2009 DOE Hydrogen Program Review

Hydrogen Storage Research

Presenters: Sesha Srinivasan/Lee Stefanakos

University of South Florida

May 18-22 2009

Arlington, Virginia

Project ID#
STP_23_Stefanakos

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. Niemann, P. Choudhury

Projects

Hydrogen Storage (STP 23)

• Advanced Hydride material-based technologies for on-board hydrogen storage

• Density Functional Theory calculations for complex borohydrides

• Hydrogen Production and Fuel Cell Research (Please see Project # **PDP 28**)

USF UNIVERSITY OF SOUTH FLORIDA

CERC Clean Energy Research Center

Overview

Timeline

Start: May 2004

End: August 2009

Percent Completed: 85%

Budget

Total Project Cost = $6,172,694

DOE Share = $4,938,155

USF Share = $1,234,539

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**

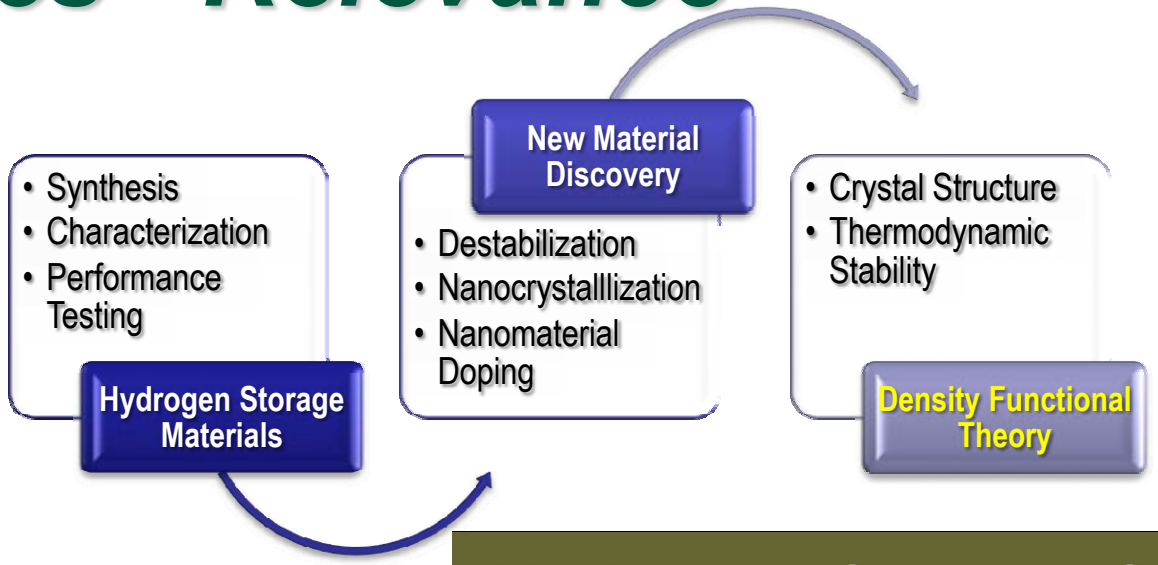
Partners

- **QuantumSphere Inc.**
- **NIST**
- **SWRI®**
- **Nano-RAM Technologies, India**
- **University of Hawaii**
- **NNRC, SRL - USF**

USF UNIVERSITY OF SOUTH FLORIDA

CERC Clean Energy Research Center

Objectives - Relevance



Technical Targets (2010)

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

Hydrogen Storage Systems January 2008 – May 2009

TASK 1	TASK 2	TASK 4
$LiMgBNH_x$ Complex Multinary Hydrides	$Li(MnBH_4)_3$ + Xmol% MgH_2 Complex Borohydrides	Polyaniline Nanostructures

TASK 3 DFT Modeling

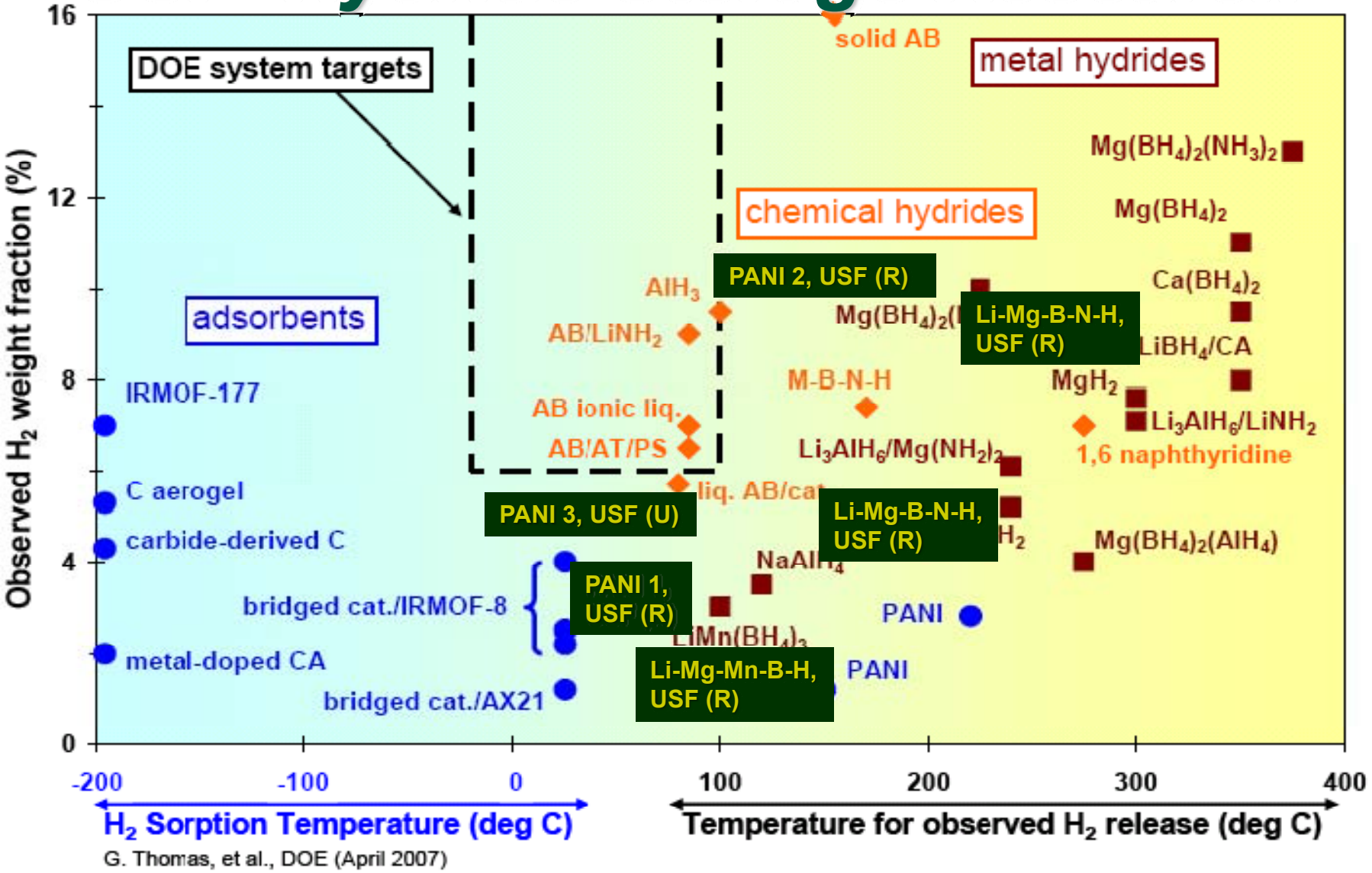
USF UNIVERSITY OF SOUTH FLORIDA

Milestones (Go/No-Go)

Critical Assumptions	TASK 1 Li-Mg-B-N-H	TASK 2: $LiMn(BH_4)_3$ – Xmol% MgH_2	TASK 4: 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
DOE Targets Met	YES	YES	YES
Status	80% complete	70% complete	60% complete

TASK 3 Density Functional Theory Calculations to predict, validate and optimize the hydrogen storage properties of complex hydrides and nanostructures [System: $Mn(BH_4)_2$] – Status: 60% complete

USF Hydride Storage Research



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

R = Reversible Hydride
U = Hydrogen Uptake

USF UNIVERSITY OF SOUTH FLORIDA

CERC Clean Energy Research Center

Approach (Experiment)

- Mechanochemical Milling methodology
- Nanomaterial doping
- Destabilization

Schlenk manifold

Ball mill

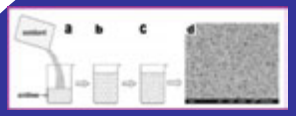
Glove Box

PCT

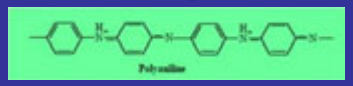
SDT

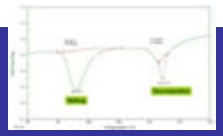
- Dehydrogenation Kinetics
- Pressure-Composition Isotherms
- Life cycle, Heat of reaction

DSC

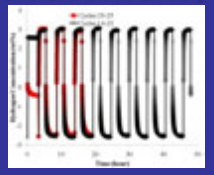


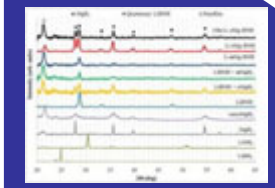
Selection and Synthesis



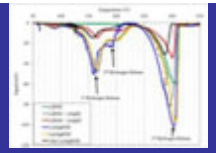


Volumetric and Gravimetric Measurements

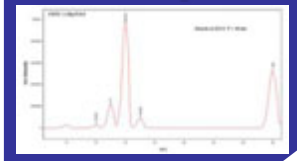




Characterization



Gas Quantification Analysis



- Gas Chromatography
- Thermal Programmed Desorption
- Mass Spectrometry

GC

- Phase Analysis
- Grain Size Analysis
- Surface Morphology
- Pore size Distribution

XRD

TEM

SEM

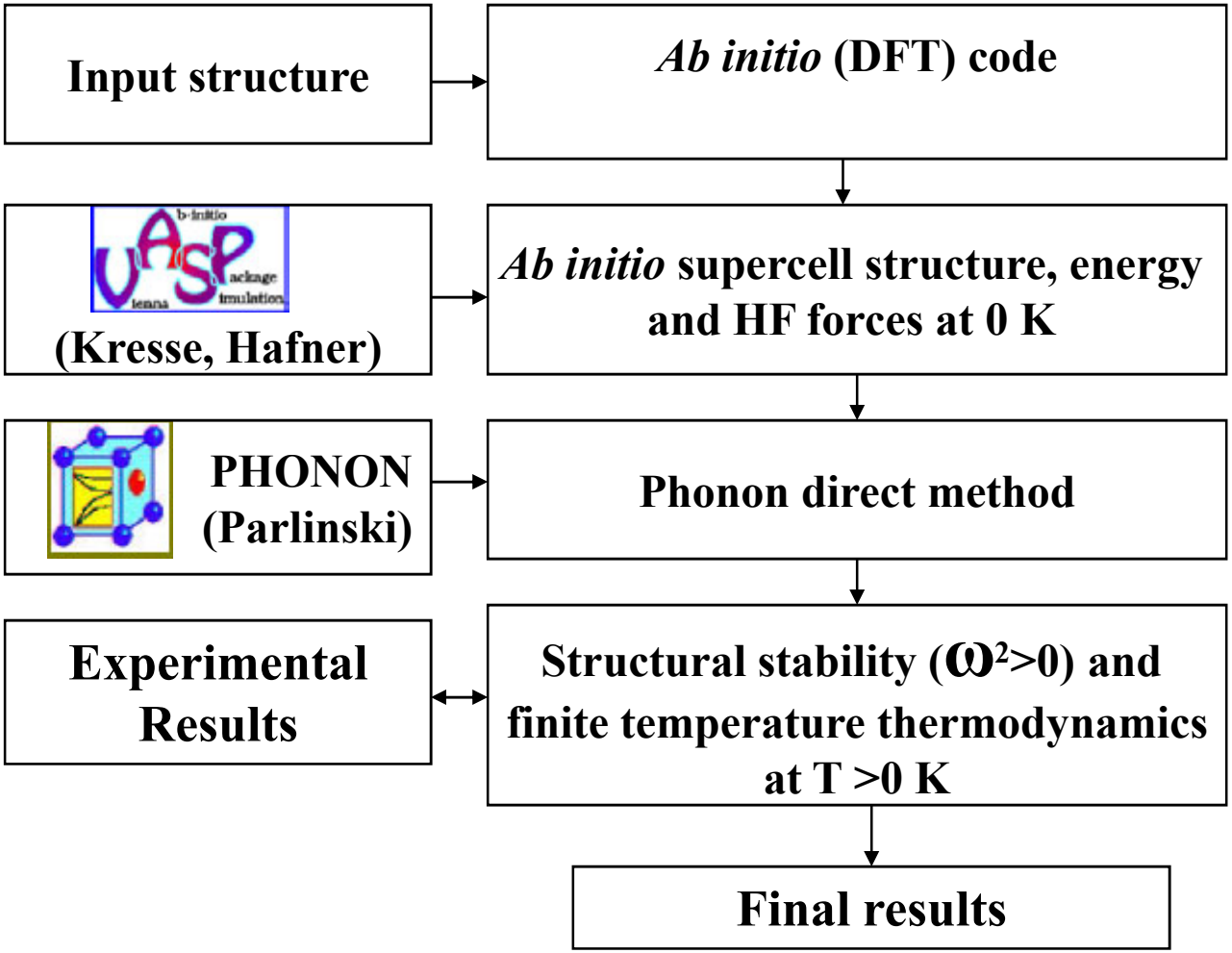
AFM

TPD

USF UNIVERSITY OF SOUTH FLORIDA

CERC Clean Energy Research Center

Approach (Theory)



Approach – Complex Hydrides

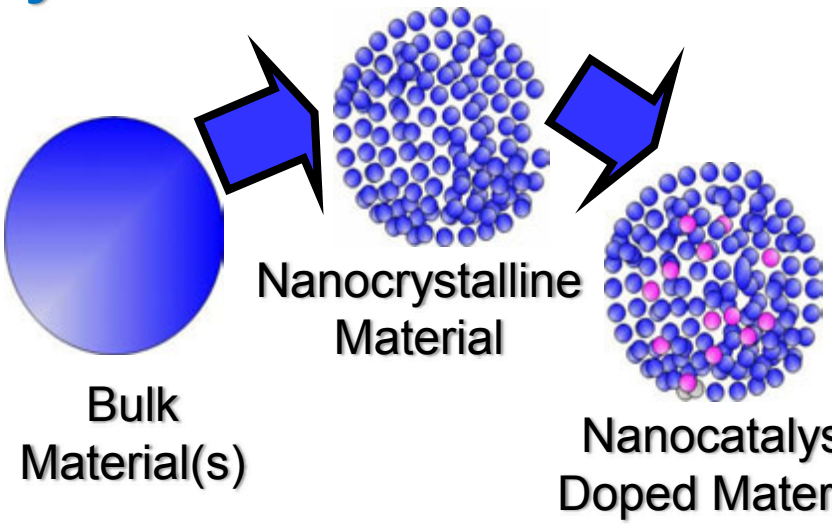
Materials

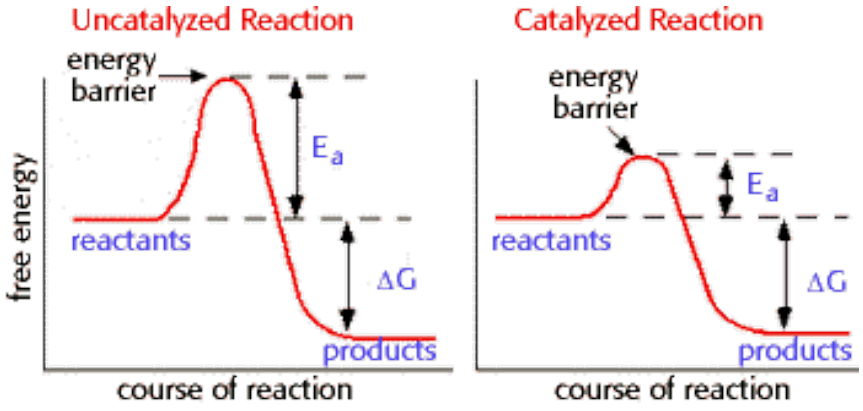
- $LiBH_4$ – 18.5wt%
- MgH_2 – 7.6 wt%
- $LiNH_2$ – 8.0 wt%

Destabilization

- Lower temperature for hydrogen release
- Greater hydrogen storage capacity
- Cyclic reversibility of reaction

