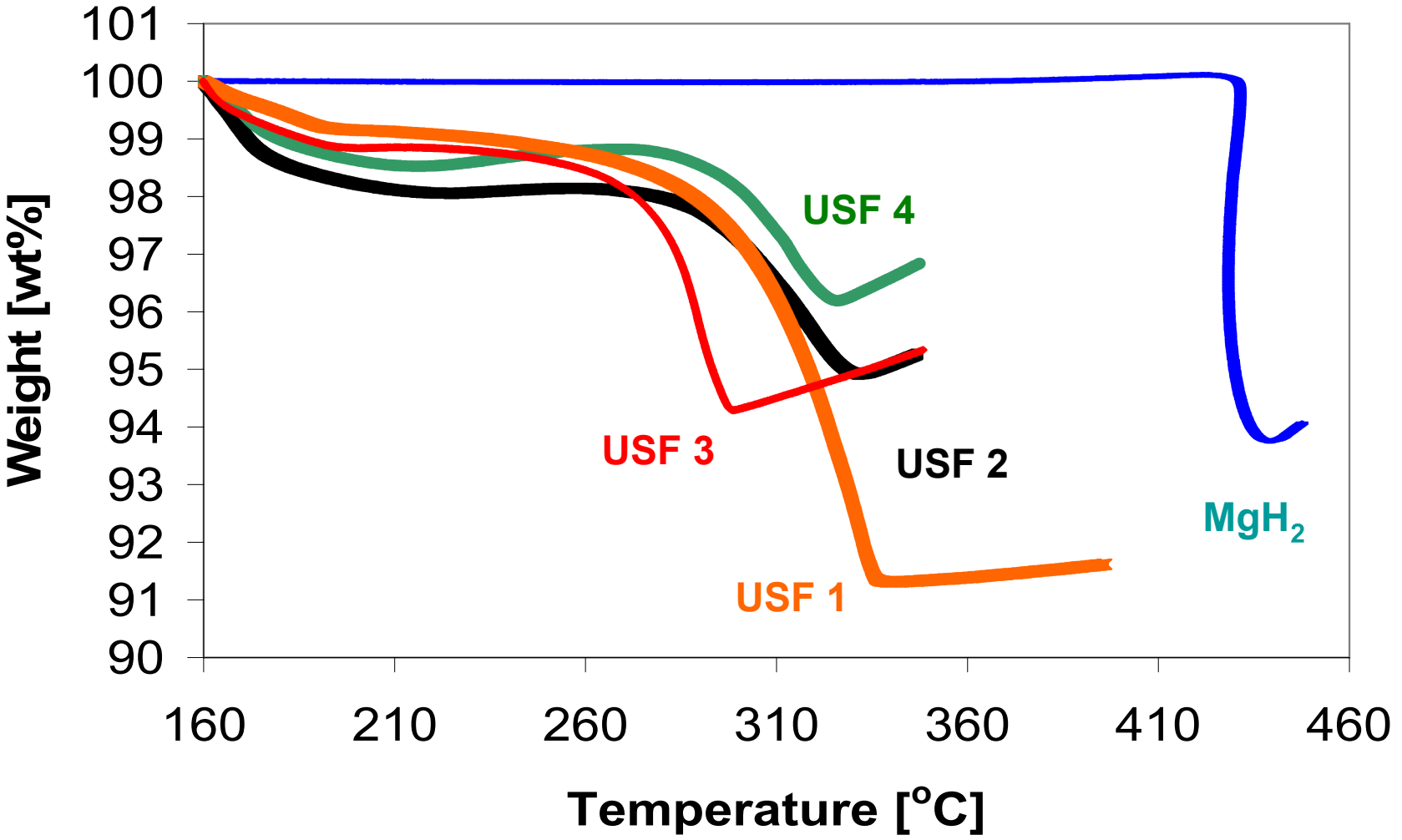
Total and partial DOS of $Mn(BH_4)_2$: zero energy is considered as Fermi energy level.

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

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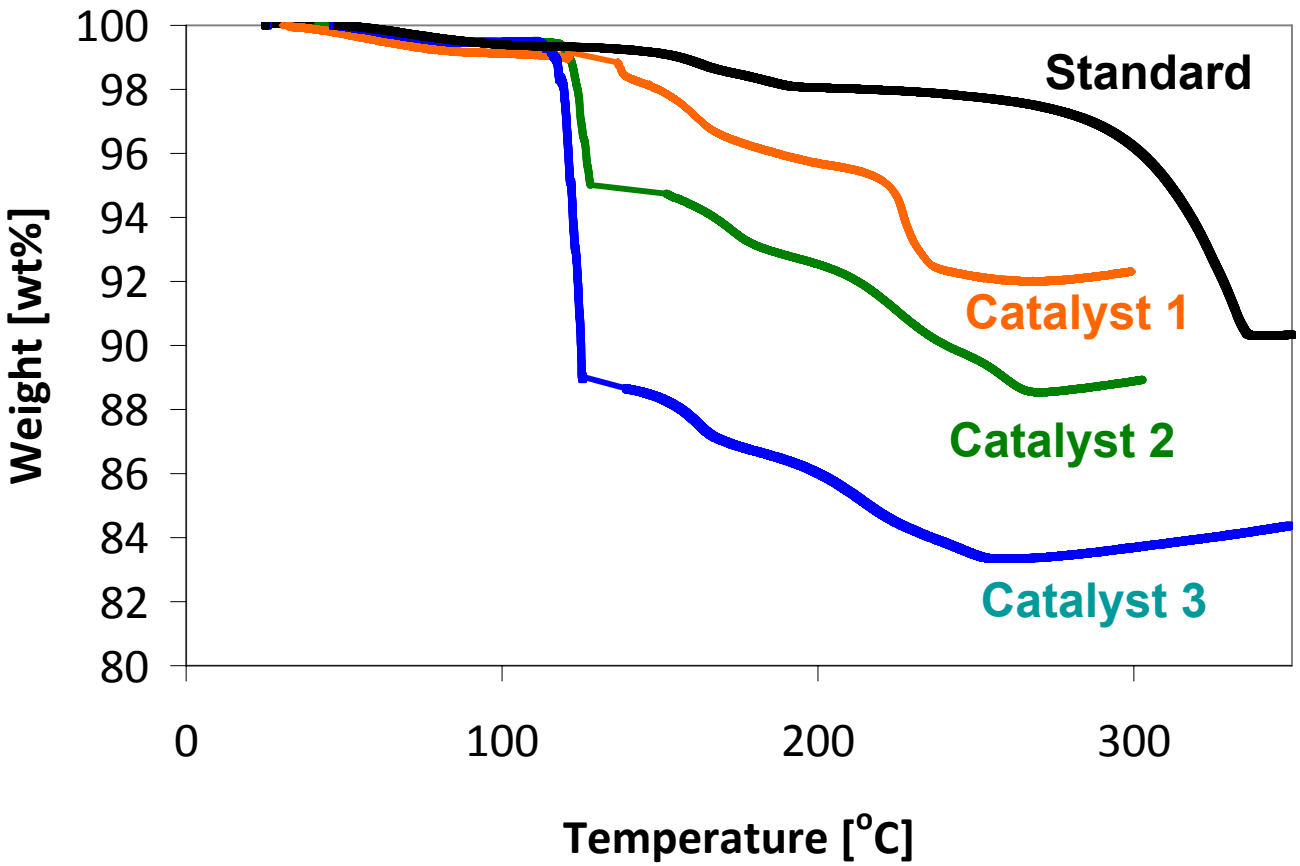
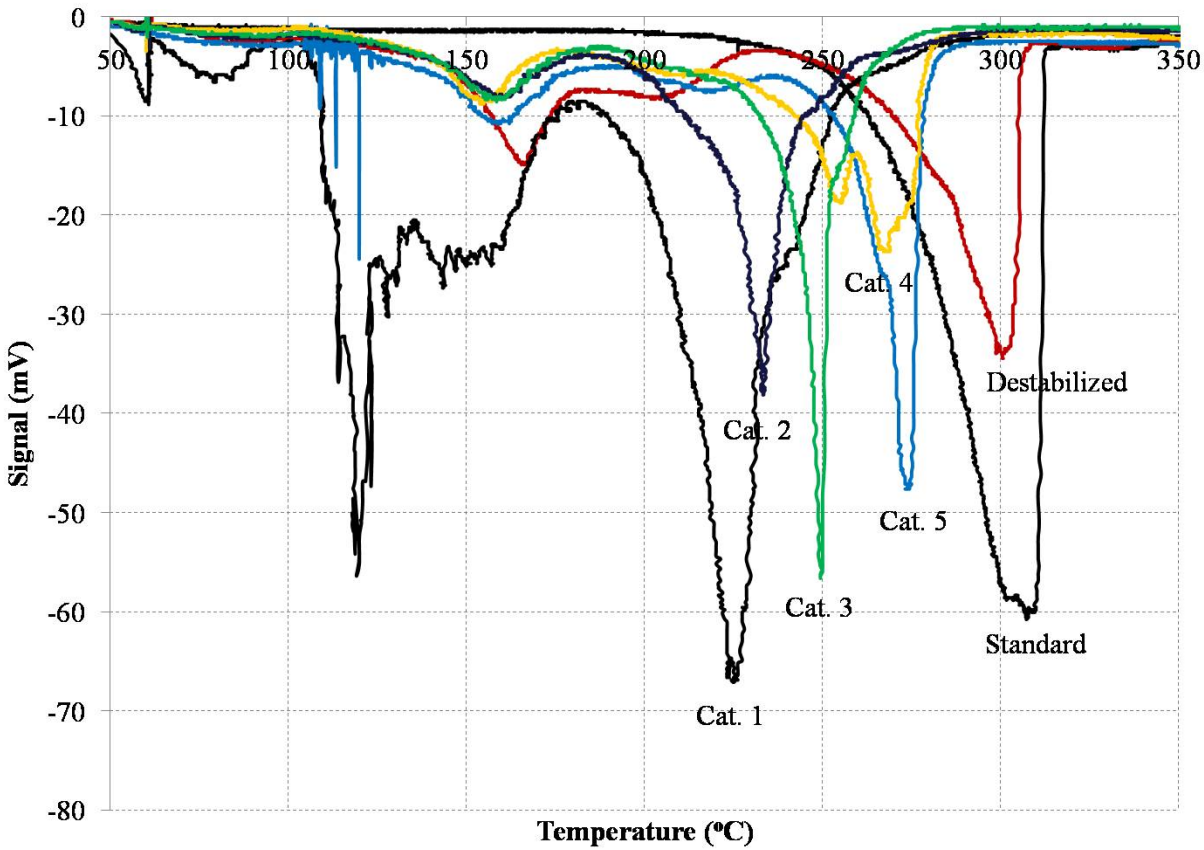
Li-Mg-B-N-H / Catalysts - TGA



