Development of Metal-N-H Systems for Hydrogen Storage

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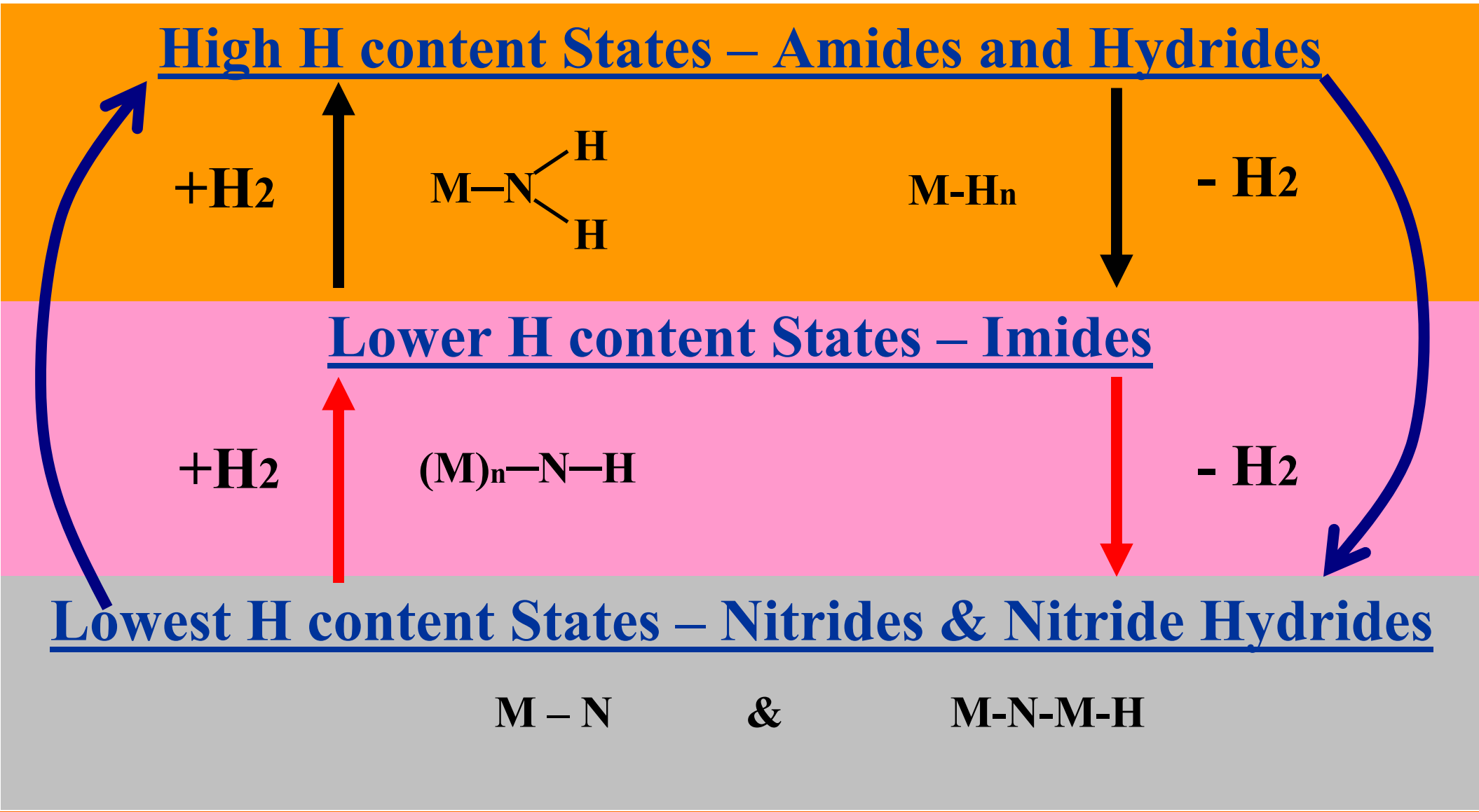
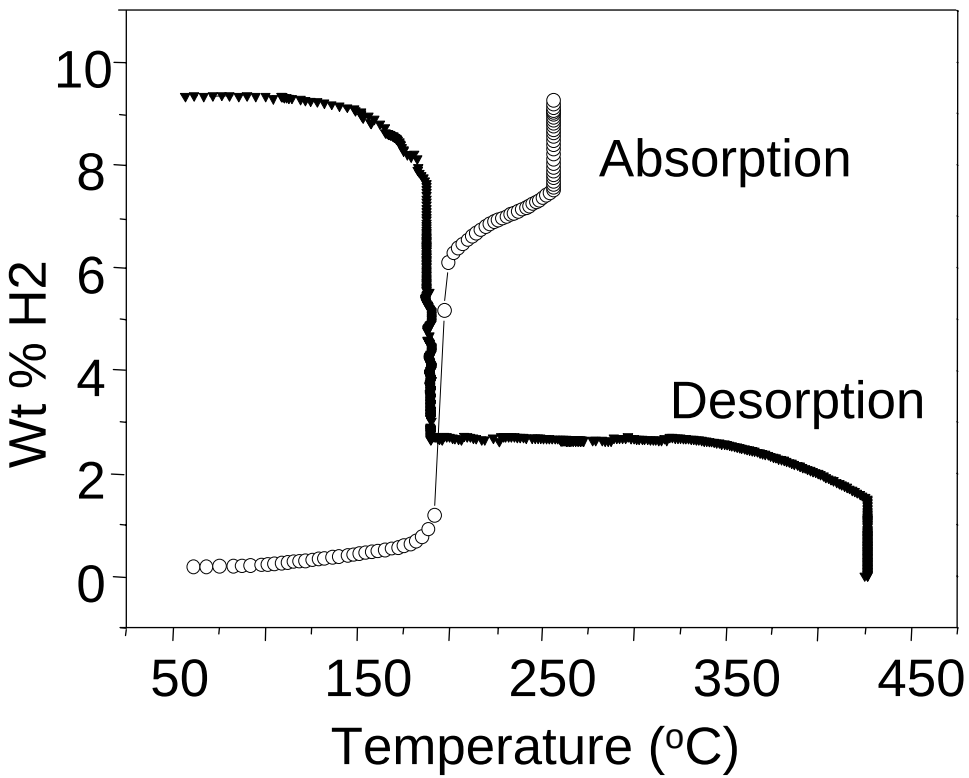
Contents