Synthesis – Mechano-chemical milling





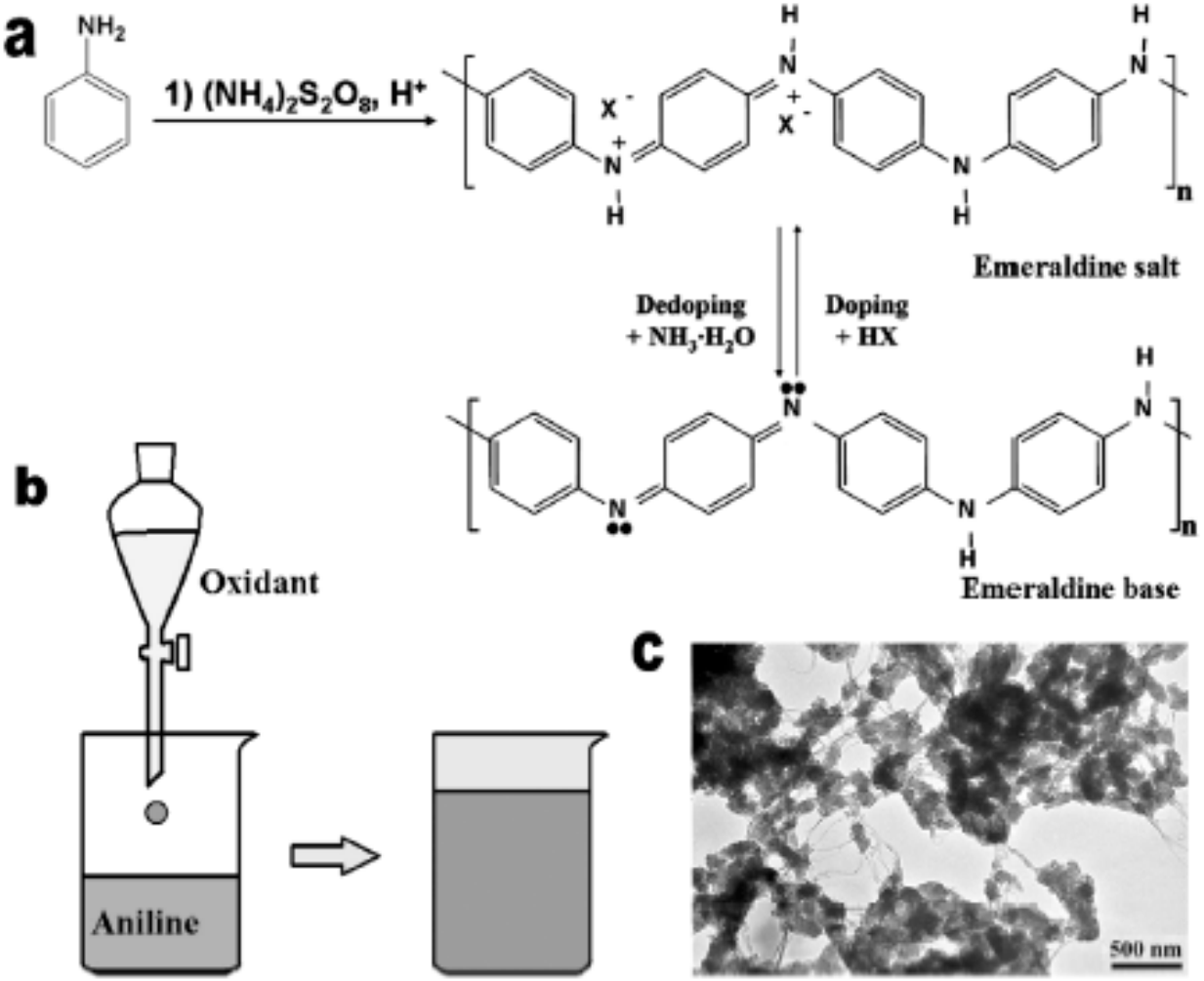
Destabilization Strategies

- Particle size reduction
- Lattice substitution
- Catalyst doping
- Ad-mixing different matrices

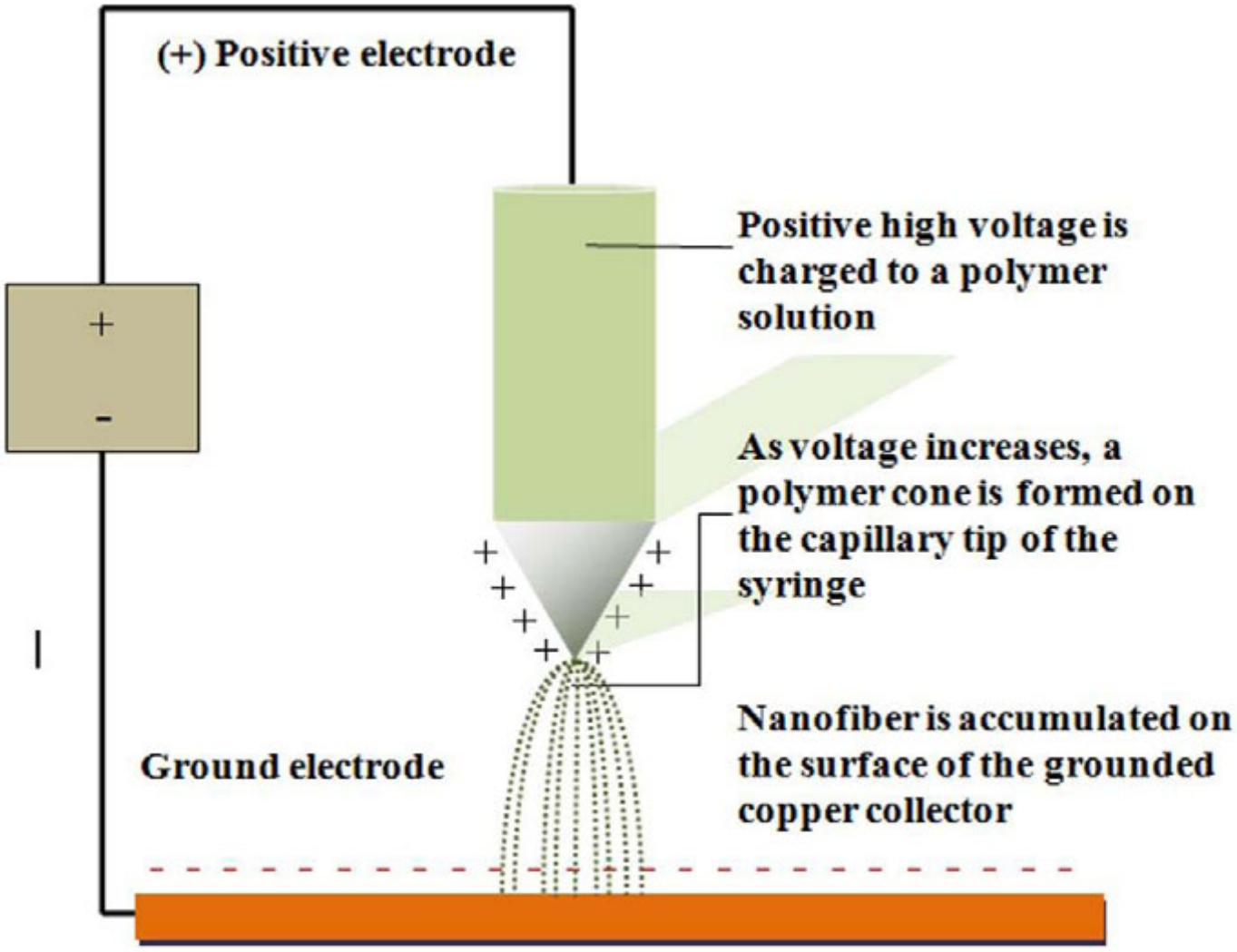
USF UNIVERSITY OF SOUTH FLORIDA

CERC Clean Energy Research Center

Approach: PANI Nanostructures – Chemical Method



Approach: PANI Nanofibers – Electrospun



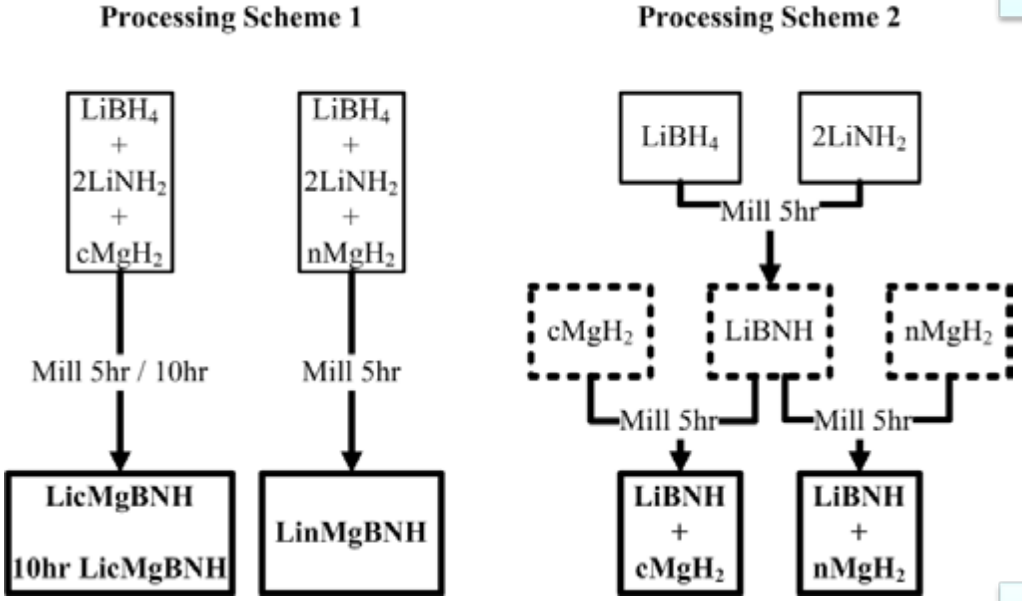
Accomplishments

- Successfully synthesized multinary complex hydrides involving $LiNH_2$, $LiBH_4$ and MgH_2 using solid state mechano-chemical process. Unique approach and adopting various processing conditions to prepare these Li-Mg-B-N-H complexes lead to efficient and reversible hydrogen storage capacity >6 wt.% at 150-175 ^oC. ***(Acer Transactions, 2009; Manuscript Submitted to JPC, 2009)***
- Independent validations of PCT characteristics such as H_2 storage capacity, sorption kinetics and gas evolution analysis by SWRI® of USF processed Li-Mg-B-N-H complex hydrides. Close match of results were obtained from both SWRI® and USF experimental analysis. No evolution of ammonia and di-borane gases have been observed from the Mass-Spec studies by SWRI®. ***(SWRI® Report to USF, 2009)***
- Accomplished Insitu-RAMAN characteristic spectra of $LiBNH+MgH_2$ samples at NIST. There exist close match of RAMAN and FTIR analyses by both USF and NIST measurements for the identification of B-H and N-H stretches. ***(NIST Report to USF, 2009)***

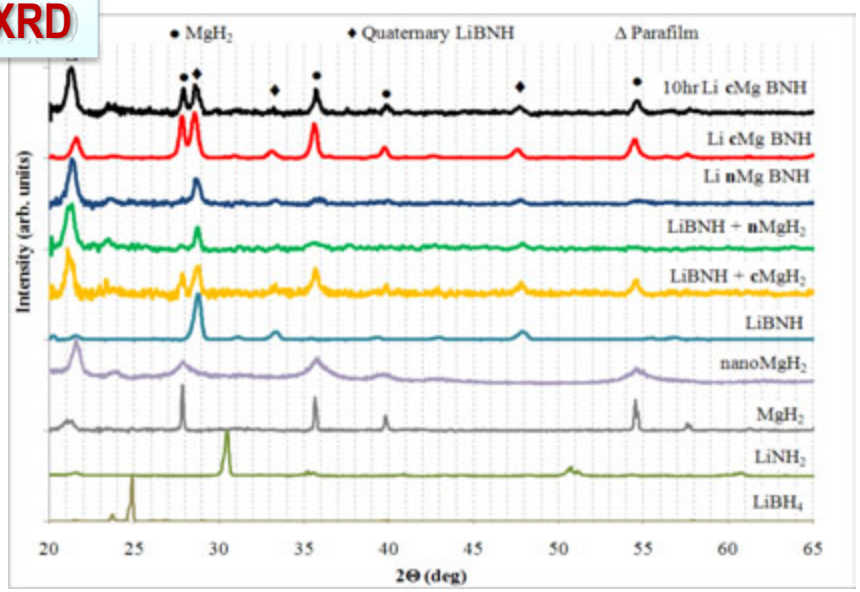
Accomplishments (contd.)

- Successfully synthesized complex borohydrides $LiMn(BH_4)_3$ mechanical milling of $LiBH_4$ and $MnCl_2$. Accomplished reversibility of hydrogen sorption cycles in non-reversible hydrides $LiMn(BH_4)_3$ by self catalyzing effects using Xmol% MgH_2. ***(Manuscript Accepted in IJHE, 2009)***
- Nanomaterials doping and co-doping on the effective hydrogenation and dehydrogenation behavior of mulitinary complex hydrides (Li-Mg-B-N-H) and Li-Mn-B-H. ***(USF -QuantumSphere Inc. Report 2009)***
- Established the structure of new $Mn(BH_4)_2$ phase and calculated the thermodynamic stabilities by Density Functional Theory. ***(Manuscript submitted to JPC, 2009)***
- Synthesized polyaniline nanostructures such as nanofibers and nanospheres using chemical and electrospun processes. Accomplished reversible hydrogen storage capacity of 3-10 wt.% from room temperature to 100 ^oC ***(J. Nanomaterials, 2008, J. Nanoscience and Nanotechnology, 2009, J. Nano Research, 2009)***

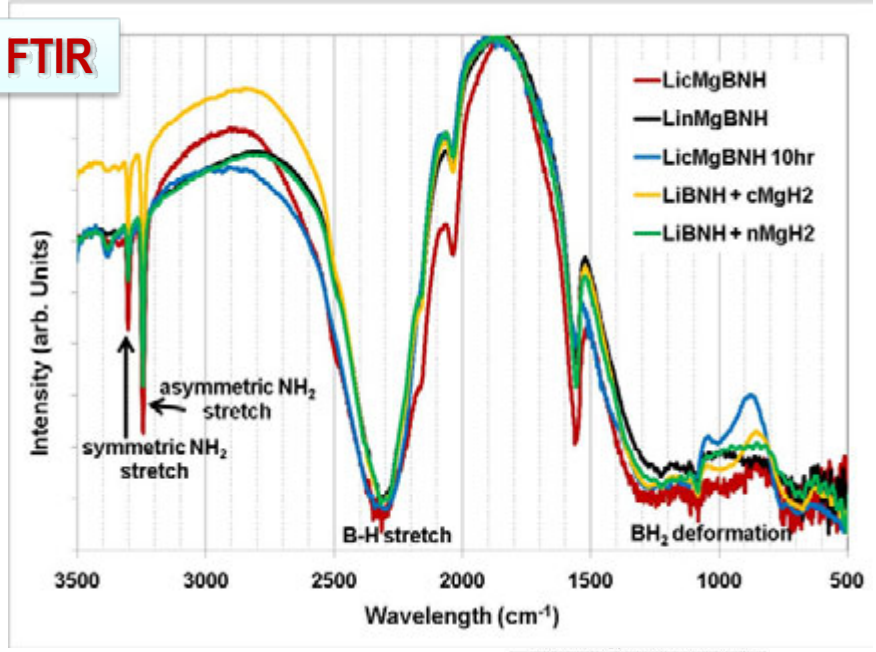
Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$



XRD



FTIR



- Various processing conditions (schemes) have been investigated
- XRD shows the appearance of quaternary complex hydride with MgH_2
- Nano MgH_2 loaded LiBNH exhibit finely dispersed nanoparticles of MgH_2
- FTIR shows the B-H and N-H stretches due to $LiBH_4$ and $LiNH_2$

USF UNIVERSITY OF SOUTH FLORIDA

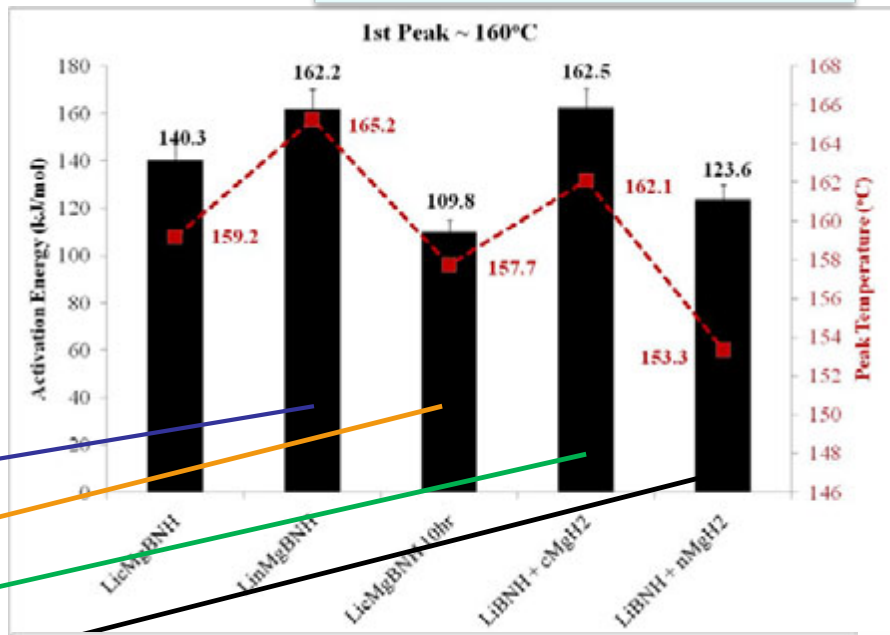
Task 1

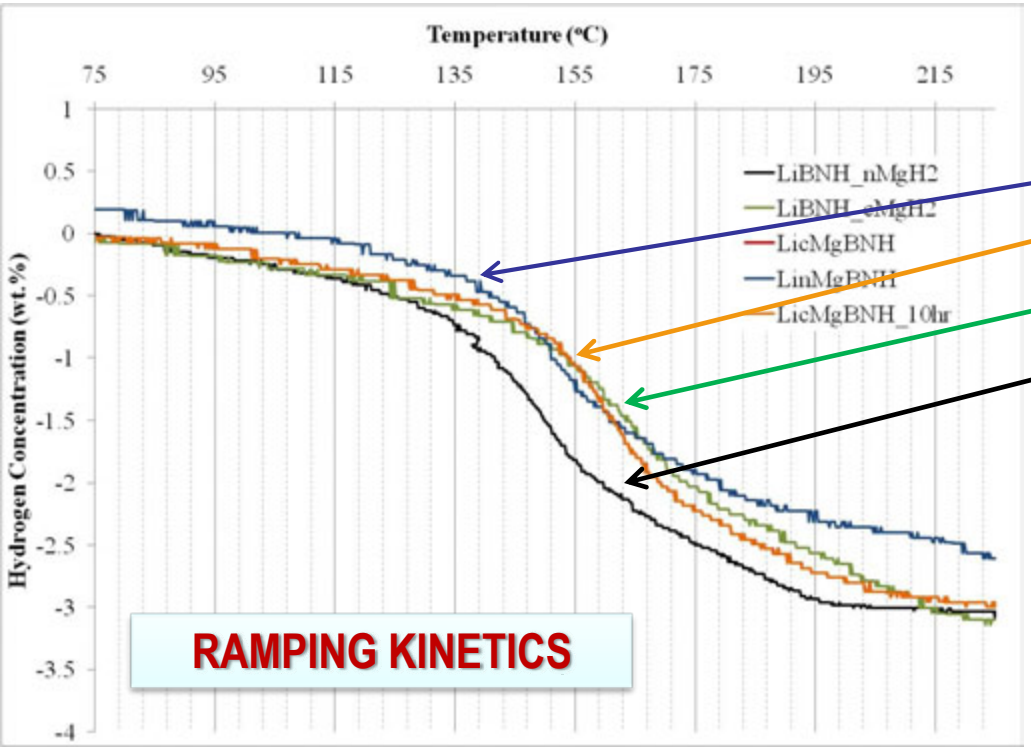
Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$