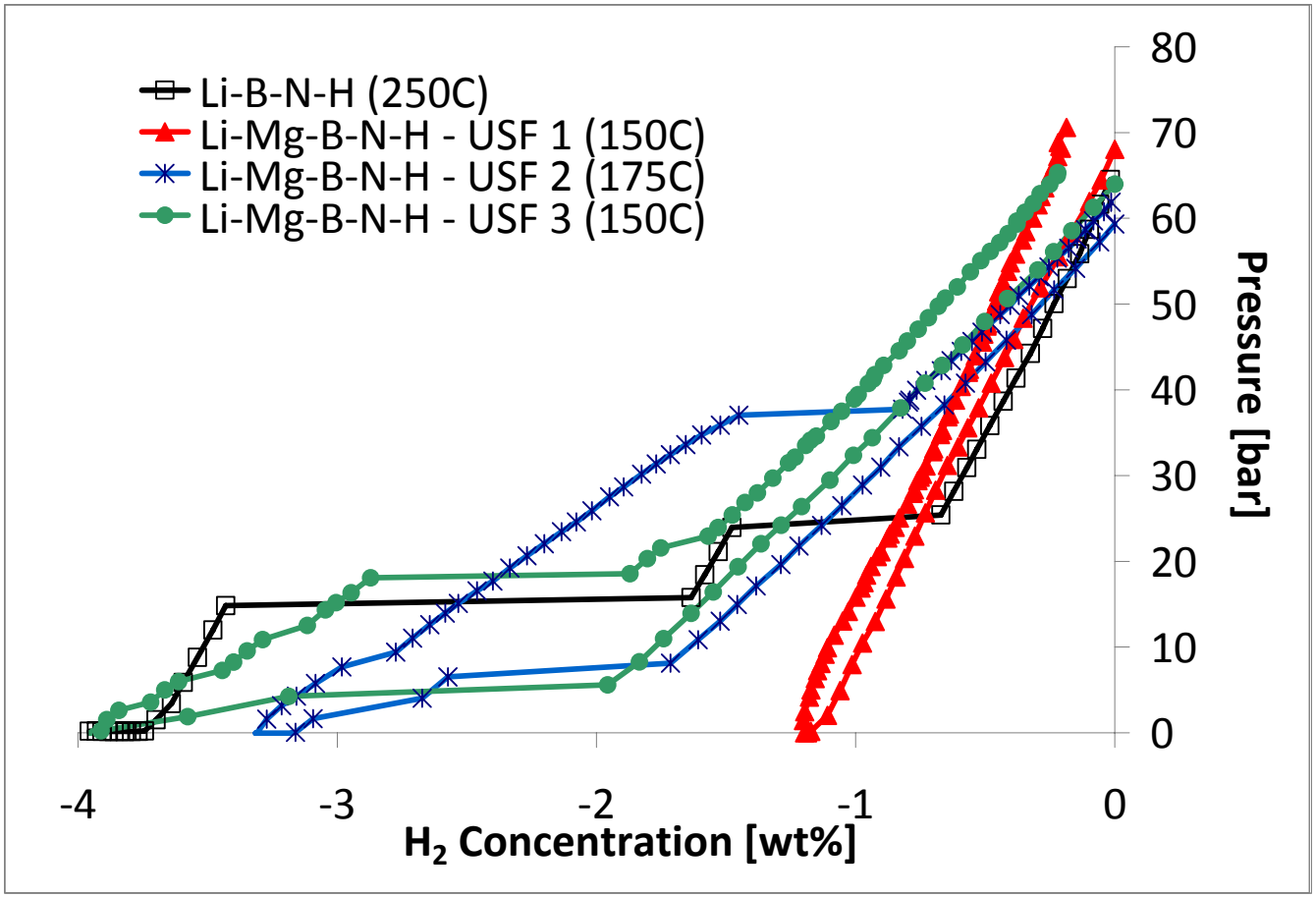
- Decomposition temperature reduced
- Gravimetric weight loss increased significantly
- Hydrogen performance testing underway

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



- Standard destabilized with 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%

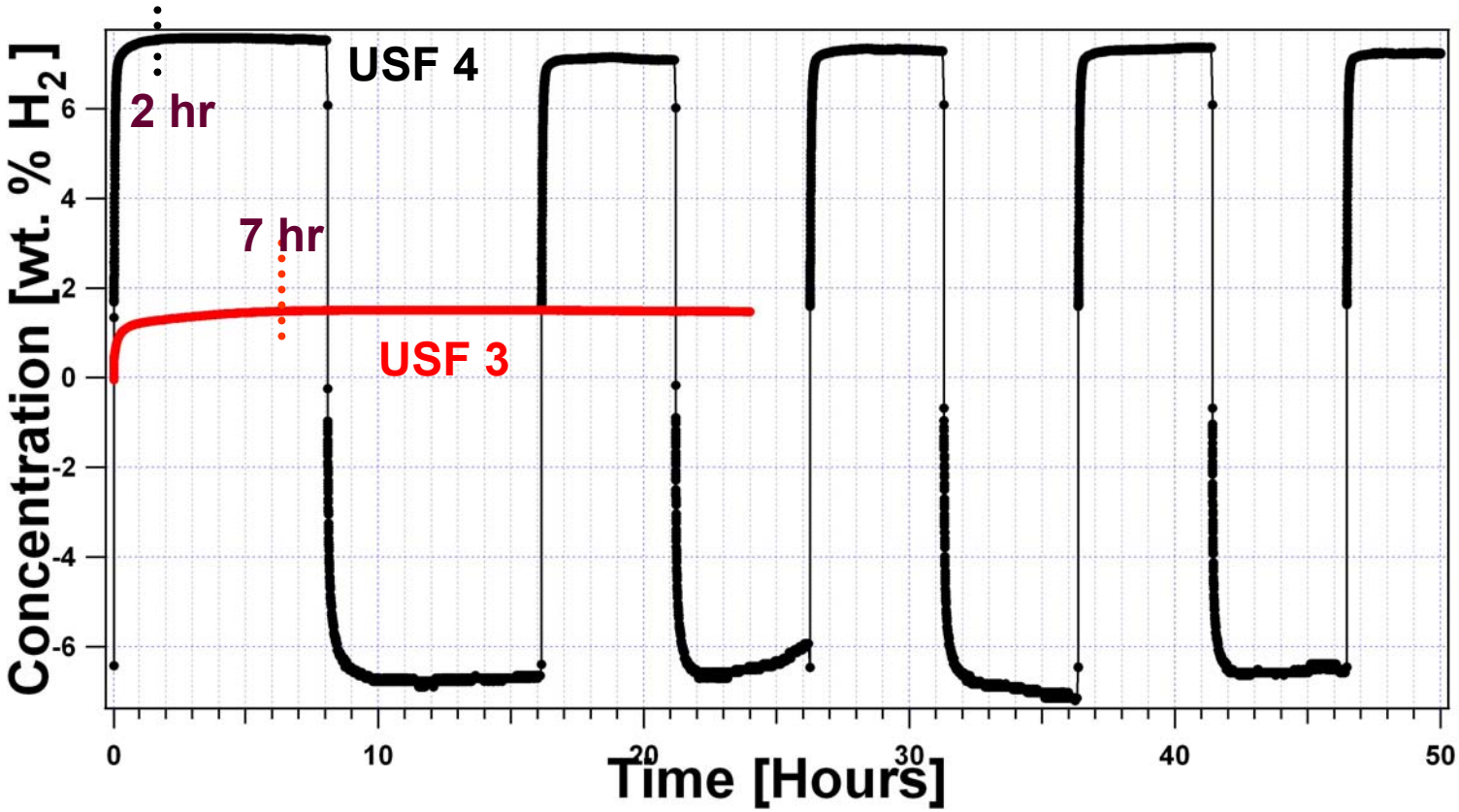
Li-Mg-B-N-H (USF 1)
- reversibility at 150 °C
- 1.2 wt%
- 4 hr for 1.2 wt%

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%

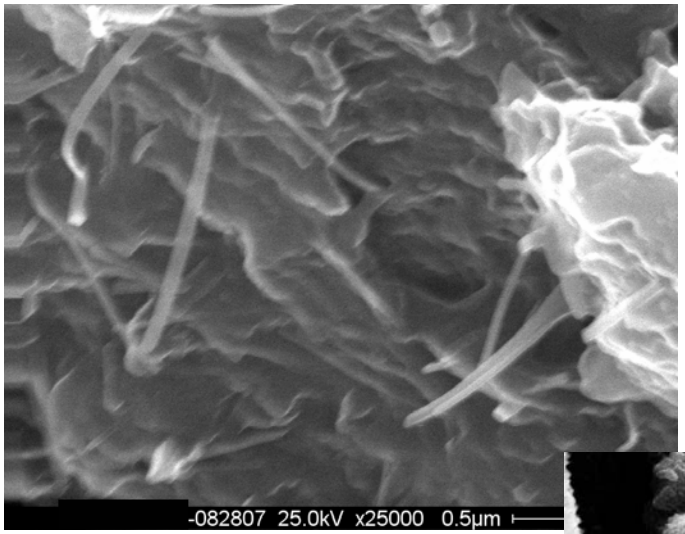
Temperature decreased from 250 °C to 150 °C; Reversibility increased from non-reversible to reversible