Correlation between Activation Energy and Temperature of complex hydrides prepared under different processing conditions

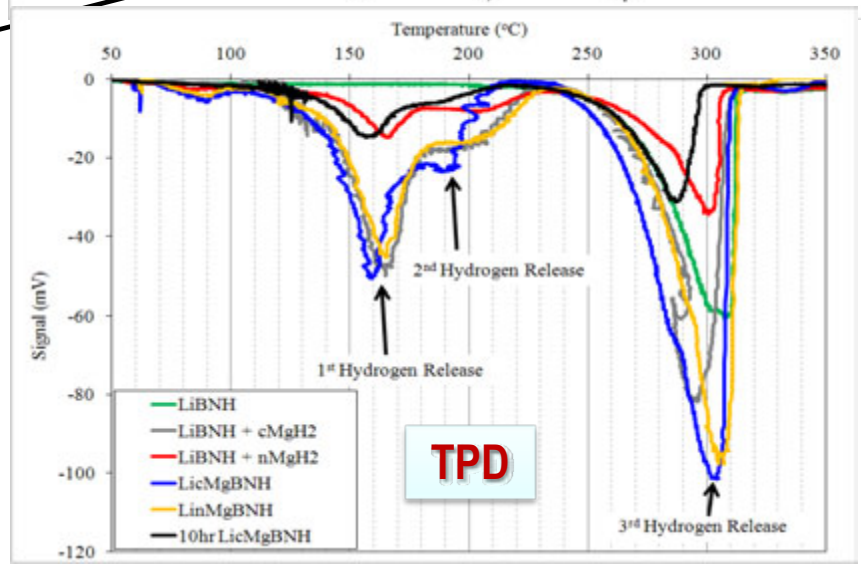
LiBNH + $nMgH_2$ hydride exhibit lower temperature of desorption among the other processed materials (both kinetics and TPD)

ACTIVATION ENERGY





RAMPING KINETICS

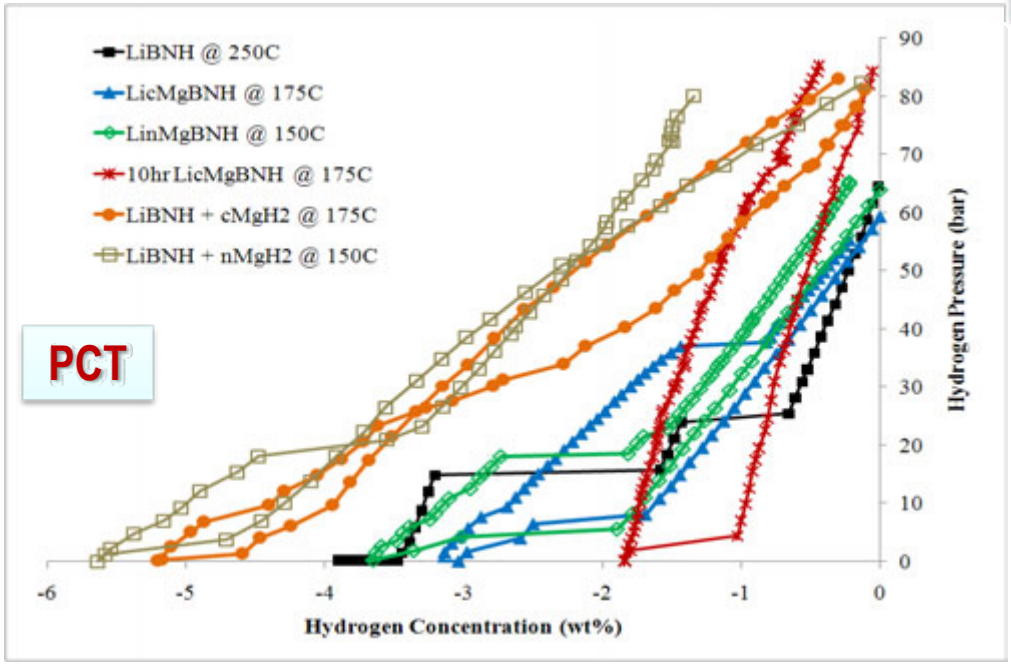


TPD

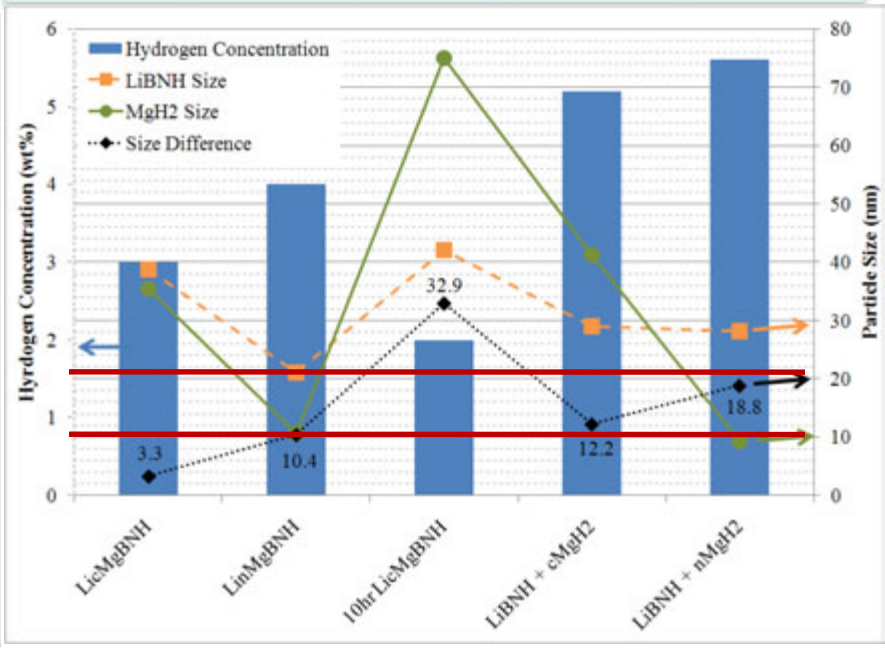
USF UNIVERSITY OF SOUTH FLORIDA

Task 1

Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$



Particle size – hydrogen correlation



- Processing conditions affects PCT performance
- LiBNH + (nano) MgH_2 excel in H2 capacity of ~5-6 wt.% at T=150°C
- Reversible cyclic plateau's observed

- LiBNH particle size was found to be ~28nm
- Size difference ~ 12 – 19 nm (between LiBNH and MgH_2 to be optimal (indicated in red lines) for high H_2 storage concentration

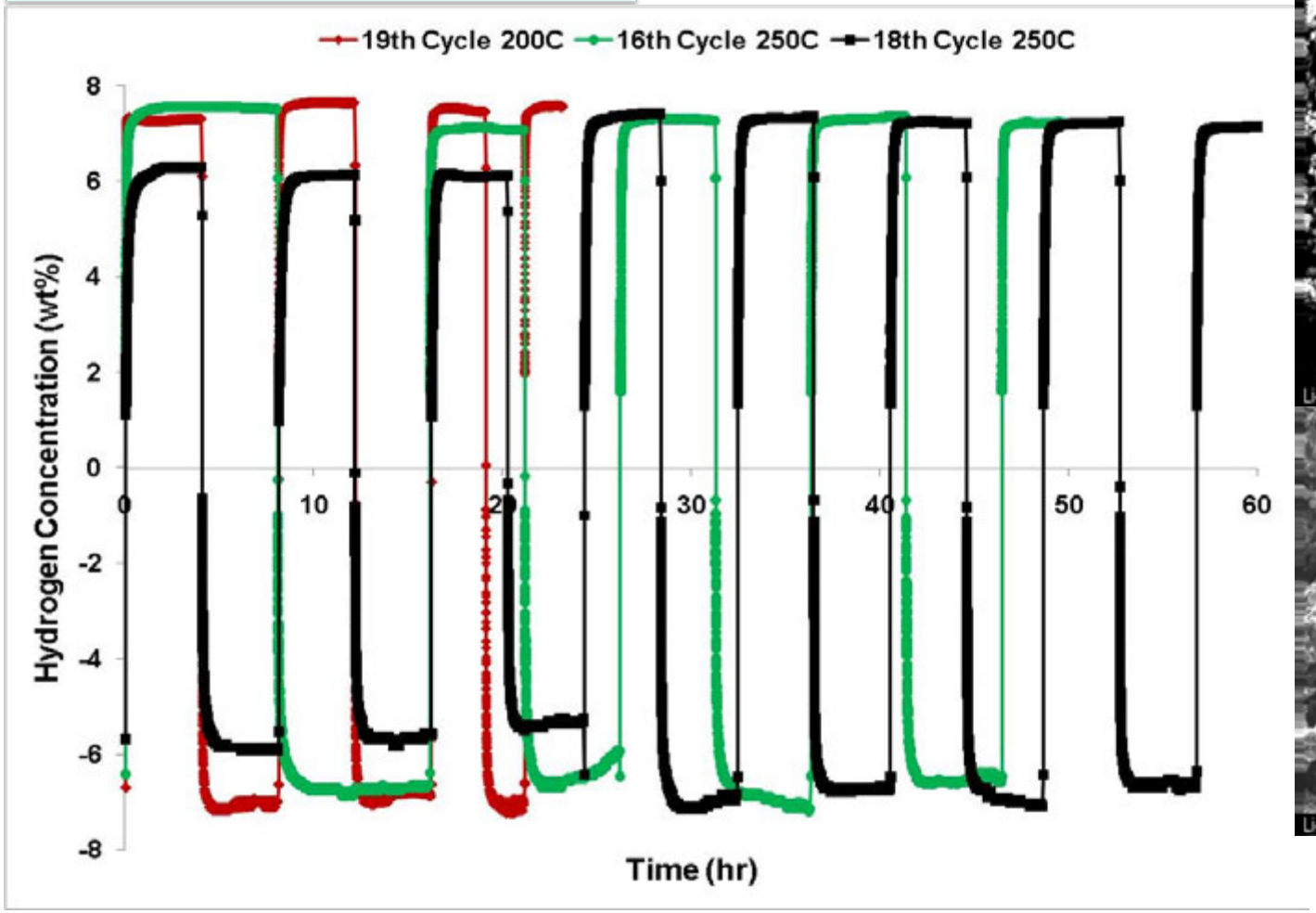
USF UNIVERSITY OF SOUTH FLORIDA

Task 1

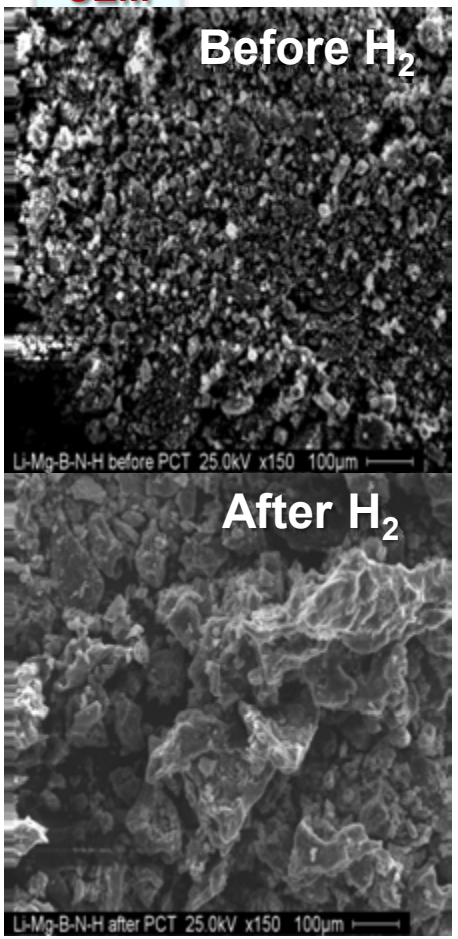
CERC Clean Energy Research Center

Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$

Life Cycle Kinetics at 250°C



SEM

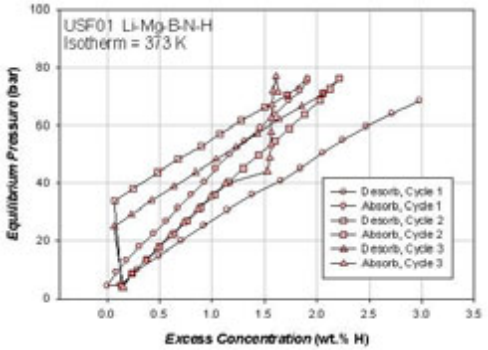


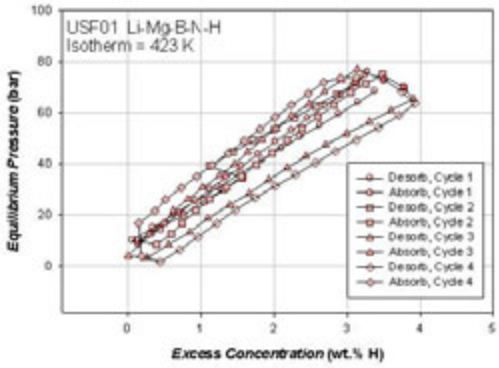
High reversible sorption kinetics (6-8wt.%) obtained in LicMgBNH comlex hydride at around 250°C

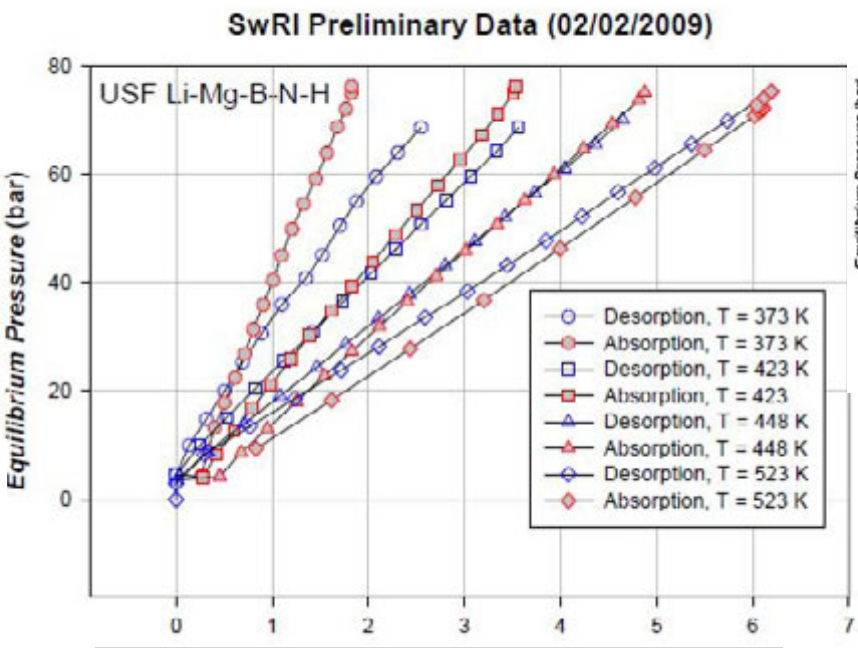
Task 1

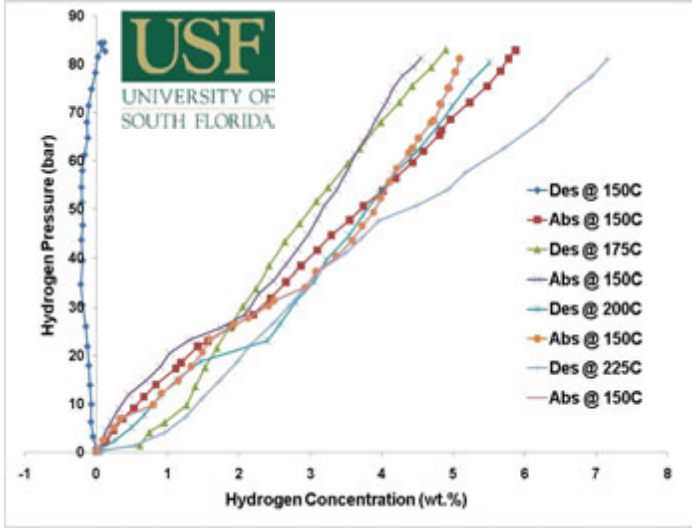
Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$

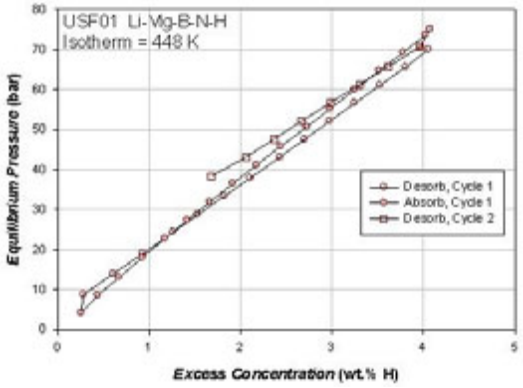
PCT

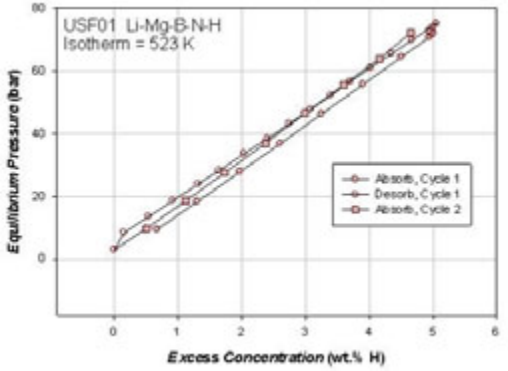












PCT characteristics of $LiBNH+cMgH_2$ – comparable results obtained by SWRI® and USF

5-7 wt% H_2 capacity achieved at T~150-250°C with high cyclic reversibility. (Minimal plateau influence observed)

USF UNIVERSITY OF SOUTH FLORIDA

Task 1

CERC Clean Energy Research Center

Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$

		LiBNH	LicMgBNH	LinMgBNH	10hr LicMgBNH	LiBNH + $cMgH_2$	LiBNH + $nMgH_2$
TPD Temperature (°C)	1st Peak	N/A	159.2	165.2	157.7	162.1	**153.3**
	Main Peak	308.5	303.6	306.6	**287.0**	298.8	300.3
Activation Energy (kJ/mol)	1st Peak	N/A	140.3	162.2	**109.8**	162.5	123.6
	Main Peak	**144.6**	197.3	245.9	237.7	145.0	148.6
H_2 Capacity (wt%)		4.0	3.0	4.0	2.0	5.2	**5.6**
H_2 Release Temperature (°C)		250.0	175.0	**150.0**	175.0	175.0	**150.0**
Plateau Pressure (bar)	Absorption	N/A	<40	**20**	N/A	<10	**21**
	Desorption	20-30	**<10**	**10**	<5	<5	<5
Reversibility		No	**Yes**	**Yes**	Less/No	**Yes**	**Yes**
Particle Size (nm)	LiBNH	60.0	38.7	**21.0**	42.1	29.0	**28.1**
	MgH_2	N/A	35.4	**10.6**	75.0	41.2	**9.3**

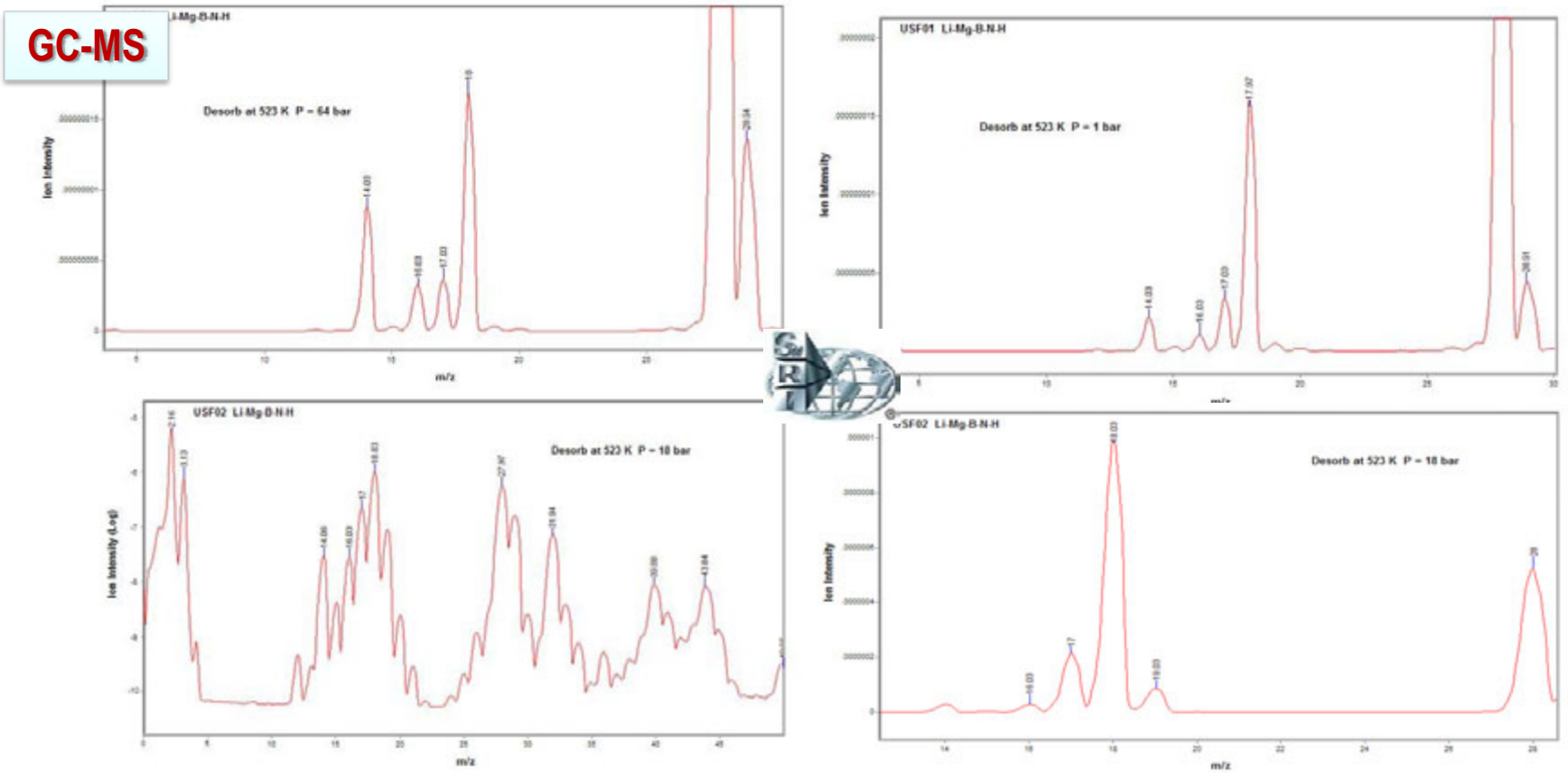
Comparison of the results for the multinary complex hydrides developed by different processing conditions (the best results are shown in bold).

USF UNIVERSITY OF SOUTH FLORIDA

Task 1

CERC Clean Energy Research Center

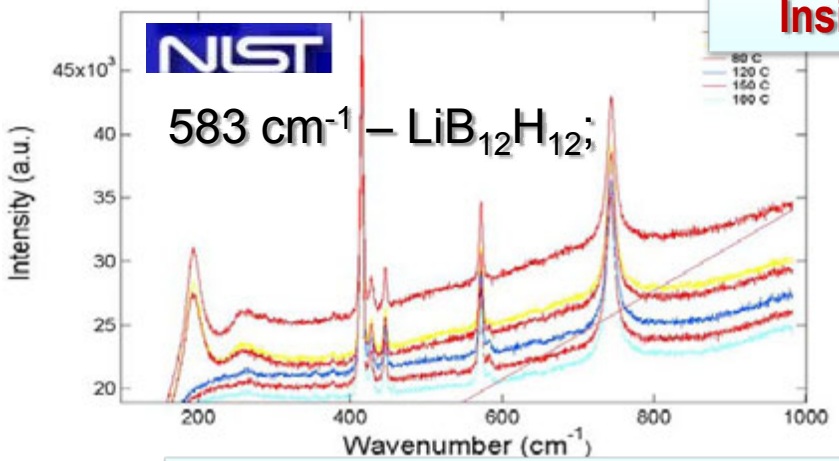
Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$



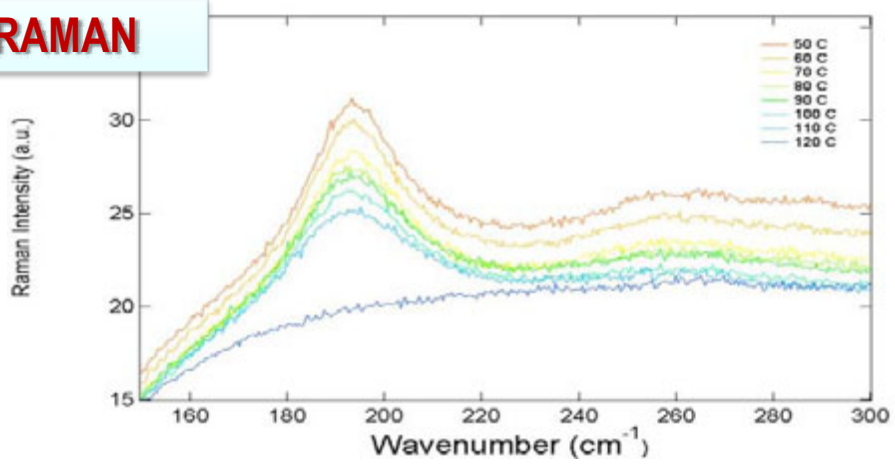
With respect to the mass spec analyses, note that the scans did not reveal any evidence for the desorption of potential parent (or daughter) species (ions); namely, NH_3, BH_3, BH_2NH_2, N_2H_4. The appearance of a species at mass 77.7 (m/z), which was only slightly above background. This corresponds to the parent ion of benzene, and its fragmentation daughter ions also appear in the spectra at the expected ratios (m/z=78, 52, 51, 50, 77; 100%:19:16:14).

Accomplishments – $LiBH_4$ vs T

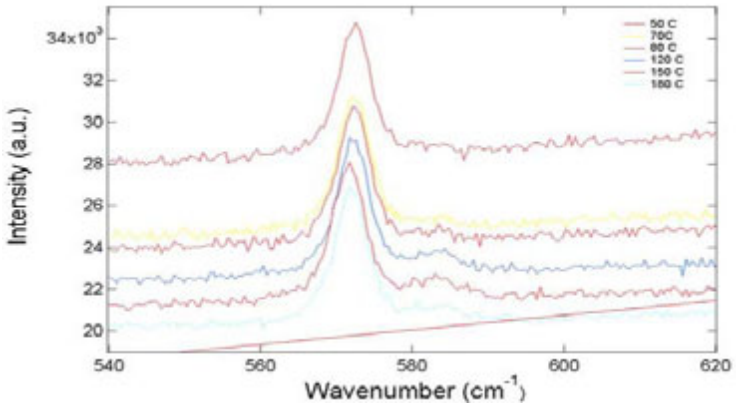
Insitu-RAMAN



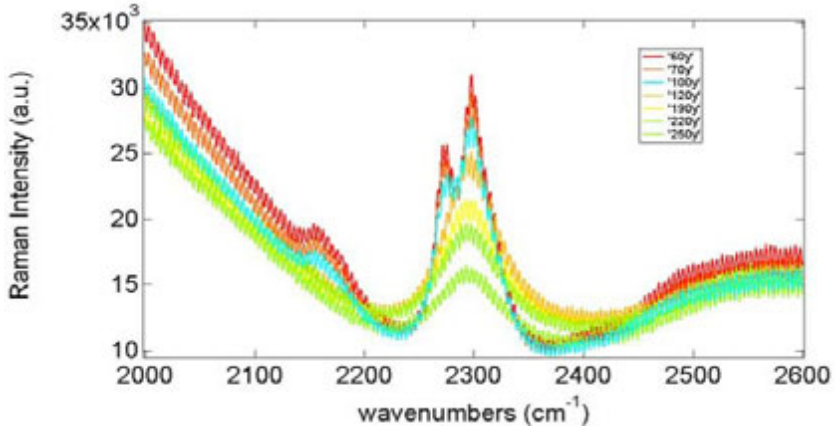
Low wavenumber Bands (global)



Low wavenumber zoomed (near edge)



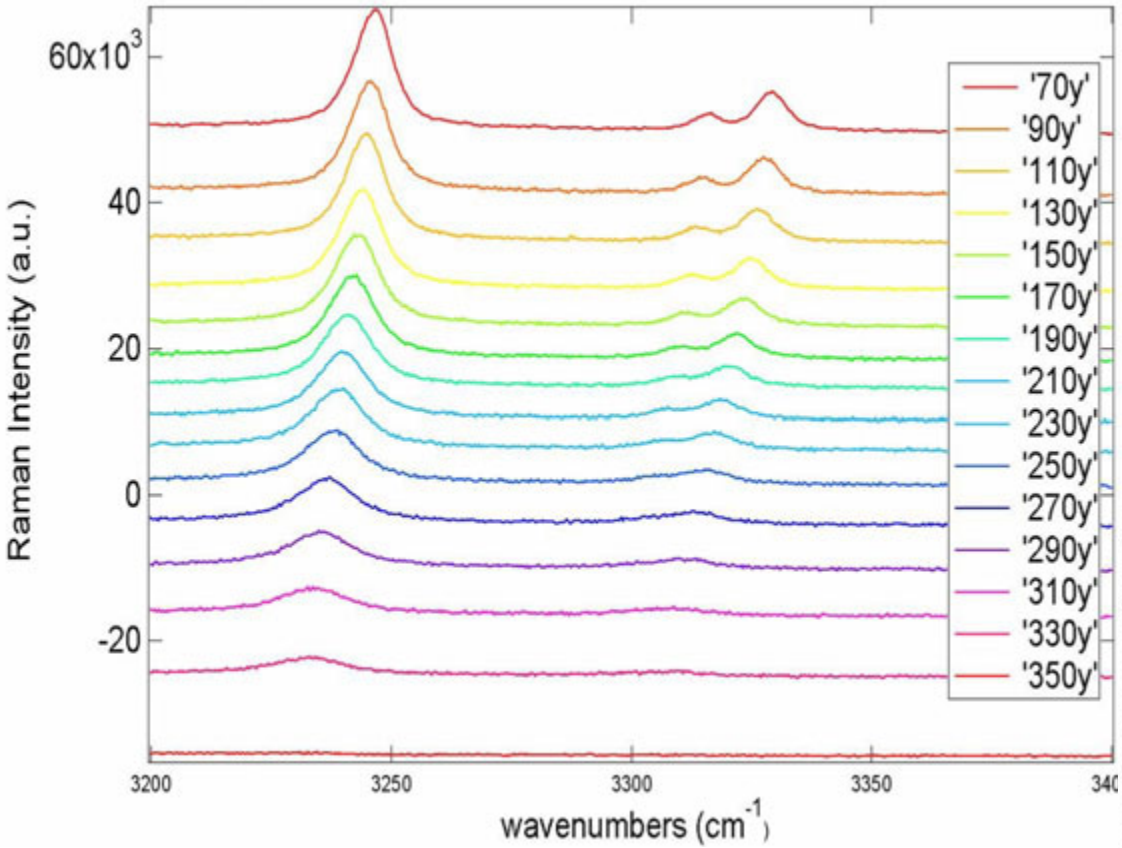
Low near a Sapphire mode

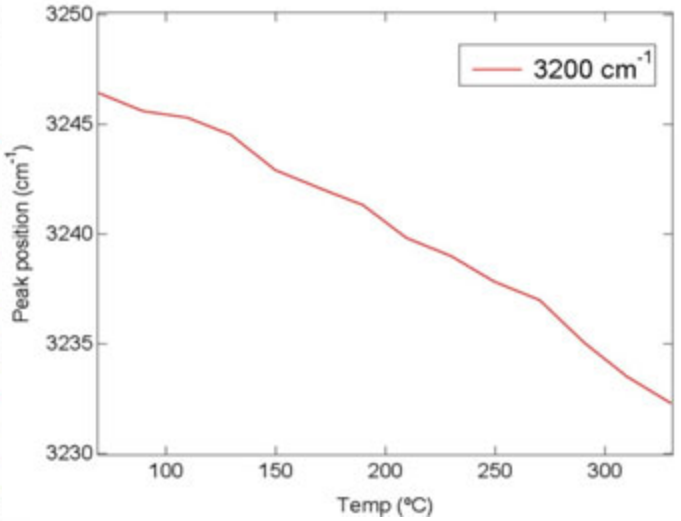


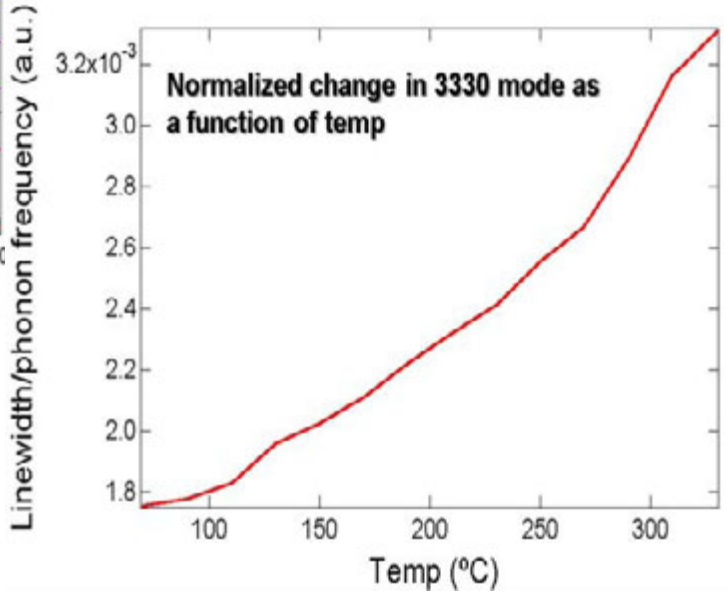
High wavenumber modes

Task 1

Accomplishments – $LiNH_2$ vs T



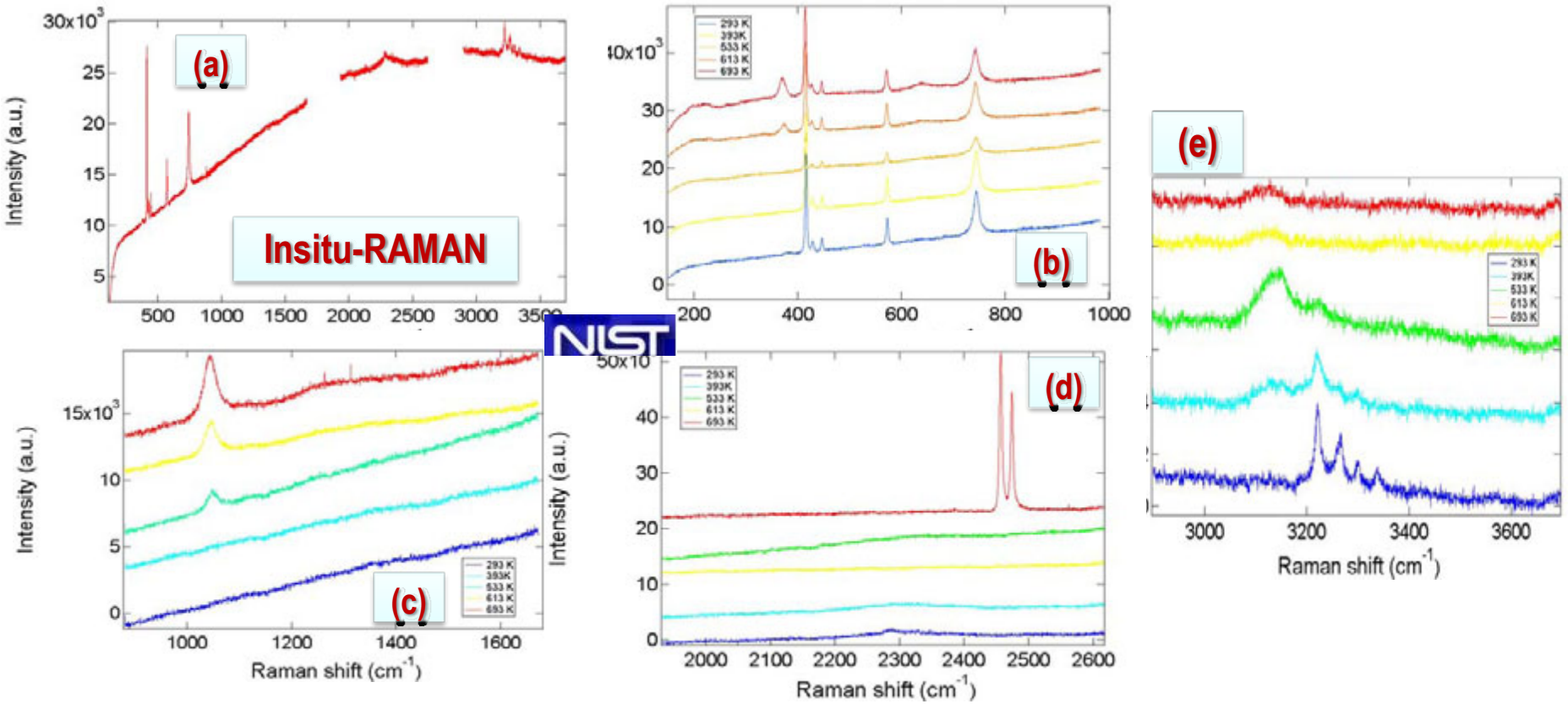




The shift in the peaks is consistent with literature, in particular Orimo, J. of alloys and compounds 370 (2004). it is roughly linear over most of the range, but H_2 release takes off around 270°C.