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

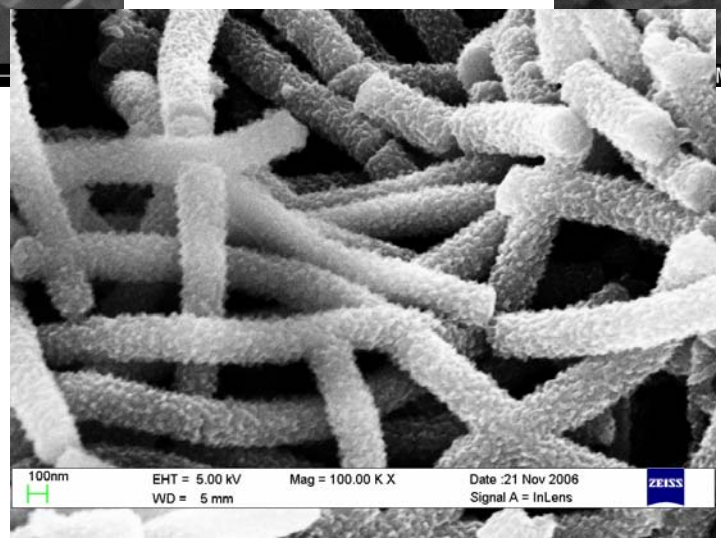


- Significant increase in capacity
- Full sorption reached after less than 2 hr compared to 7 hr for USF 1-3
- >80% capacity reached within 5 minutes

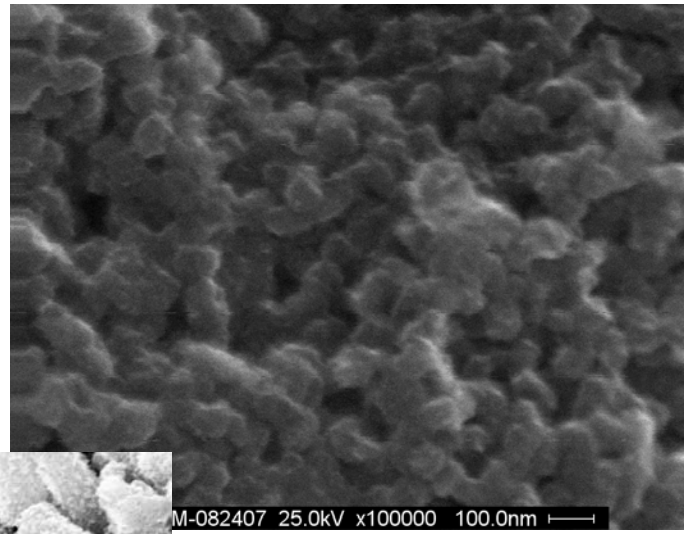
PANI Nanostructures



PANI 1



PANI 2



PANI 3

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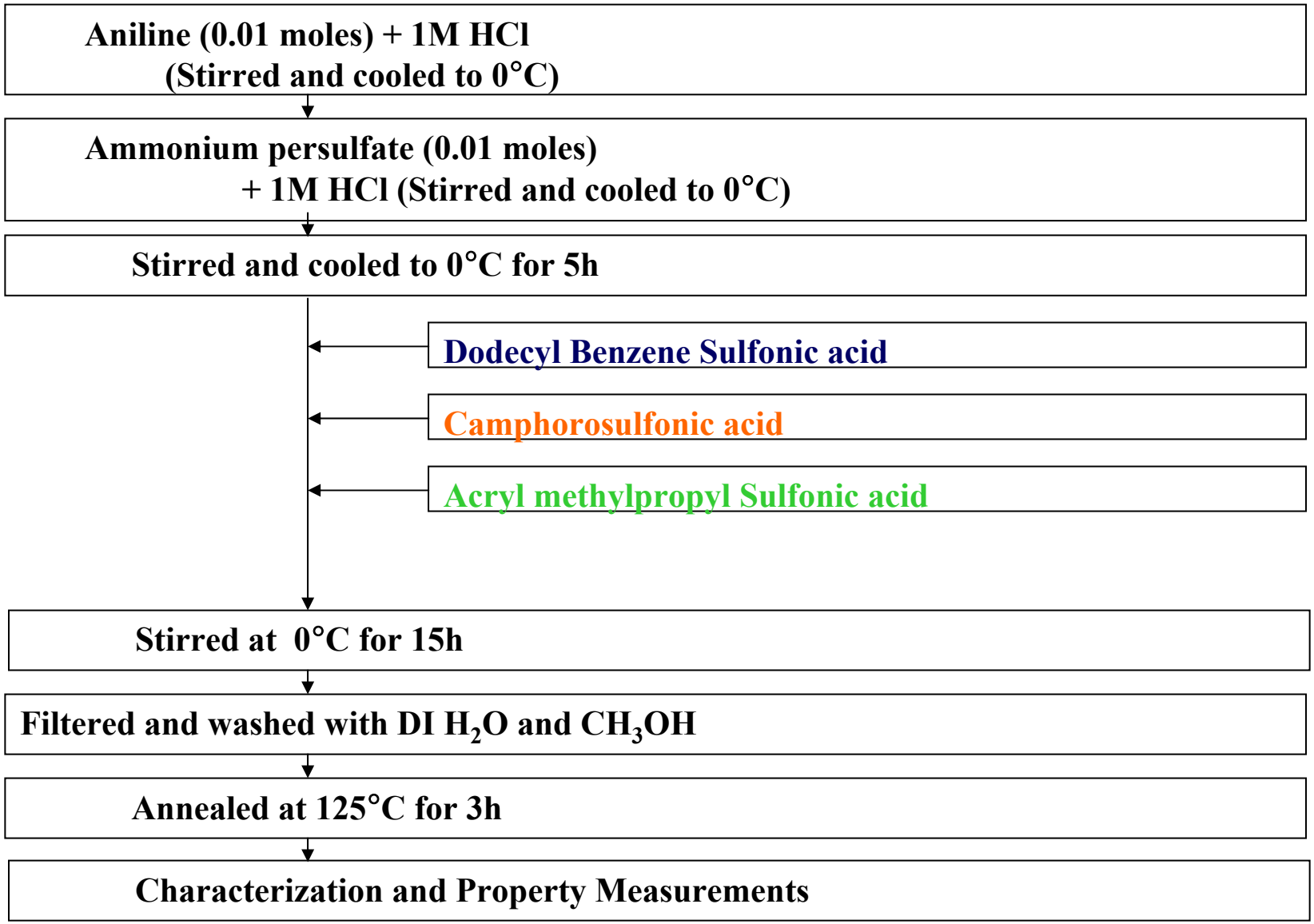
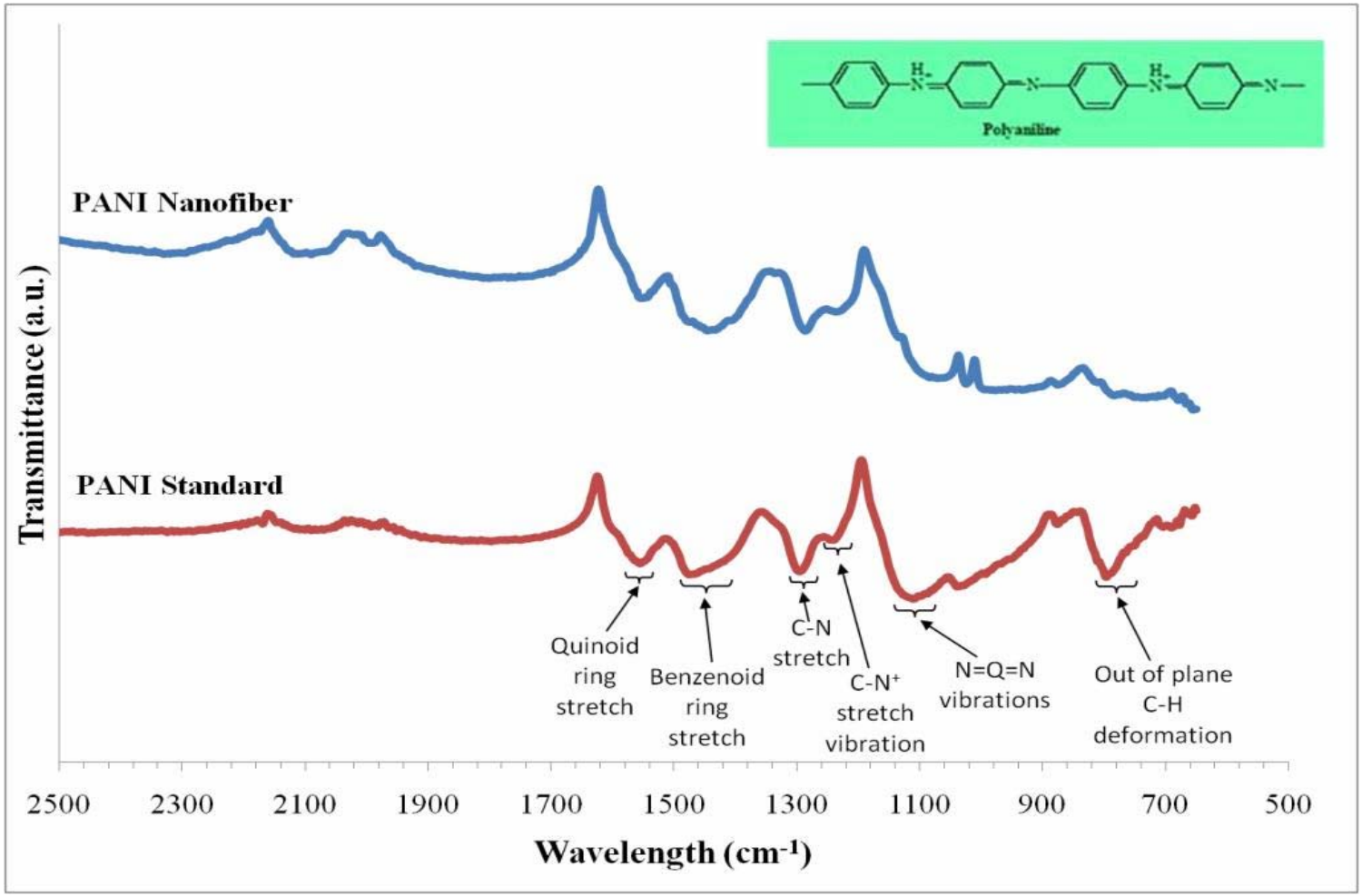
PANI1 Synthesis