Task 1

Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$



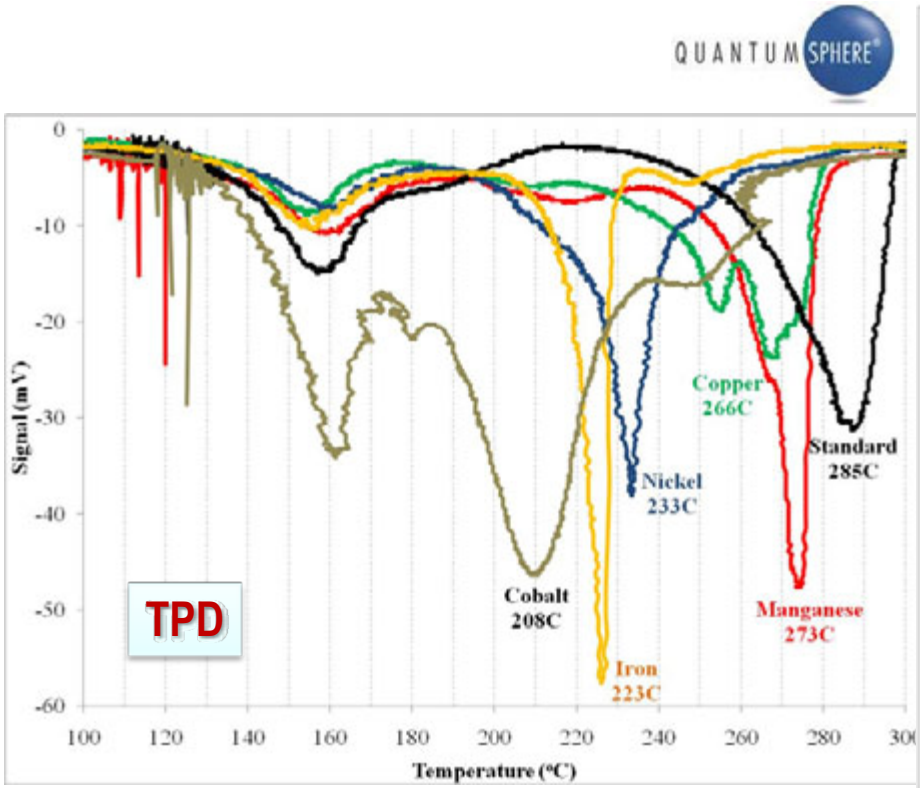
(a) Complete Raman spectra at Room Temperature (b) Temperature dependence of lowest wave number (sapphire mode and low intensity mode at 400 cm^{-1}) (c) first and second overlapping region shows pronounced peak around 180°C (d) second to highest mode region exhibit sharp peaks after heating to 360°C showing similar to those of $LiBH_4$ (e) highest wave number region, showing four N-H modes similar to FTIR and replaced with large and wide peak around 320°C and finally disappears.

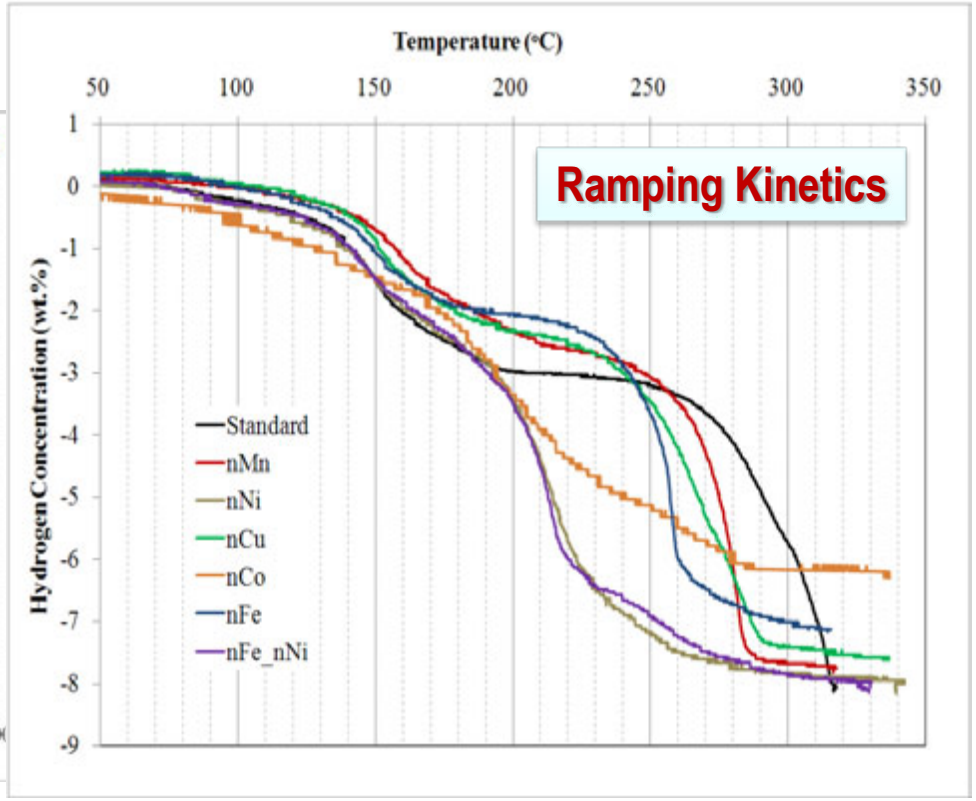
USF UNIVERSITY OF SOUTH FLORIDA

Task 1

CERC Clean Energy Research Center

Accomplishments – $LiBH_4 + LiNH_2 + MgH_2$





Thermal Programmed Desorption (TPD) profiles demonstrated lower decomposition temperature at least 100oC from the standard Li-Mg-B-N-H complex hydride. The stability is in the range of (nano) Co>Fe>Ni>Cu>Mn>Standard

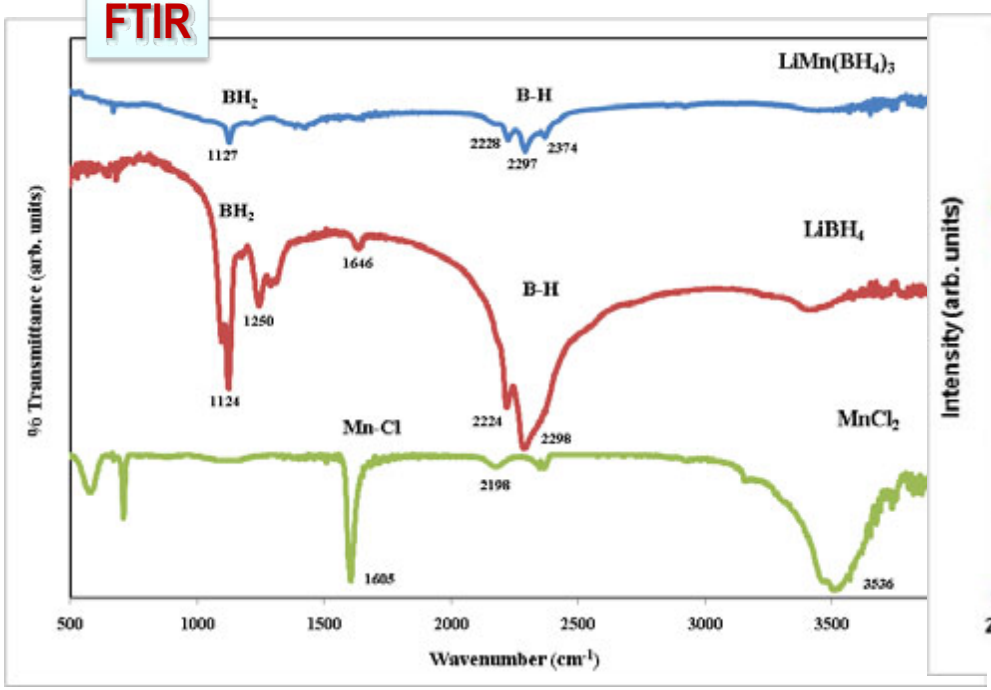
Hydrogen ramping kinetics (1°C/min) of undoped and nanomaterial doped Li-Mg-B-N-H. NanoNi and co-doped nanoNi/nanoFe materials outperformed at lower temperature of decomposition with hydrogen capacity ~8wt.%.

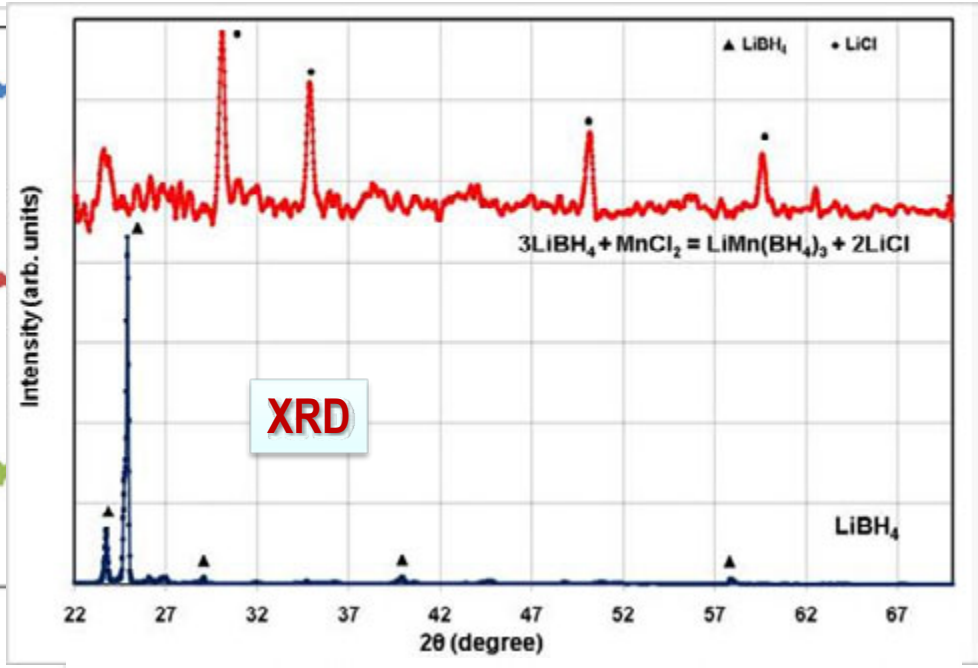
USF UNIVERSITY OF SOUTH FLORIDA

Task 1

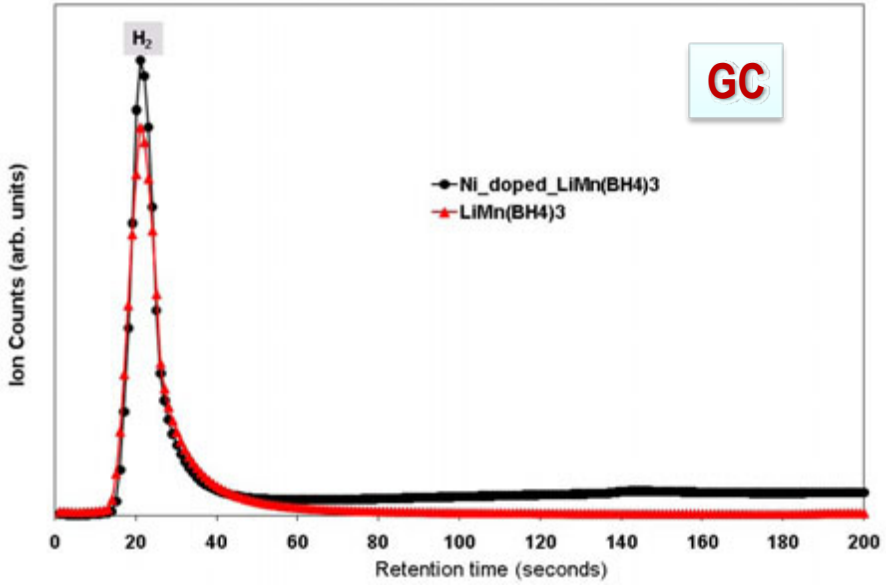
CERC Clean Energy Research Center

Accomplishments – $LiMn(BH_4)_3$





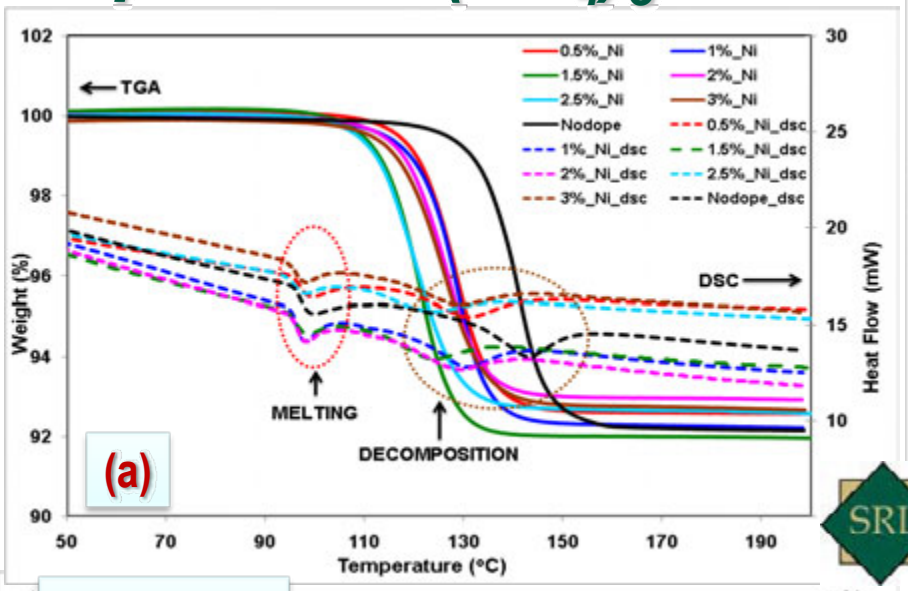
(a) FTIR spectrum of $LiMn(BH_4)_3$ shows a new B-H stretch at 2374 cm^{-1} confirms the formation of new compound based on the above reaction. (b) The formation of LiCl peaks from XRD substantially demonstrate the product is of new complex borohydride. (c) Moreover the decomposition of $LiMn(BH_4)_3$ evolves no other gases except HYDROGEN

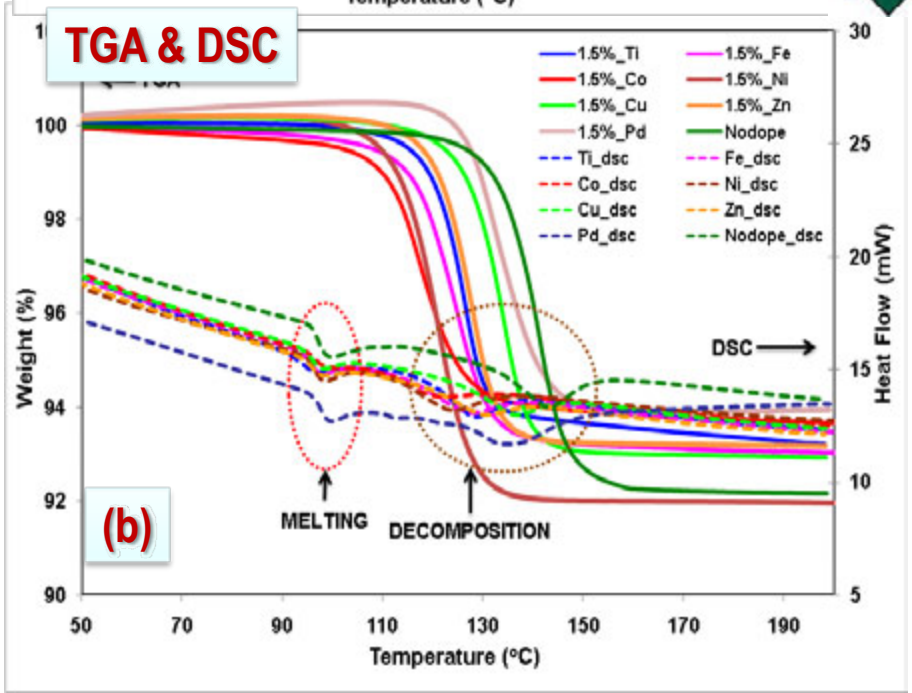


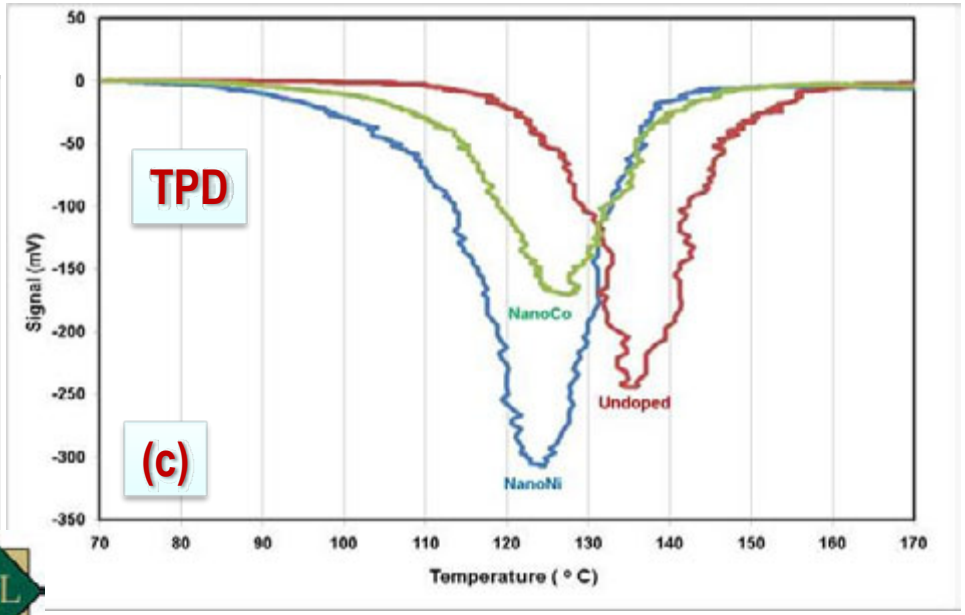
USF UNIVERSITY OF SOUTH FLORIDA

Task 2

Accomplishments – Undoped and nanomaterial doped $LiMn(BH_4)_3$







(a) TGA and DSC profiles of $LiMn(BH_4)_3$ doped with different concentrations of nanoNi – 1.5 mol% nanoNi exhibit lower decomposition temperaure.

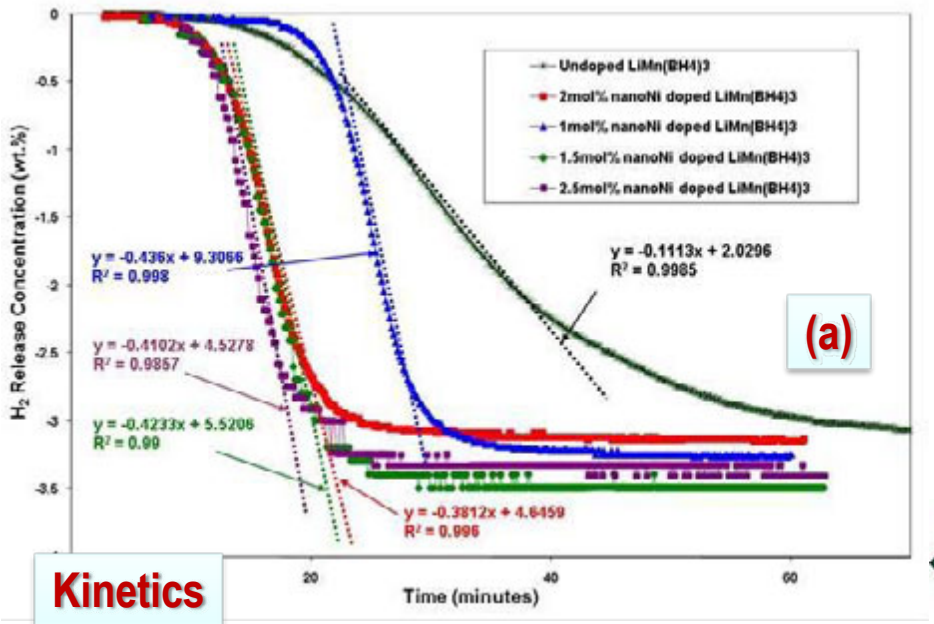
(b) TGA and DSC profiles of 1.5mol% nanomaterials (Ni, Co, Fe, Cu, Mn, Pd) shows Ni, Co and Fe are having effective and lower $T_{decomposition}$

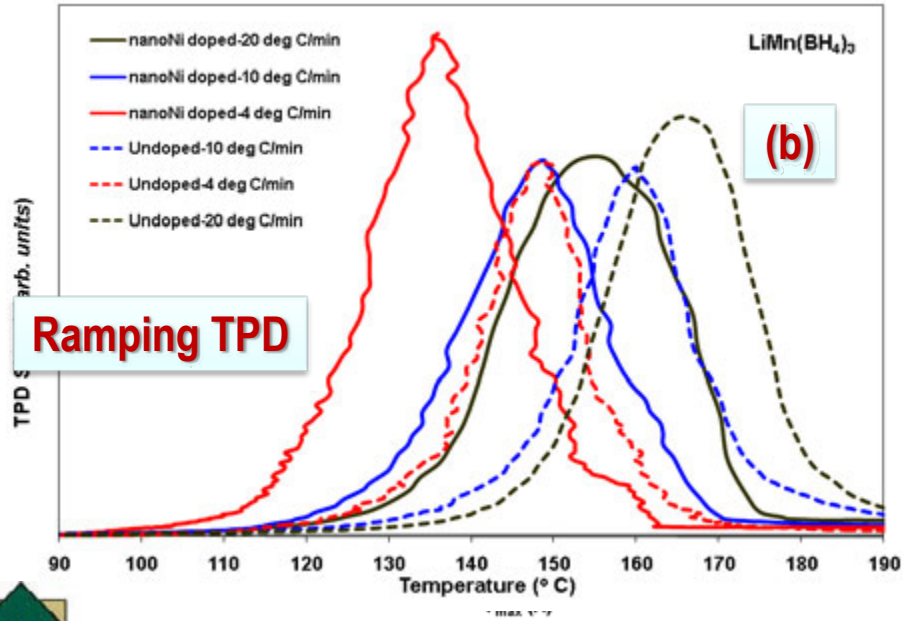
(c) TPD signal during desorption shows at least 25°C lower in the Tdecompsiton for nanomaterials doped samples.

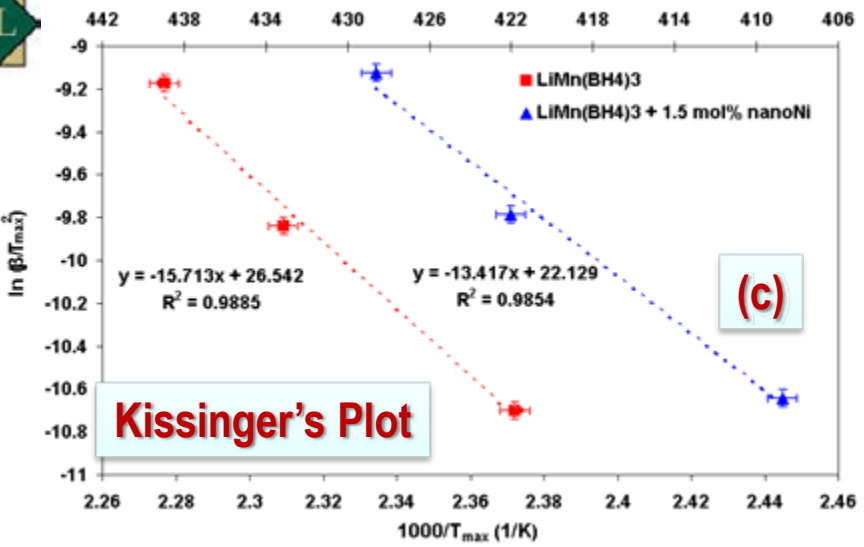
Task 2

CERC
Clean Energy Research Center

Accomplishments – Undoped and nanomaterial doped $LiMn(BH_4)_3$







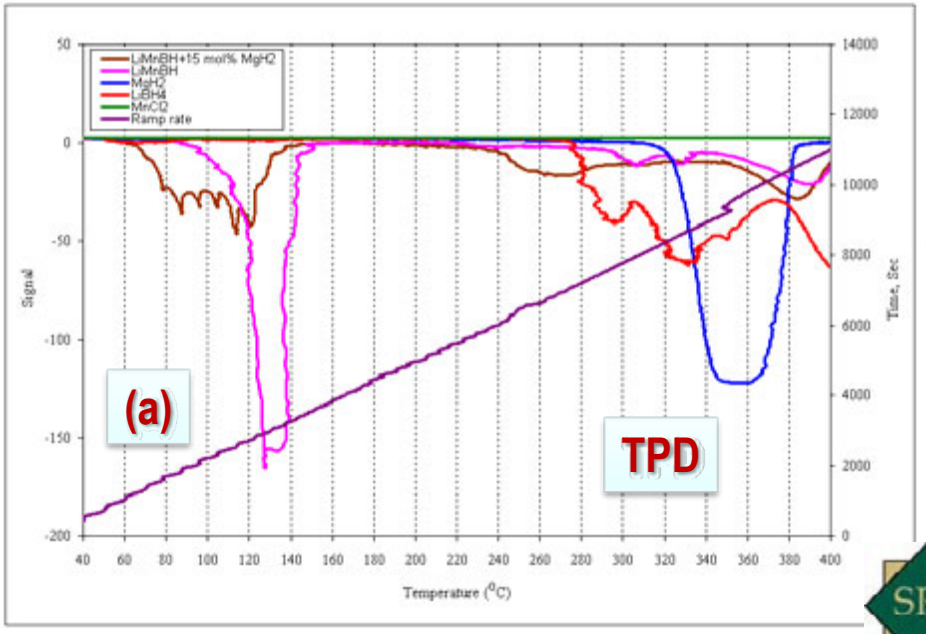
- (a) 3 to 4 fold increase of dehydrogenation kinetics of Xmol% nanoNi doped Li-Mn-B-H
- (b) Uniform shift in T_{max} value for the ramping in the order of 4>10>20°C
- (c) Activation energies have been calculated based on the Kissinger's equation

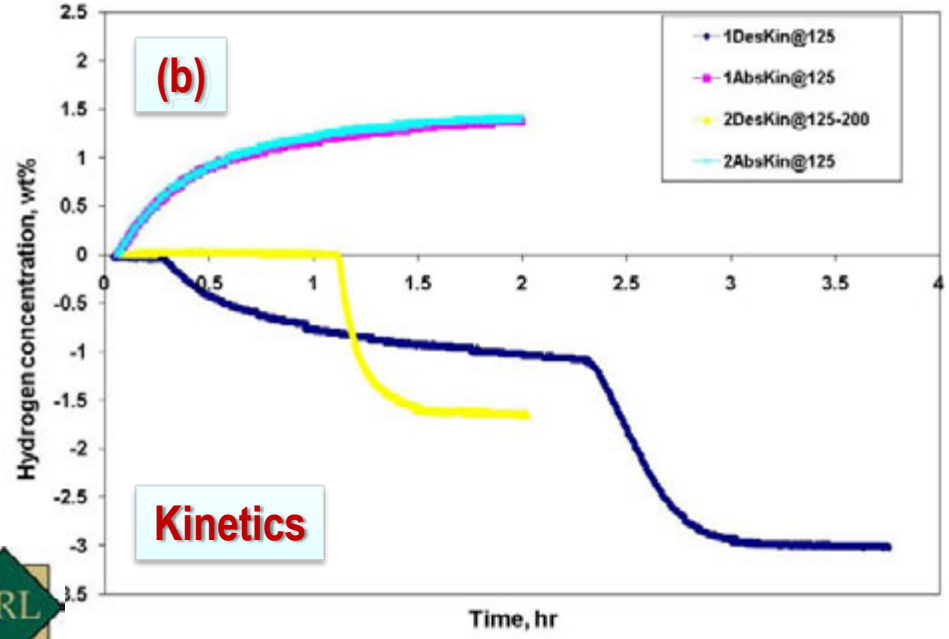
$$\frac{da}{dt} = A\exp(\frac{-E_a}{RT})f(a)$$

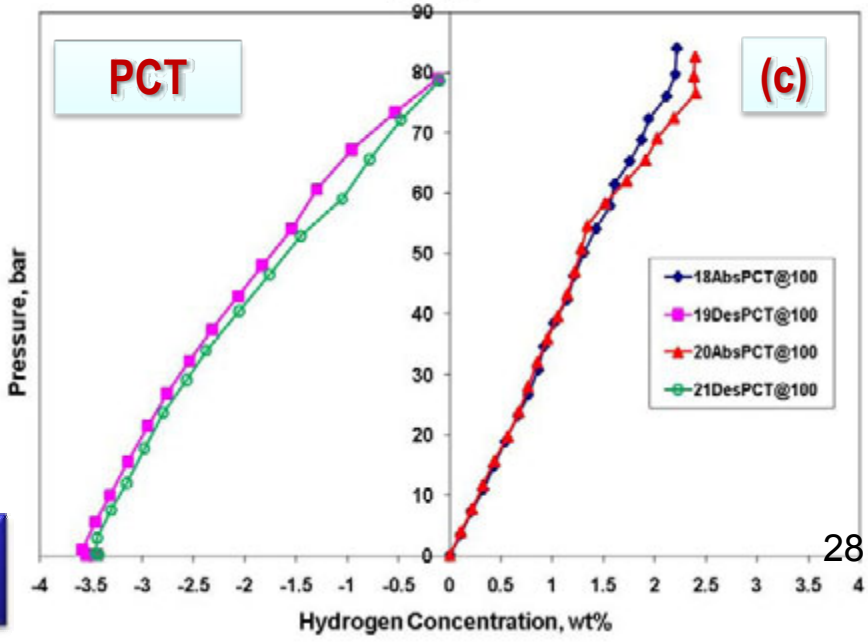
Undoped: Ea = 130.64 kJ/mol
NanoNi doped: Ea = 111. 55 kJ/mol

Task 2

Accomplishments – $LiMn(BH_4)_3$ – X mol% $nMgH_2$







(a) TPD of LiMnBH and LiMnBH-X mol%MgH_2 shows lower hydrogen $T_{decomposition}$

(b) Hydrogenation and dehydrogenation kinetic curves demonstrate the reversibilty of 2-3 wt.% at 100-125°C

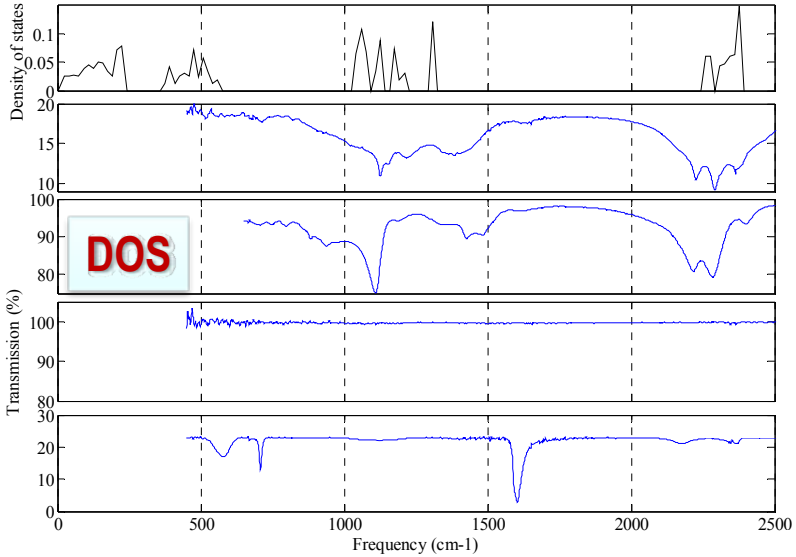
(c) PCT isotherms of $LiMn(BH_4)_3$-15mol%MgH_2 exhibit reversible sorption behavior at temperature around 100°C.

USF UNIVERSITY OF SOUTH FLORIDA

Reversibility established in non-reversible hydrides

Task 2

Accomplishments – $Mn(BH_4)_2$ – DFT Calculations

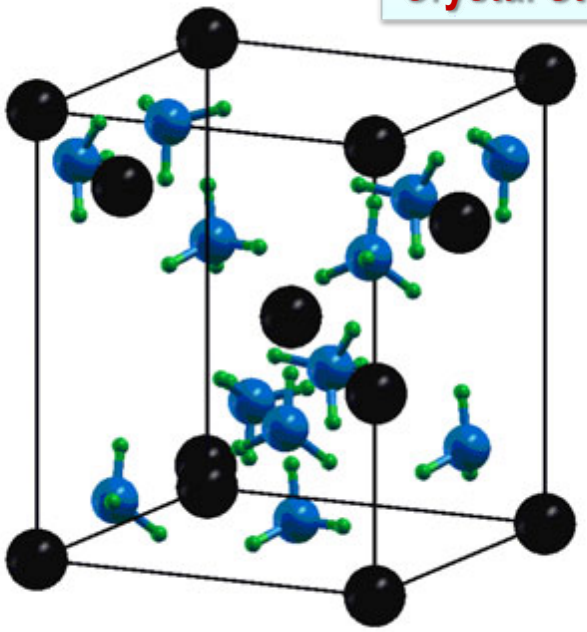


Total density of phonon states *g(w)* of $Mn(BH_4)_2$ in *I-4m2* symmetry. Total phonon density of states is normalized as $\int g(w)dw=1$.

$Mn(BH_4)_2$ of space group *I-4m2* (# 119) (Black (large), blue (middle) and green (small) spheres represent Mn, B and H atoms, respectively).