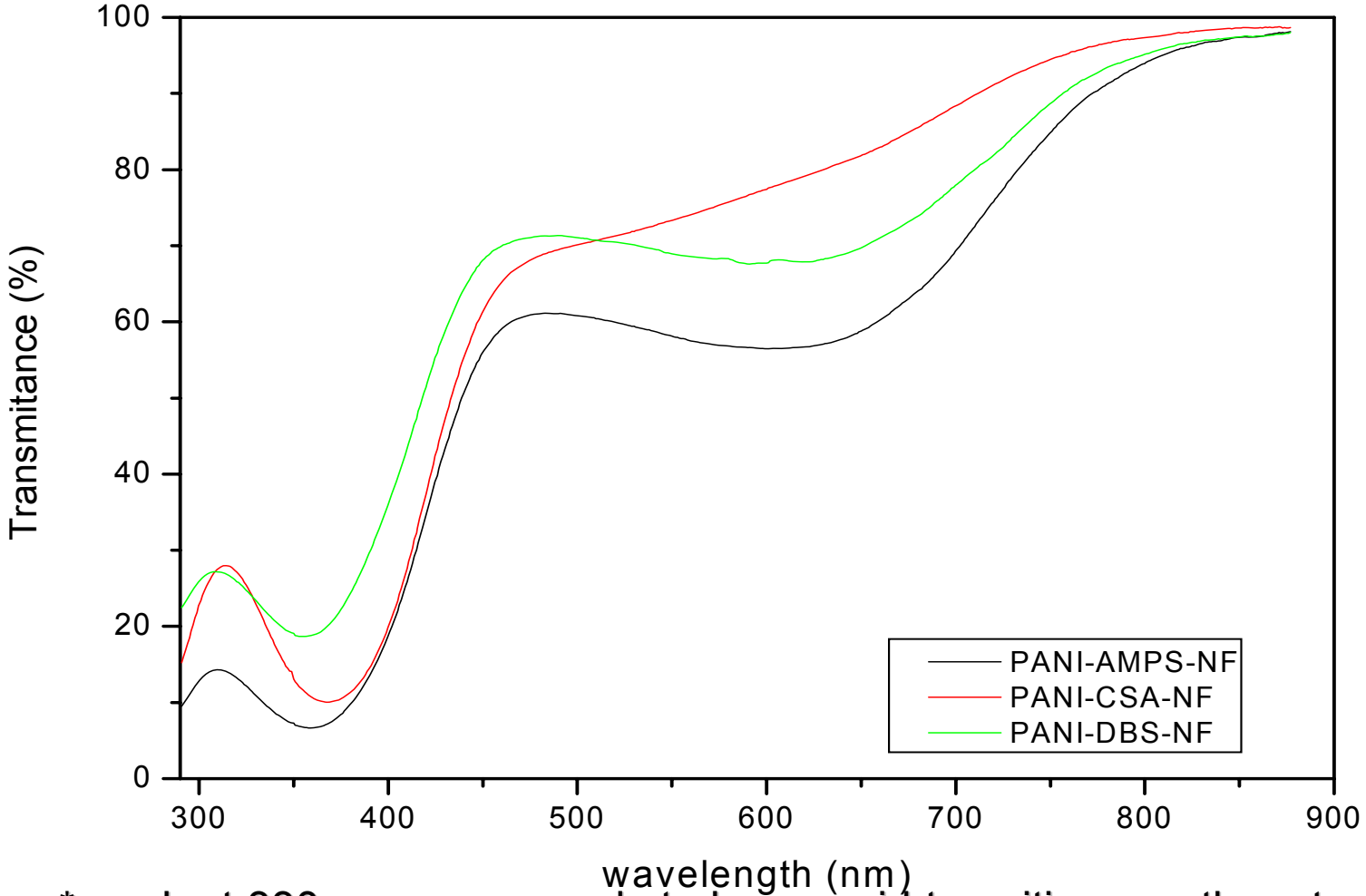


PANI1 - FTIR



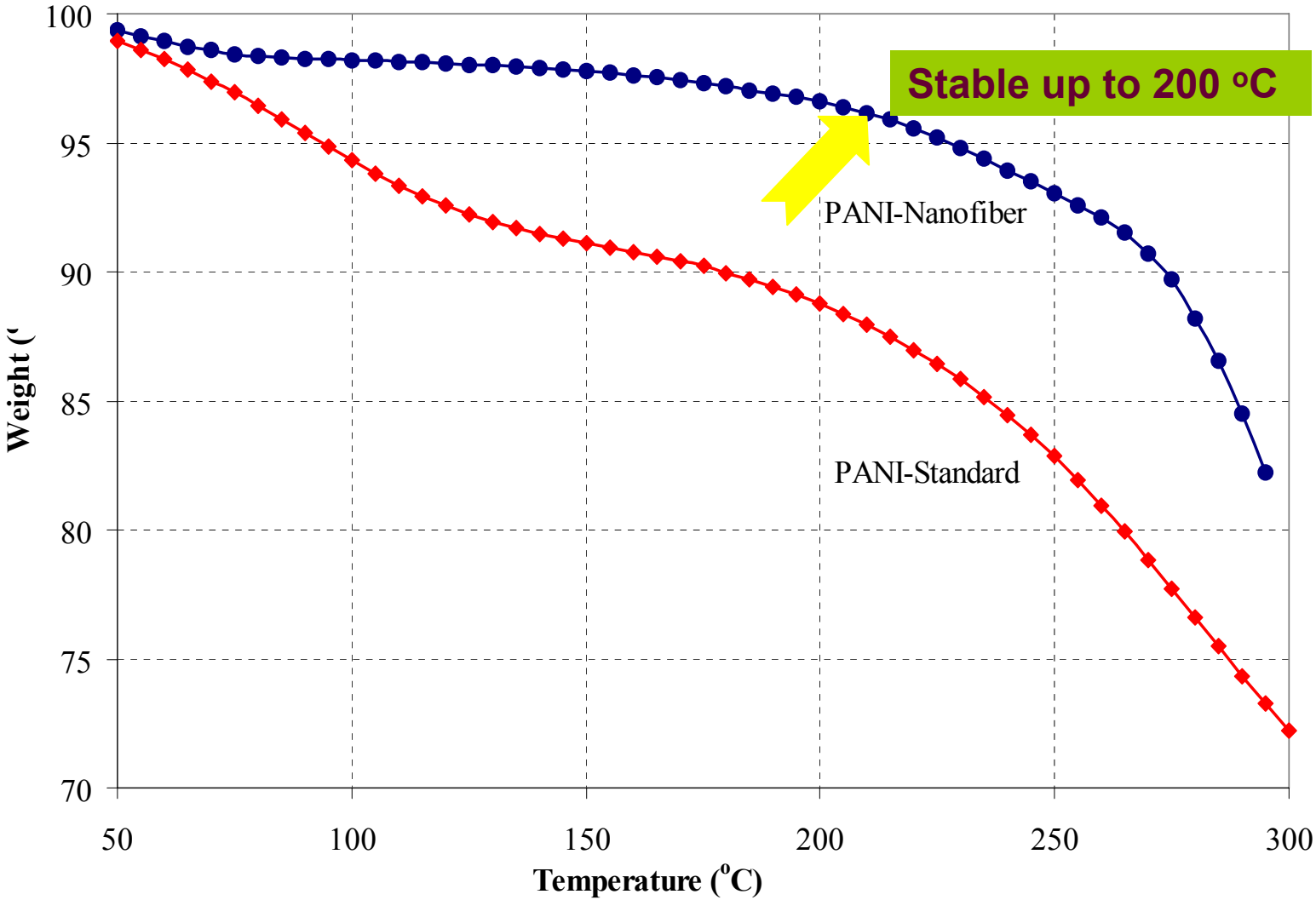
The signature bands of benzenoid and quinoid transitions in the vicinities of 1500 cm^{-1} and 1600 cm^{-1}, respectively, as evidenced from FTIR confirms the formation of polyaniline structure irrespective of the surfactants used in the precursor preparation.