- The *I-4m2* structure, it is characterized by a fourfold coordination of $[BH^4]^-$ ions around the Mn2+ ions
- Each Mn^{2+} has 8 nearest neighbor H atoms with the shortest Mn-H bond distance around 2.06 Å.
- The B-H bond lengths and the H-B-H bond angles within the [BH4]- tetrahedral of *I-4m2* symmetry are found to be $d_{B\text{-}H}$ = 1.23 - 1.24 Å and $\theta_{H\text{-}B\text{-}H}$ = 106 – 115°, respectively

Crystal Structure

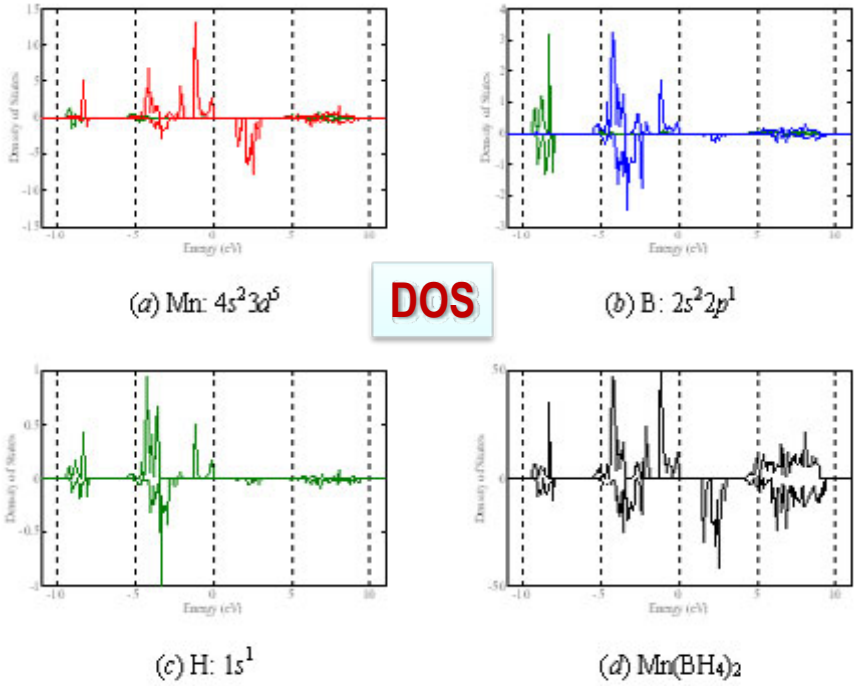


USF UNIVERSITY OF SOUTH FLORIDA

Task 3

SRL

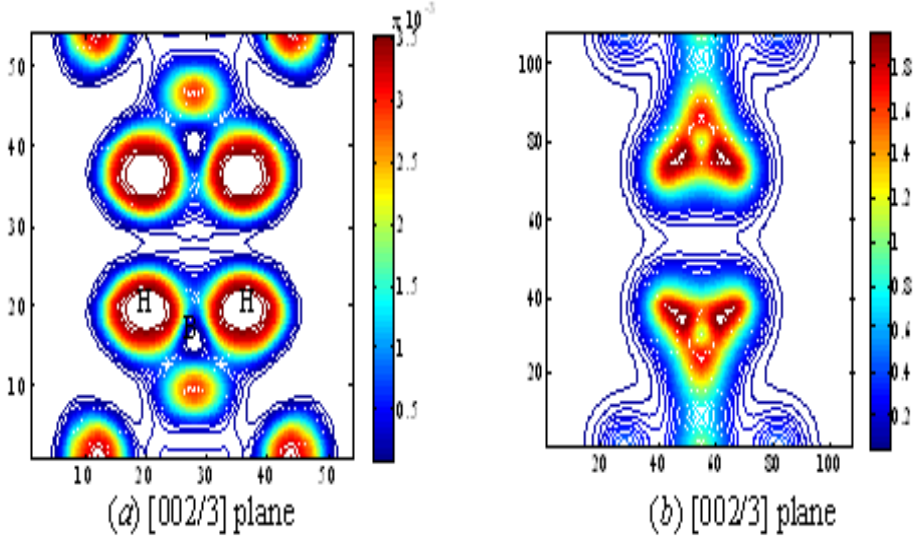
Accomplishments – $Mn(BH_4)_2$ – DFT Calculations



DOS

(*a-d*) Spin polarized total and partial DOS of $Mn(BH_4)_2$: zero energy is considered as Fermi energy level. (*s* electrons: green, *p* electrons: blue and *d* electrons: red color)

(*a-b*) Electron localization function (ELF) and Charge density of Mn(BH4)2 for *I-4m2* symmetry. The plane contains both Mn and B and H atomic sites are projected on the plane.

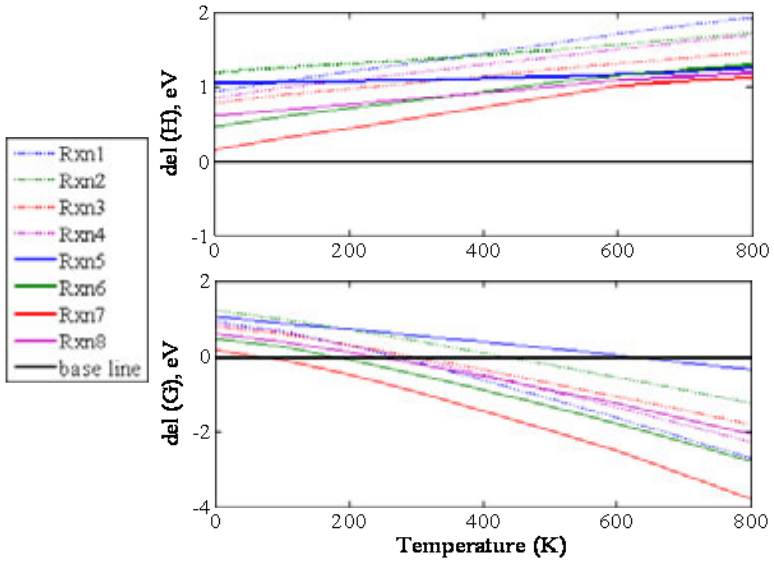


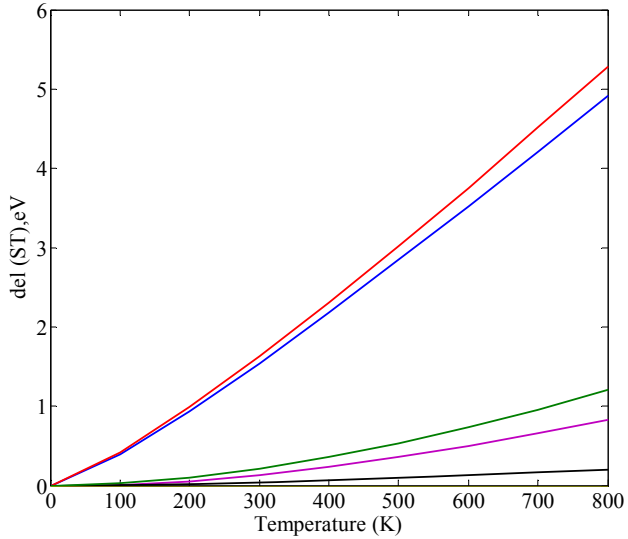
Electronic Structure

Accomplishments – $Mn(BH_4)_2$ – DFT Calculations

Possible dehydrogenation reactions:

$Mn(BH_4)_2 = Mn + 2B + 4H_2$, (1)
$Mn(BH_4)_2 = Mn + B_2H_6 + H_2$, (2)
$Mn(BH_4)_2 = MnH_2 + 2B + 3H_2$, (3)
$Mn(BH_4)_2 = ½\ MnH_2 + ½\ Mn + 2B + 7/2\ H_2$, (4)
$Mn(BH_4)_2 = MnH_2 + B_2H_6$, (5)
$Mn(BH_4)_2 = ½\ MnH_2 + ½\ MnB_2 + 7/2\ B + H_2$, (6)
$Mn(BH_4)_2 = MnB_2 + 4H_2$, (7)
$Mn(BH_4)_2 = ½\ MnH_2 + ½\ MnB_2 + ½\ B_2H_6 + 2H_2$ (8)



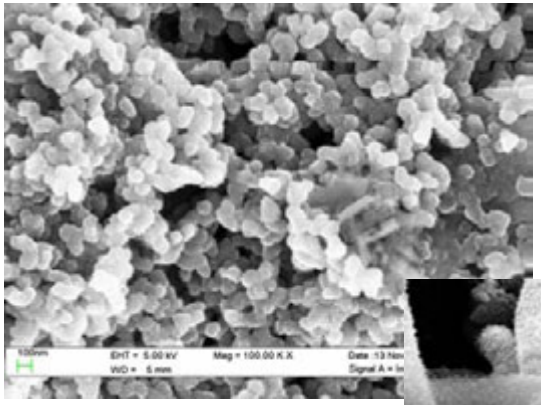


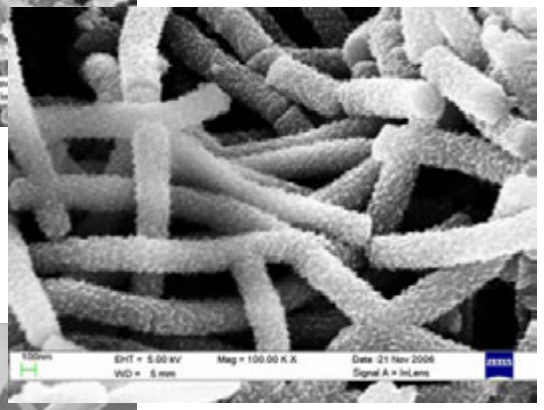
Entropy contribution:
$Mn(BH_4)_2 = MnB_2 + 4H_2$

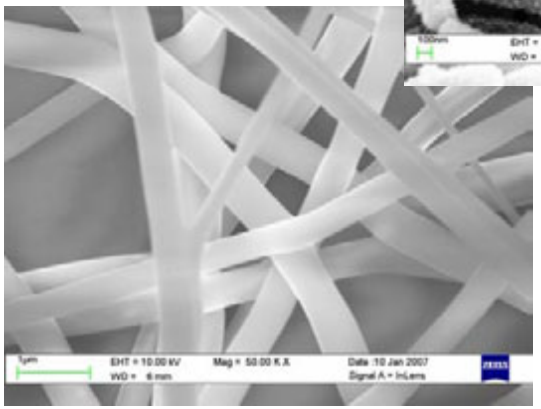
The total entropy contribution for the reaction (1*g*) $\Delta(TS)_{p\text{-}r}$ (blue line), for H_2 *molecules* $4T\Delta S(H_2)$ (red line), for MnB_2 *(purple line), for Mn (black line) and for the* $Mn(BH_4)_2$ *(green line)*

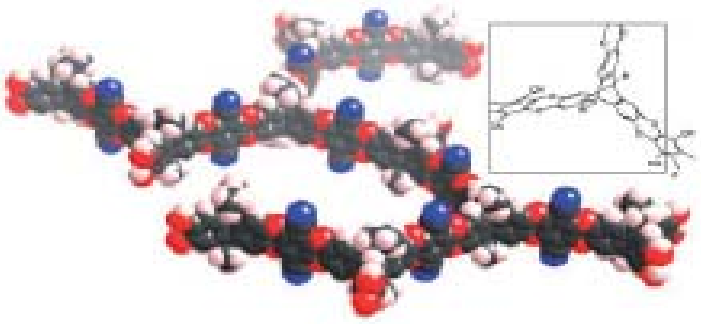
PANI Nanostructures

- **PANI Nanospheres – Chemical Method**
- **PANI Nanofibers – Chemical Method**
- **PANI Nanofibers – Electrospun Method**

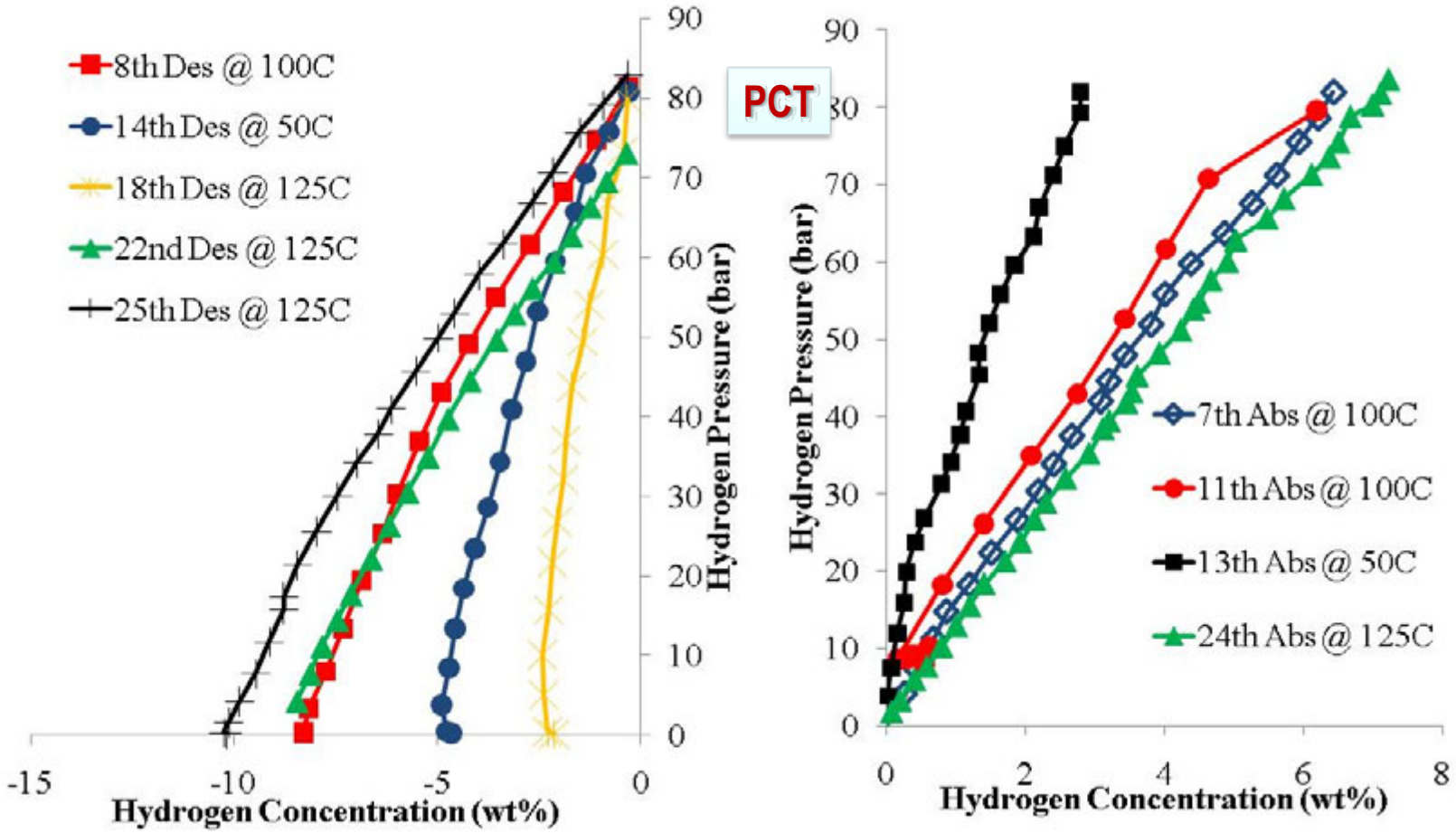








Accomplishments – Electrospun Polyaniline Nanofibers



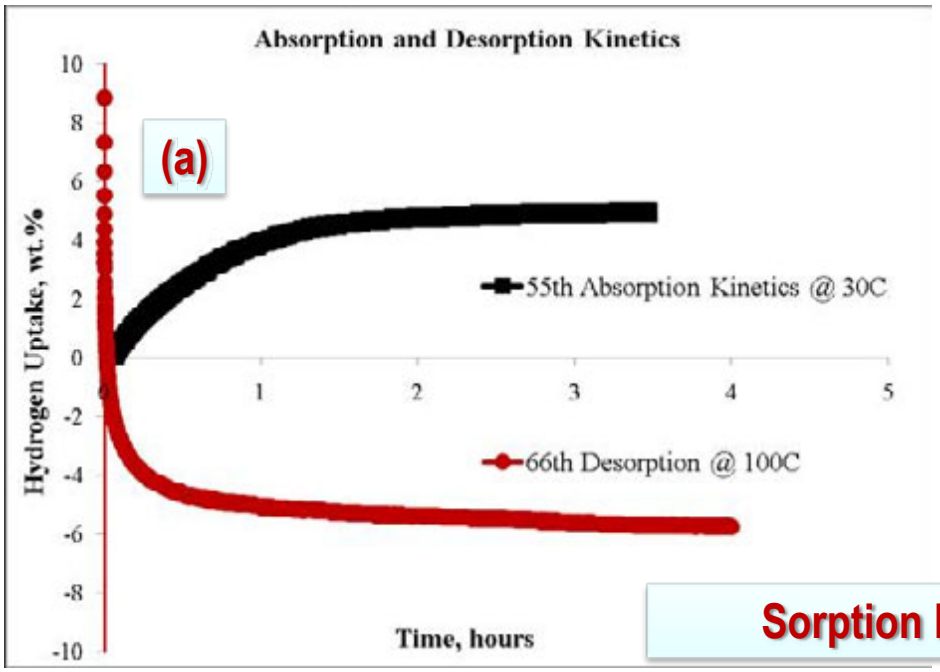
It can be seen that approximately 8wt% of hydrogen is absorbed at 80bar of hydrogen pressure at a temperature of 100-125°C. Note that these PANI nanofibers show reversible hydrogen storage capacities (25 cycles performance) of 8-10 wt.% at 100-125°C.