PANI1 – UV-Vis



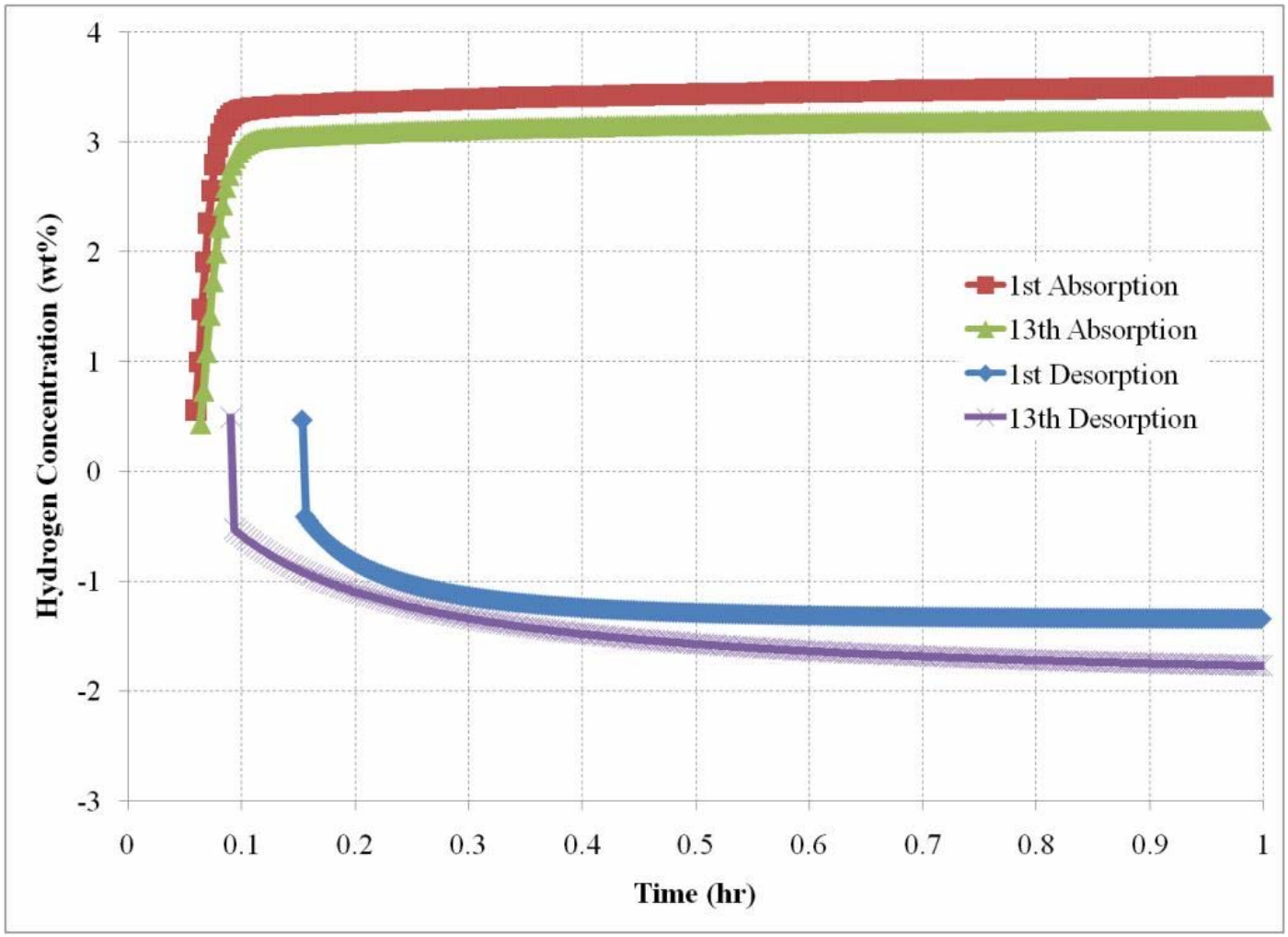
Strong π-π* peak at 330 nm corresponds to benzenoid transition, another strong π-π* peak at 630 nm corresponds to benzenoid to quinoid transition indicating the synthesized polymer was polyaniline in oxidized form.

PANI 1- TGA



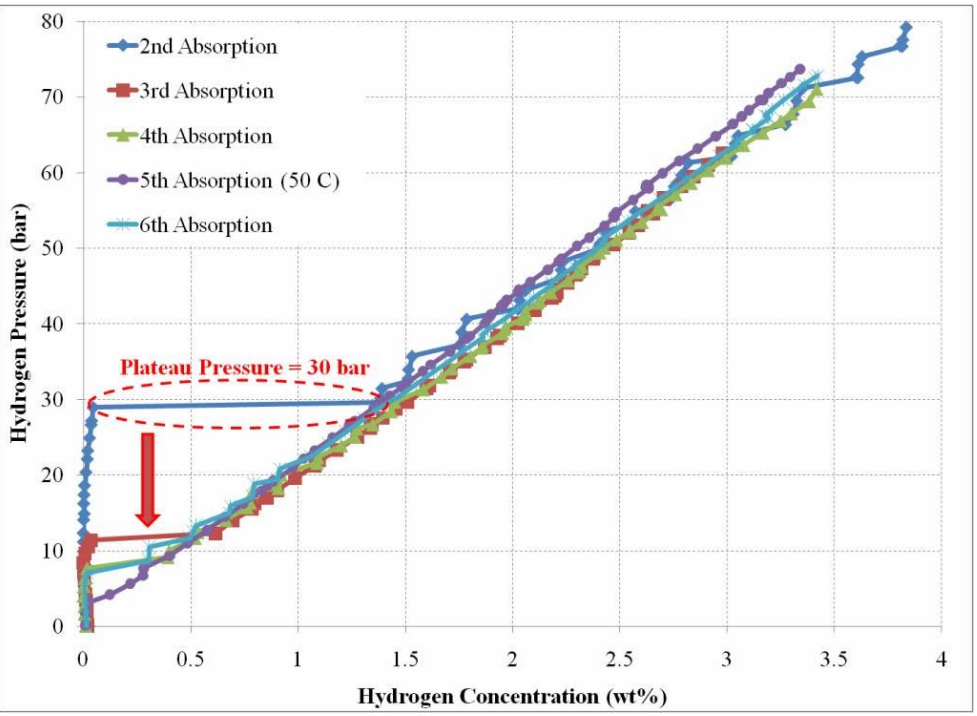
The thermogravimetric analysis reveals that these PANI nanofibers are stable up to 200 oC due to their high density nanofibrous matrix.

PANI 1 – KINETICS at Room Temperature



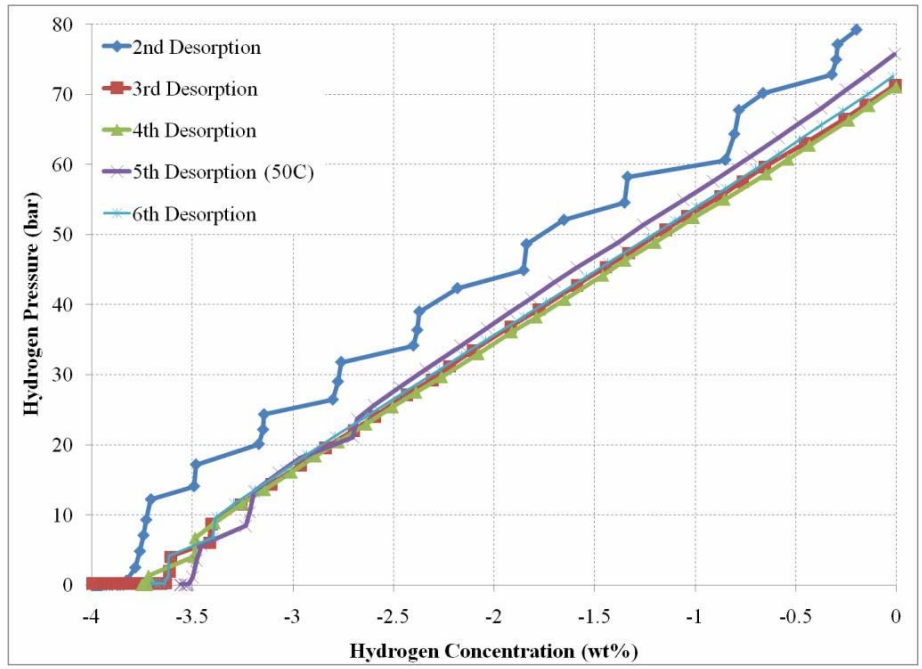
Hydrogen absorption and desorption kinetics of PANI-NF in initial (1st) and 13th cycle: 3 wt/% of hydrogen absorbed by the sample at room temperature.