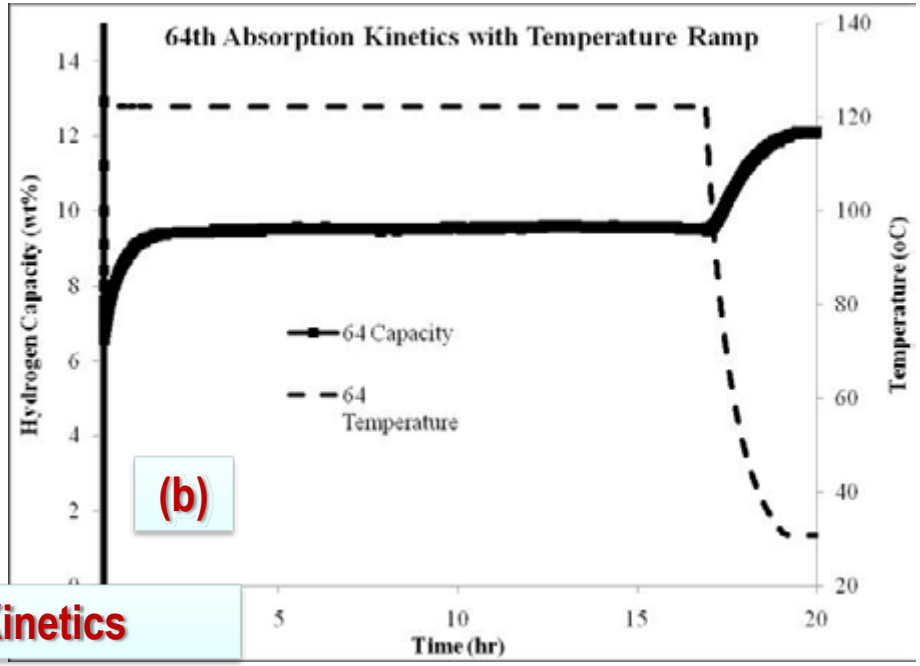
USF UNIVERSITY OF SOUTH FLORIDA

Task 4

CERC Clean Energy Research Center

Accomplishments – Electrospun Polyaniline Nanofibers



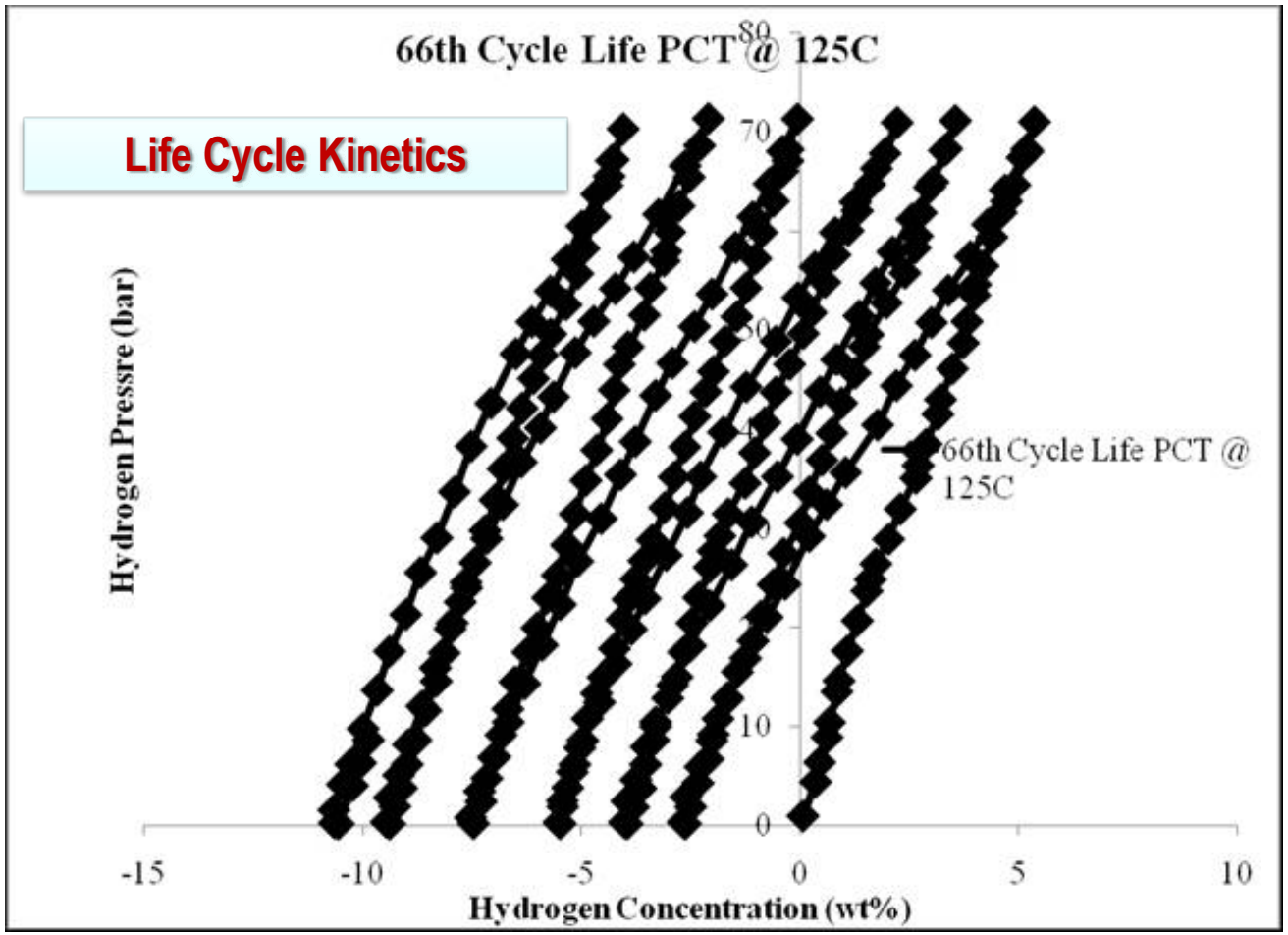


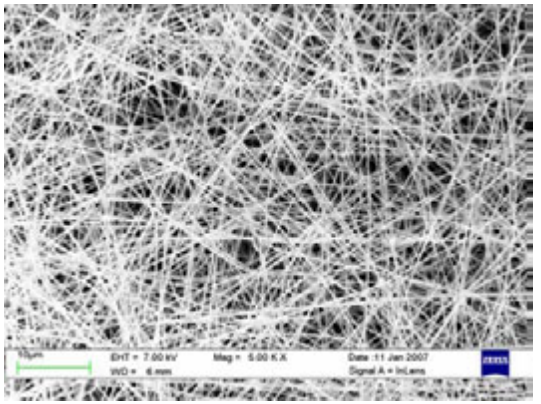
Sorption Kinetics

(a) The hydrogen absorption kinetics of the PANI nanostructure after 55 previous absorption / desorption cycles at 30°C. It can be seen that after approximately 2 hours at 80bar of H_2 pressure close to 5wt% of hydrogen is absorbed. Additionally, the hydrogen desorption after 66 cycles at 100°C. Reveals that the kinetics are rather rapid, with most of the hydrogen being released in less than 30 minutes for a total hydrogen release of close to 6wt%.

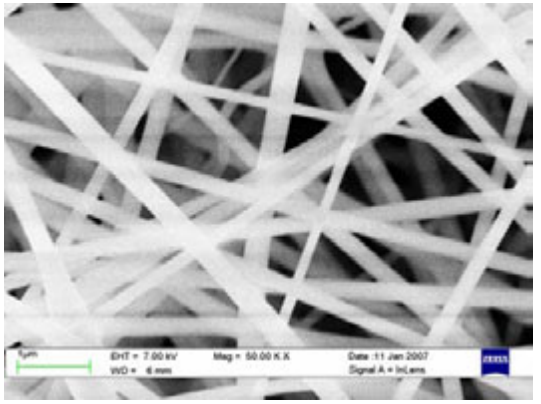
(b) The absorption kinetics (64th cycle) of hydrogen at 80bar of hydrogen pressure with varying temperature. Initially, the hydrogen is absorbed at 125°C with saturation occurring after approximately 2 hours (solid line). After 18 hours, the temperature (dotted line) is reduced to 30°C, whereupon another 3wt% of hydrogen is absorbed.

Accomplishments – Electrospun Polyaniline Nanofibers





SEM



Cyclic PCT measurements are shown in the 66th cycle of the material. It can be seen that approximately 6wt% are reversibly absorbed and released with increasing and/or decreasing pressure at 125°C.

USF UNIVERSITY OF SOUTH FLORIDA

Task 4

CERC Clean Energy Research Center

Summary – LiMgBNH Complex Hydride

Material	Capacity	Reversibility	Temperature	Activation Energy
LicMgBNH	3.2 wt%	Reversible	175°C	140.3 kJ/mol
LinMgBNH	3.8 wt%	Reversible	**150°C**	162.2 kJ/mol
LicMgBNH 10hr	1.9 wt%	Reversible	175°C	**109.8 kJ/mol**
LiBNH + cMgH_2	**5.2 wt%**	Reversible	175°C	162.5 kJ/mol
LiBNH + nMgH_2	**5.6 wt%**	Reversible	**150°C**	123.6 kJ/mol

- Processing Conditions
  - No effect on chemical structure – intimate mixture of LiBNH + MgH_2
  - Large effect on temperature
  - Large effect on capacity
  - Small effect on microstructure
  - Particle size **difference** – vital parameter needs to be optimized
- LiBNH + nano MgH_2 best candidate for further study

Summary – LiMnBH and LiMnBH+nMgH_2

Xmol% nanoNi doped $LiMn(BH_4)_3$	DSC melting transition (ºC)	TGA On-set decomposition Temperature (ºC)	TGA Peak decomposition Temperature (ºC)	Weight loss (%)
Undoped	99	125	143	7.8
0.5	98	112	131	7.3
1.0	98	110	131	7.7
1.5	98	107	123	8.0
2.0	98	108	130	7.0
2.5	98	107	123	7.2
3.0	98	108	129	7.1

Undoped LiMnBH: Ea = 130.64 kJ/mol
NanoNi doped LiMnBH: Ea = 111. 55 kJ/mol

The stability of hydride was found to be ((nano)Ni>Co>Fe>Cu>Mn>Pd>Standard

10-15mol% of nanocrystalline MgH_2 doped with LiMnBH hydride shows cyclic reversibility of 3-4 wt.% at Temperature ranges from 100-125ºC

Summary – DFT Calculations of $Mn(BH_4)_2$

- These calculations establish a stable structure of $Mn(BH_4)_2$ at finite temperature
- From electronic structure calculations, ionic interaction between Mn and $[BH_4]^-$ and strong iono-covalent B–H interaction within the $[BH_4]^-$ tetrahedral structure are revealed.
- Electronic density of states studies reveal that the $Mn(BH_4)_2$ is a half-metallic hydrogen storage material due to the presence of half filled *d* orbital of Mn
- Standard Gibbs energy calculations reveal that reaction, *i.e.*, $Mn(BH_4)_2 \rightarrow MnB_2 + 4H_2$ is the most favorable dehydrogenation reaction and no borane families
- The calculated standard enthalpy of reaction was found to be always positive over the entire temperature range, indicating that the dehydrogenation reaction is endothermic (need to address reversibility issue by experiments!!!)
- The methodology outlined in this work can be extended to study other forms of complex hydride materials

Summary – PANI Nanostructures

Material	Capacity	Reversibility	Temperature	Comments
PANI Bulk	0.4 wt%	Small	125°C	
PANI NS-CM	6 wt%	Decreases to 0.5 wt%	30°C	Slow kinetics (hours)
PANI NF-CM	3 wt%	Reversible	30°C	Fast Kinetics (<10min)
PANI NF-ES	10wt%	Reversible with PCT, capacity decreases with kinetics measurement	100°C (kinetic) 125°C (PCT)	Kinetics combination of physisorption (rapid) and chemisorption (slow)

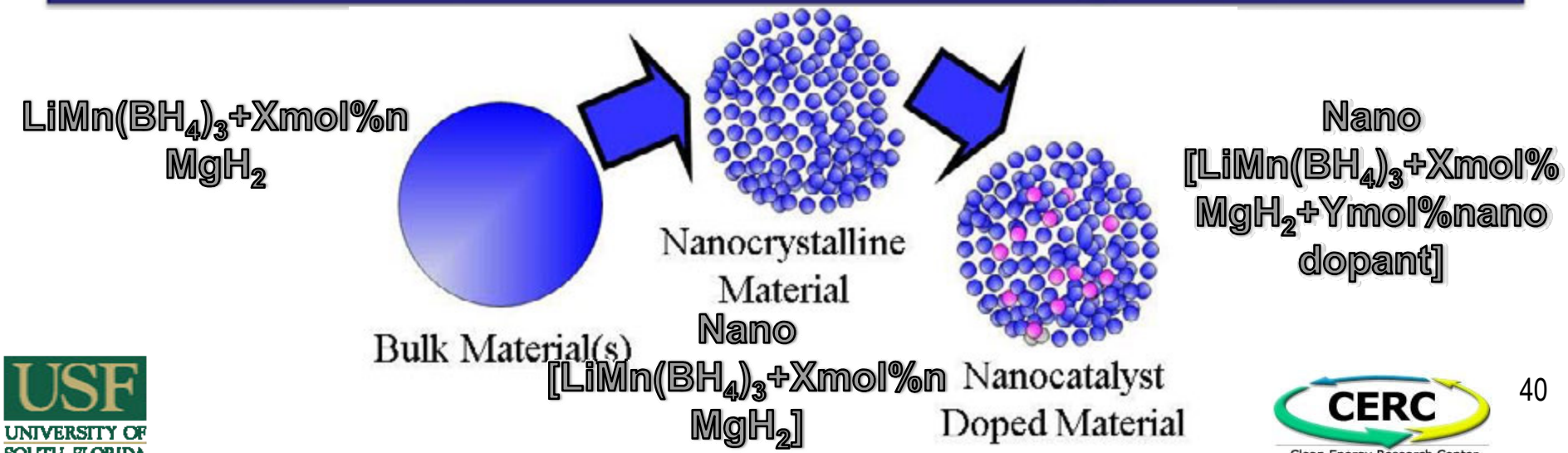
- PANI nanostructures combine physisorption and chemisorption
- Reversible storage of >3wt% possible at room temperature
- Reversible storage of <10wt% possible at 100°C

Proposed Future Research

Task 1: LiMgBNH and nanomaterial doped LiMgBNH

- Investigate hydrogen performance of nanomaterial dopant enhanced complex multinary hydrides
- Investigate activation energy and the mechanism of hydrogen release from nanomaterial doped complex hydrides using Kissinger method
- Insitu RAMAN, XRD, FTIR, TEM studies of the dehydrogenation and reversible rehydrogenation of undoped and nanomaterial doped Li-Mg-B-N-H ***(NIST Collaboration)***
- Gas evolution analysis insitu during the cyclic hydrogen sorption measurements.

Task 2: LiMnBH and Xmol% LiMnBH having nano additives

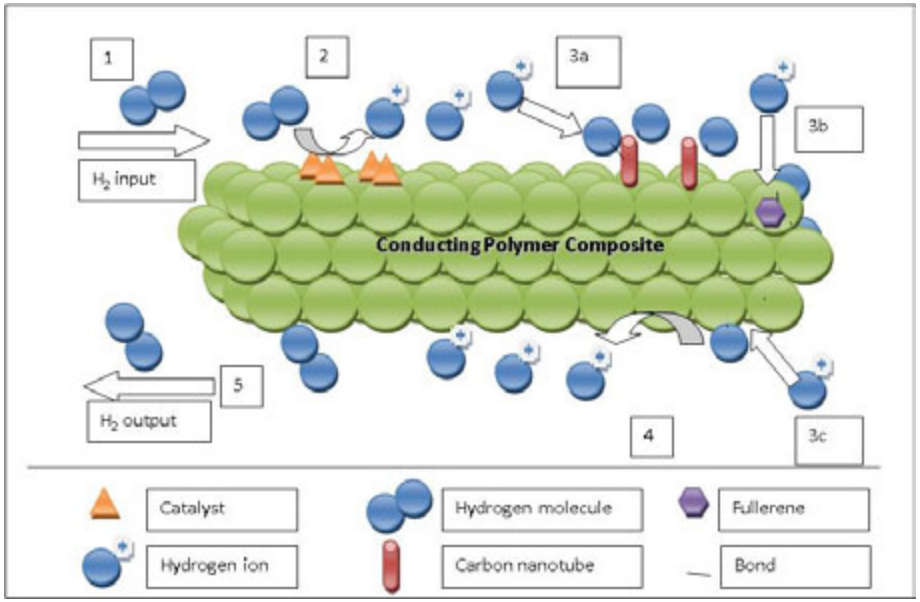


Proposed Future Research

Task 3: DFT calculations of $Mn(BH_4)_2$ and related systems

- Establish the structure of new $LiMn(BH_4)_3$ phase and calculate the thermodynamic stabilities by Density Functional Theory.
- Investigate the effects of nanomaterial additive on the dehydrogenation and reversible rehydrogenation characteristics of $LiMn(BH_4)_3$ by finding the cohesive energies and bond strength information.
- Demonstrate and correlated the analysis results of DFT calculations with the experimental investigations carried out in previous tasks.

Task 4: Polyaniline Nanostructures: Functionalization



Mechanistic approach to enhance the hydrogen storage characteristics of PANI nanostructures by incorporating various materials such CNT, Fullerene, SnO_2 and Titanium during chemical and electrospinning processes.

Collaborations

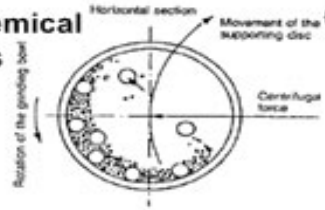
USF UNIVERSITY OF SOUTH FLORIDA

Nanomaterials and Nanomanufacturing Research Center

NNRC

QUANTUM SPHERE

Mechano-chemical Process



Complex Hydrides Development

Characterization

QSI-Nano® Process

Nanomaterials Development

CERC

Clean Energy Research Center

Materials Synthesis

Nanocatalyst Development

PANI

Polyaniline Nanostructures Synthesis & Characterization

Nano-RAM Technologies

b-initio VASP Vienna Simulation Package

Density Functional Theory of Complex Hydrides

SRL

Insitu- RAMAN
Insitu FTIR
PGAA, PCT

NIST

High Pressure (Gpa) Hydrogen insitu RAMAN

SRI

PCT, Kinetics, Life cycle and Gas analyses

New complex borohydrides

FIU

UNIVERSITY of HAWAI'I MĀNOA

Hydrogen Safety

- Handling reactive chemicals, catalysts, solvents and high pressure gases
- Transfer and loading/unloading the materials for characterization studies
- Mechano-chemical synthesis and doping under reactive gas environment
- Hydrogenation and dehydrogenation with high pressure hydrogen gas regulations
- Methodologies for disposing/deactivating chemicals, alloys, hydrides
- Safety and Risk Management training
- Regular monitoring of lab safety by the EHS&RM officials
- Complying with MSDS date sheet
- Adhering to vendor instructions for PCT operation
- H_2/He leak testing with in-built automated alarm system and external leak check procedures for PCT operation
- Trained personnel for the safe operation of high pressure systems, reactive gases and explosive materials
- Standard operating procedures (protocols) establishment and regular maintenance/repair of the equipment