PANI 1 – PCT at Room Temperature



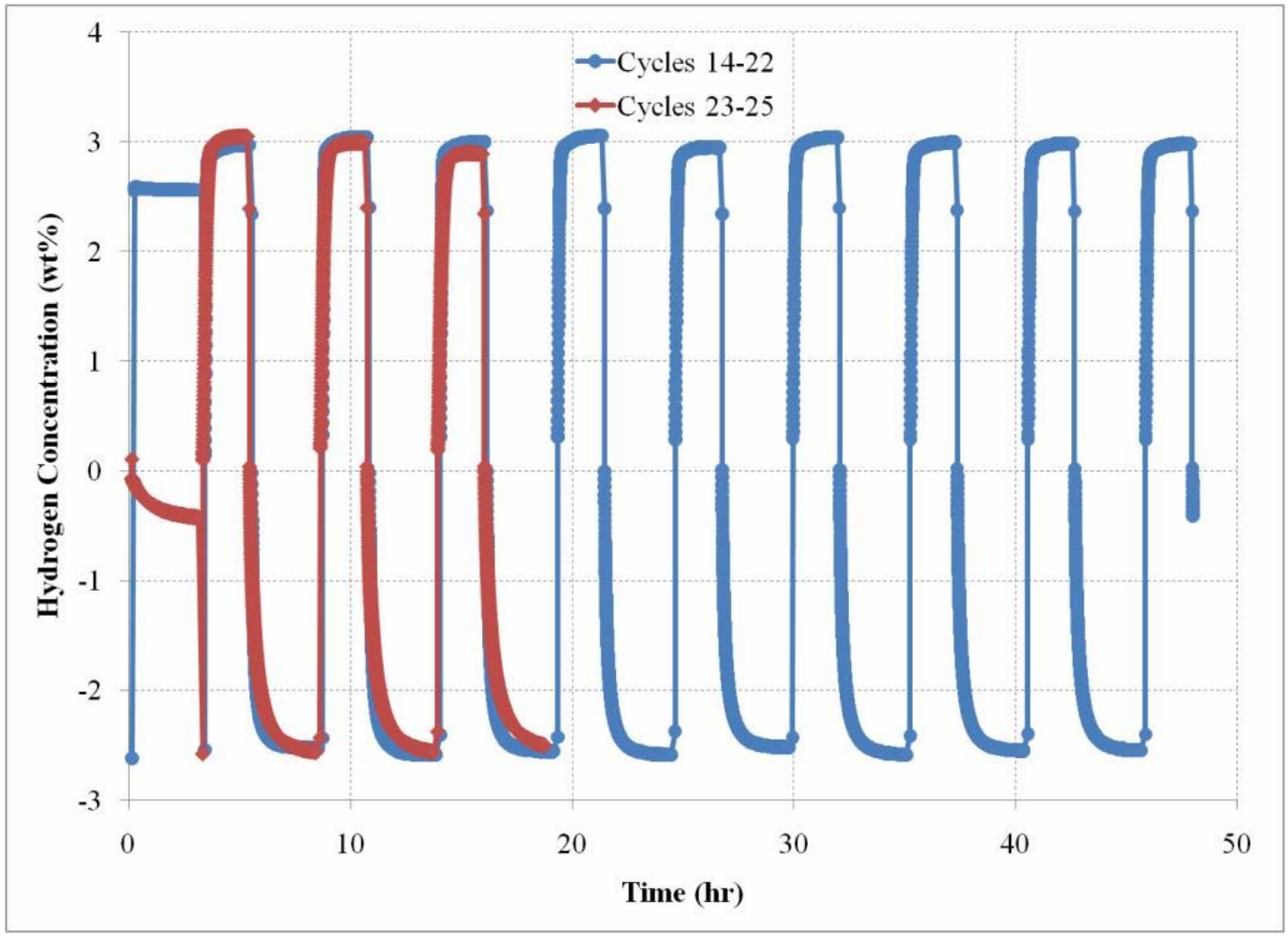
ABSORPTION

DESORPTION



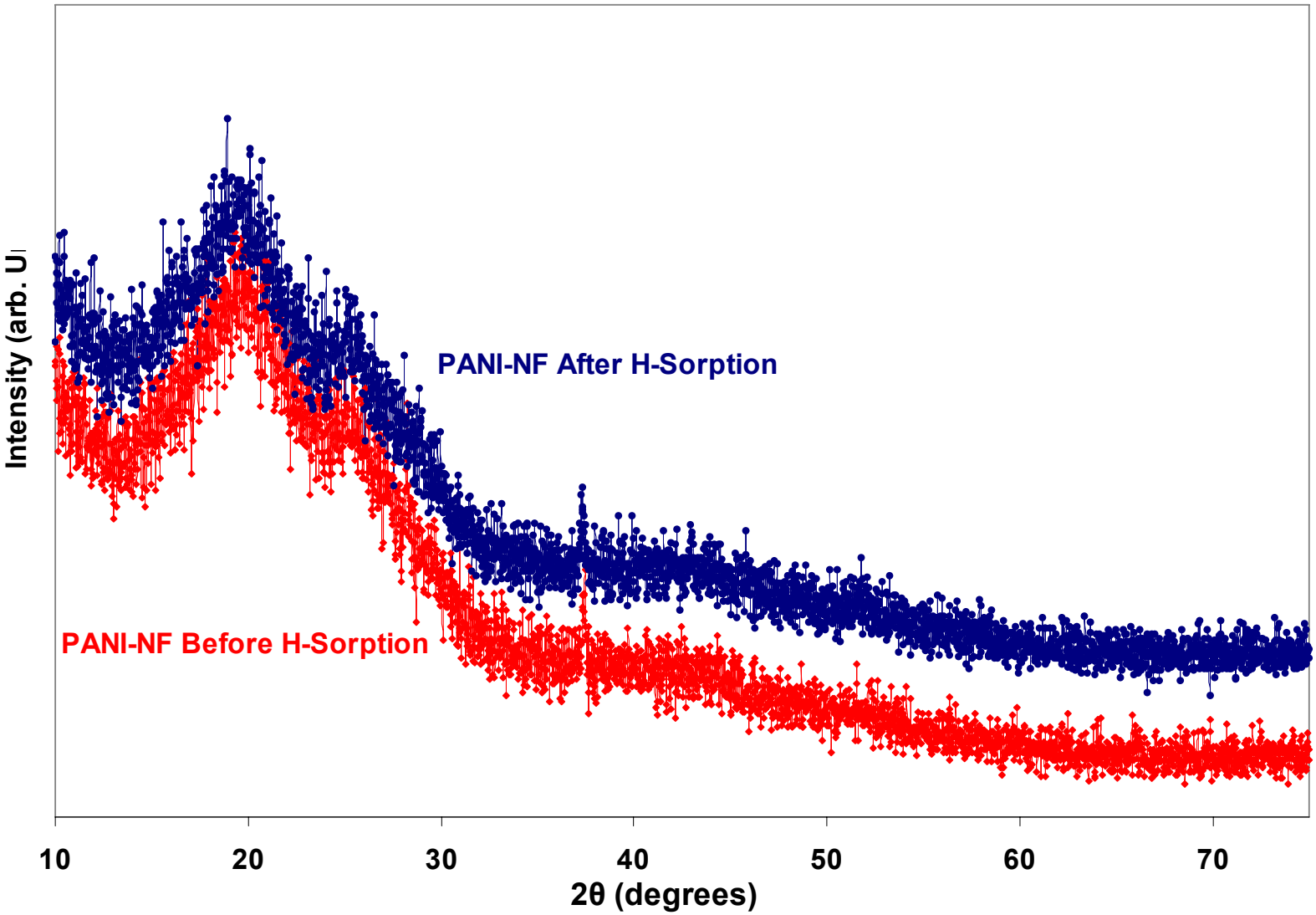
Pressure-Composition Isotherms of PANI-NF at room temperature from 2nd to 6th (a) absorption (b) desorption cycles; Hydrogen absorption plateau pressure of 30 bars was clearly seen in the 2nd absorption PCT and it reduces in the subsequent sorption cycles

PANI 1 - LIFE CYCLE KINETICS at Room Temperature



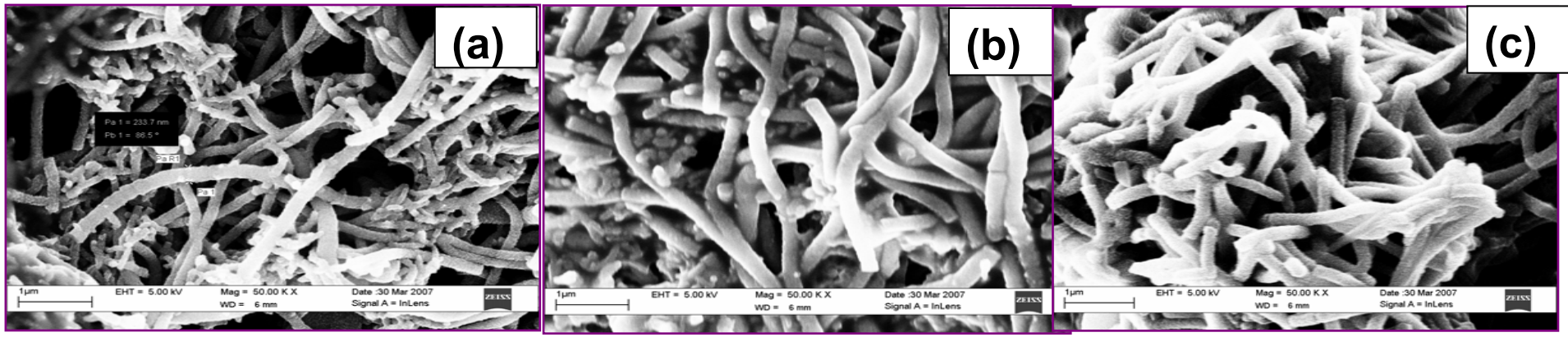
Hydrogen sorption kinetics at room temperature from 14th cycle to 25th cycle. No degradation in the hydrogen sorption kinetics and storage capacity was observed.

PANI 1 - XRD



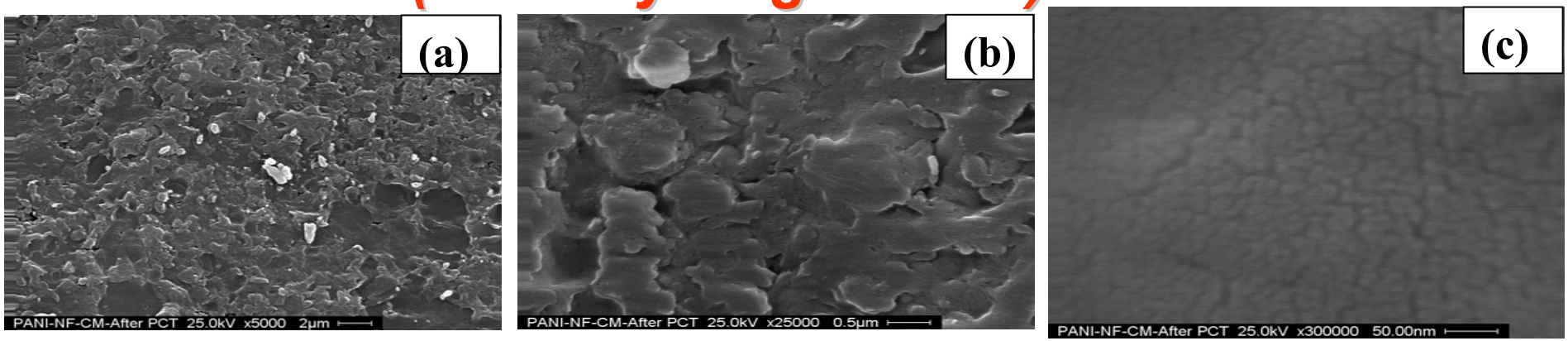
XRD profiles of PANI 1 before and after hydrogen sorption cycles; No structural changes observed

PANI 1- SEM (Before Hydrogenation)



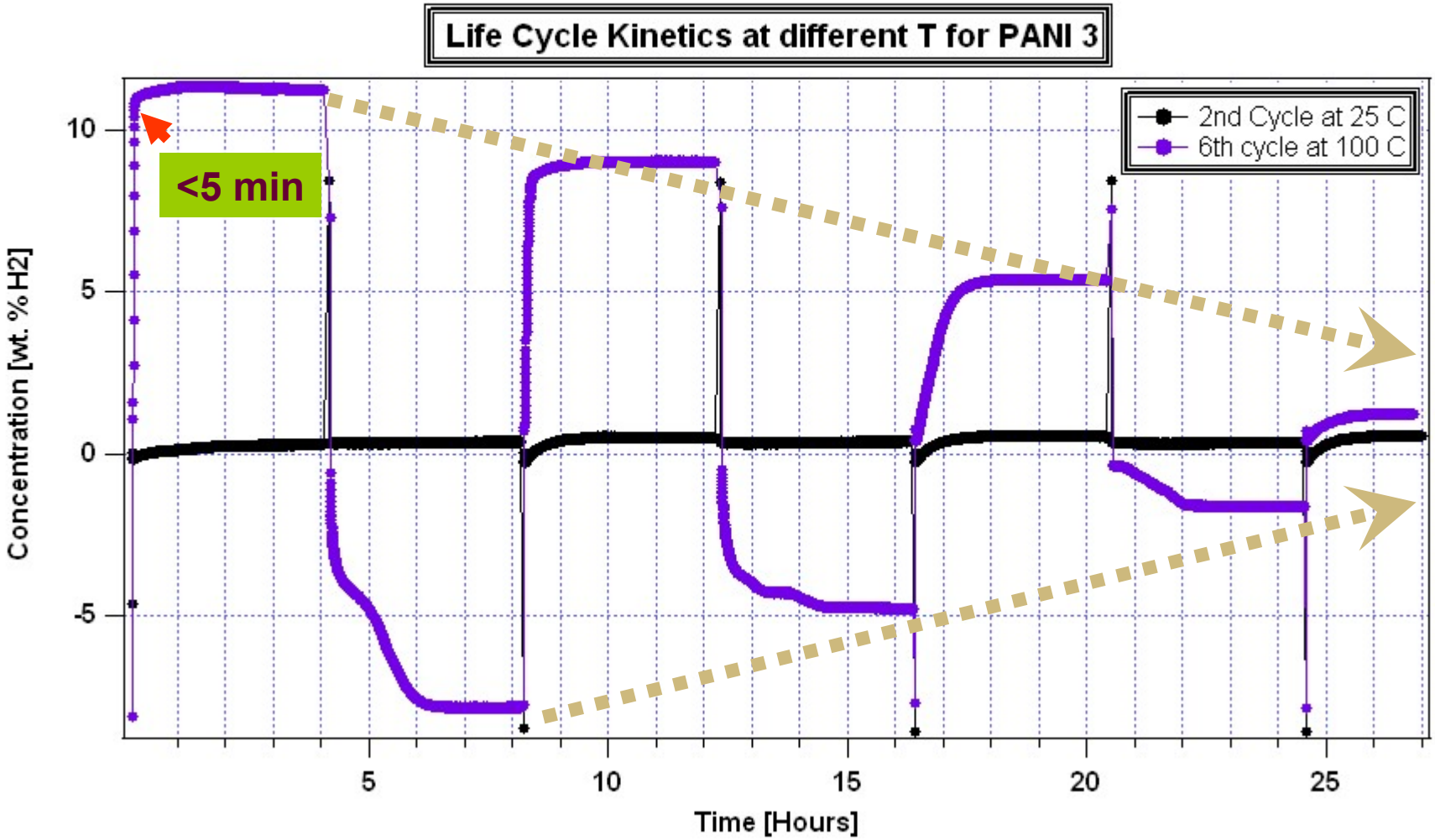
Scanning electron micrographs of polyaniline nanofibers grown at room temperature in aqueous medium with different surfactants (a) Dodecybenezenessulfonic acid (b) Acrymethylpropyl sulfonic acid (c) camphorosulfonic acid using ammonium persulfate as oxidizing agent

PANI 1- SEM (After Hydrogenation)



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

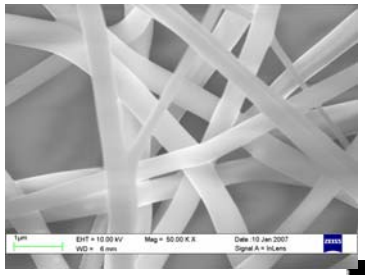
PANI 2 - CYCLE LIFE KINETICS AT DIFFERENT TEMP.

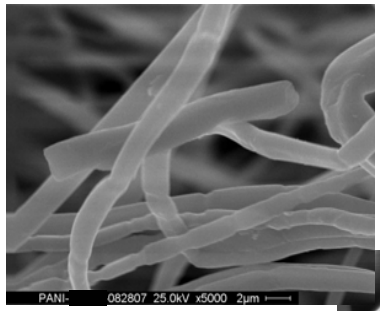


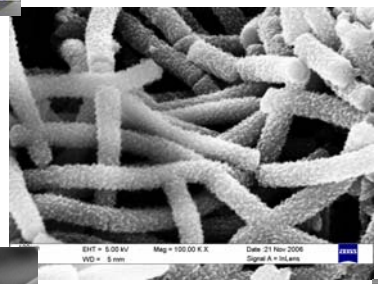
Fast kinetics with high capacity of ~10 wt% at 100 °C; Capacity decreases with number of Abs. and Des. cycles

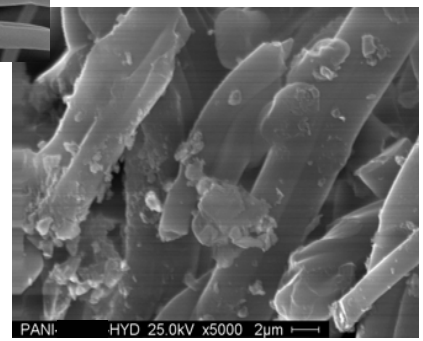
Accomplishments

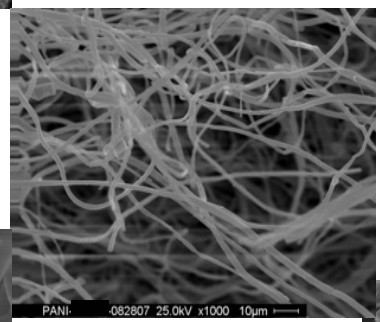
PANI 2
SEM

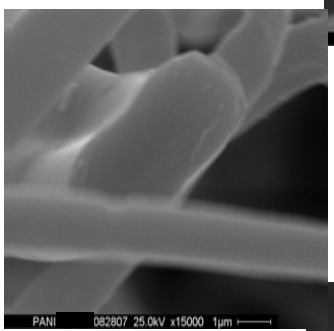


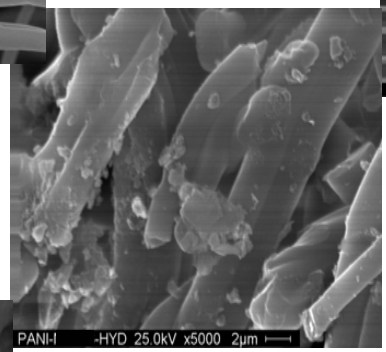


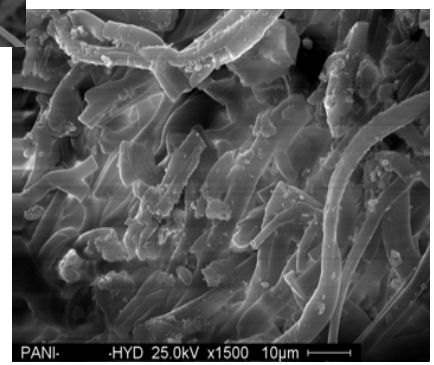


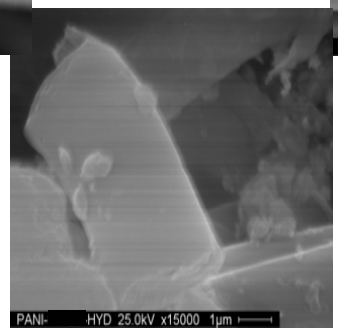










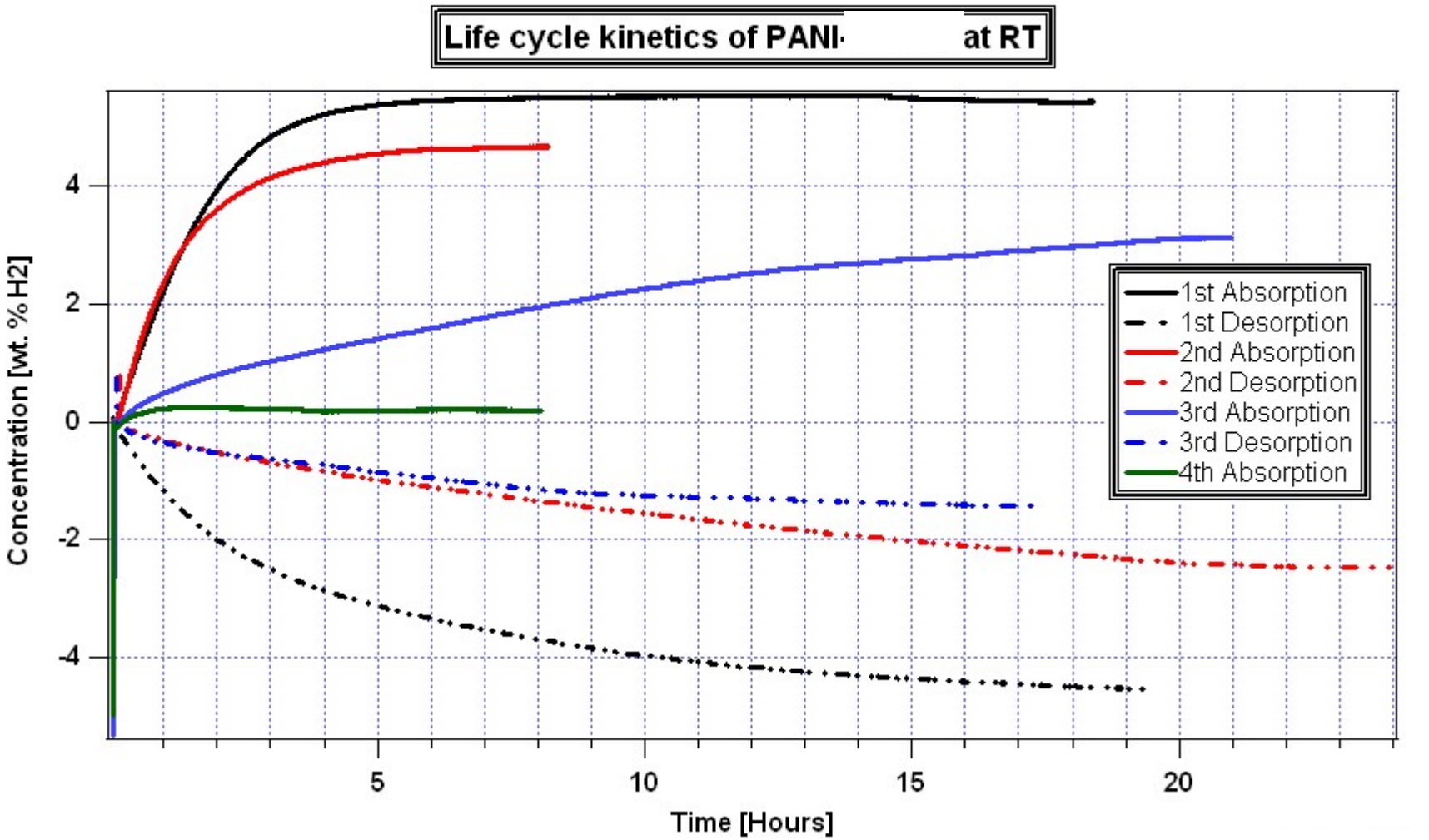


USF UNIVERSITY OF SOUTH FLORIDA

Accomplishments

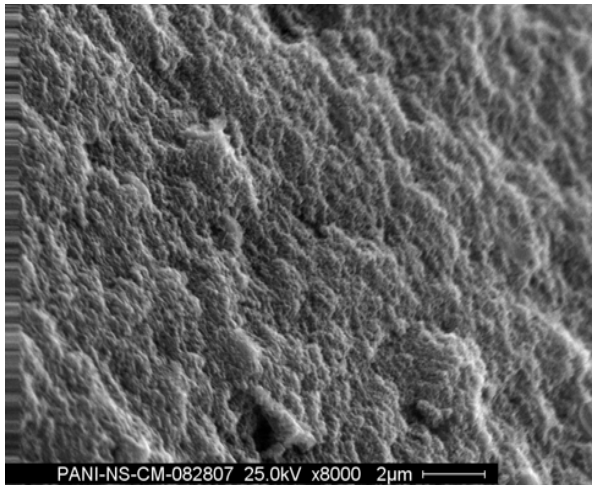
CERC Clean Energy Research Center

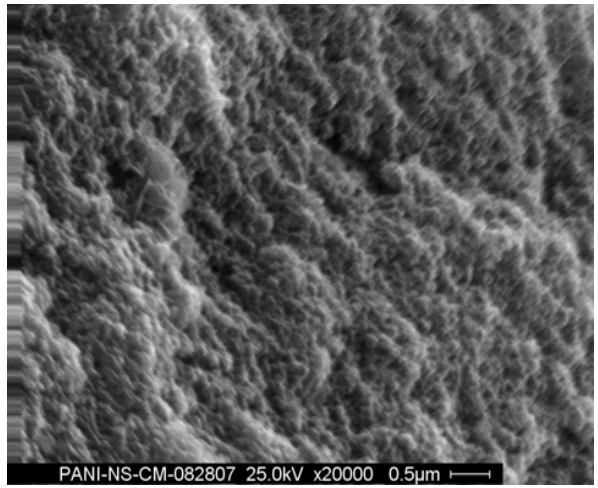
PANI 3 - CYCLE LIFE KINETICS at Room Temp.

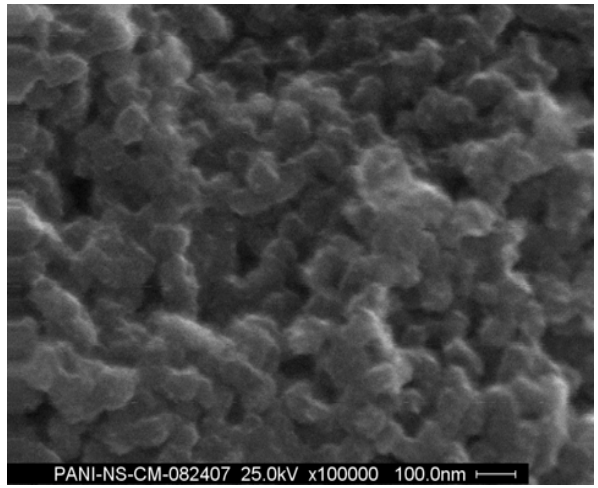


Hydrogen sorption capacity of ~4.5 wt% at 1st cycle and it decreases with cycling

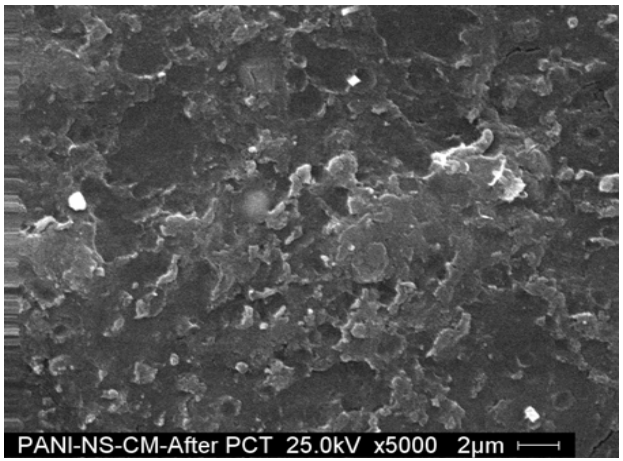
PANI 3- SEM (Before Hydrogenation)

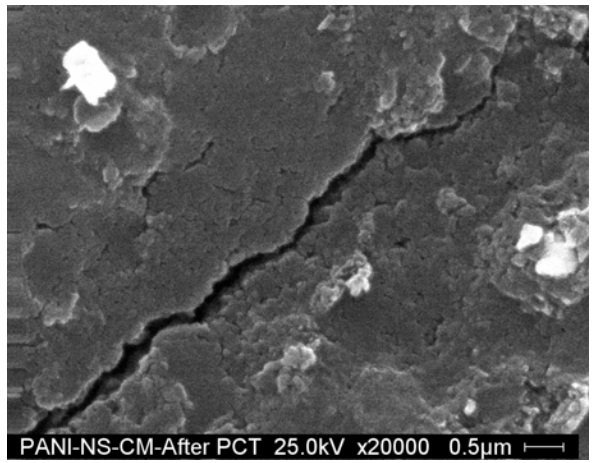


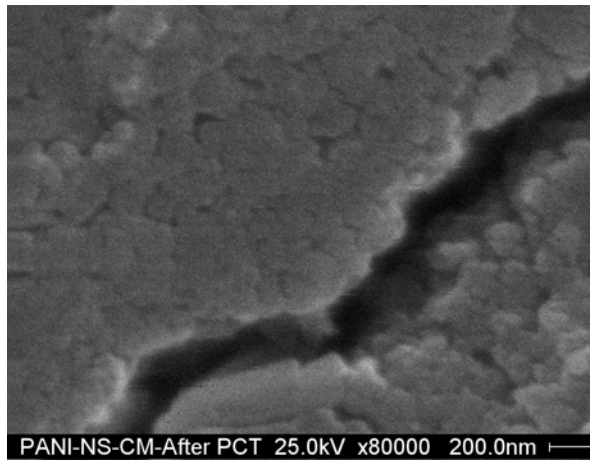




PANI 3- SEM (After Hydrogenation)







Micro-cracks observed after hydrogen sorption indicated effective hydrogen reaction

Summary

Subtask 1 & 2: $Mn(BH_4)_2$ (Experiment and Theory)

- An optimum milling duration of 30 minutes was sufficient to complete the reaction $2NaBH_4 + MnCl_2 \rightarrow Mn(BH_4)_2 + 2NaCl$
- An optimum milling duration of 90 minutes was sufficient to complete the reaction $2LiBH_4 + MnCl_2 \rightarrow Mn(BH_4)_2 + 2LiCl$
- For the $3LiBH_4 + MnCl_3$ samples, the melting and decomposition temperatures lowers down to 98 and 112 ^oC
- 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 $Zn(BH_4)_2$ 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 of150-250 ^oC
- 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: $Mn(BH_4)_2$

- Analysis of the residual gas after thermal decomposition of $Mn(BH_4)_2$ by GC/MS
- Kinetic and thermodynamic characteristics optimization of $Mn(BH_4)_2$ 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