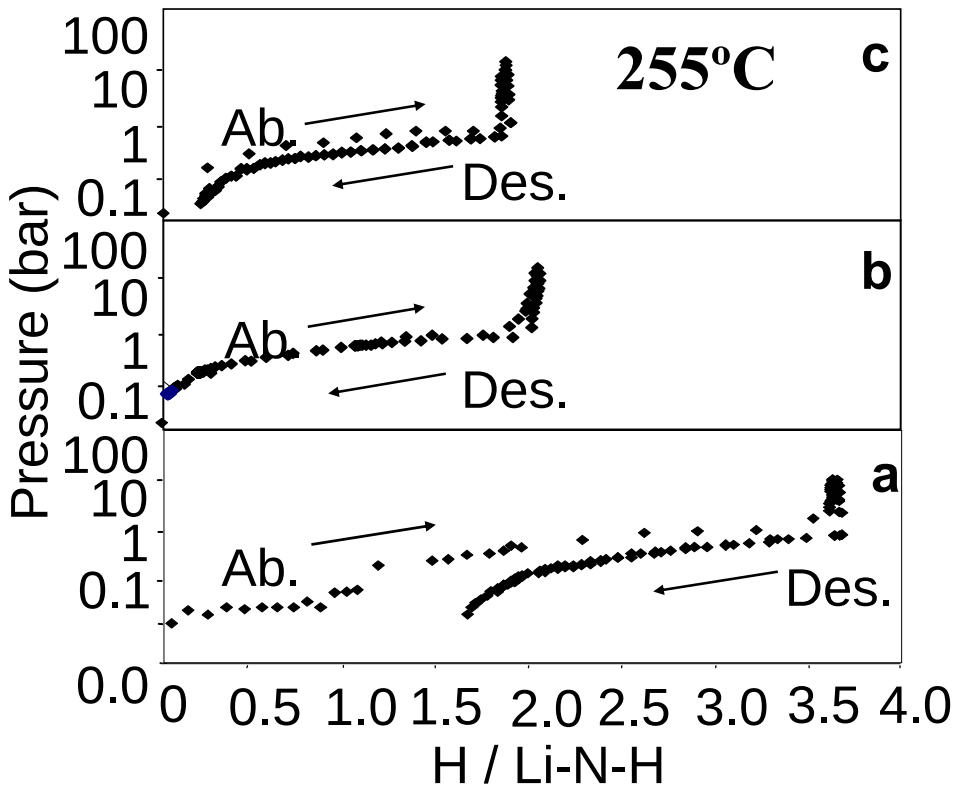
I. Material Scope



II. Binary Systems

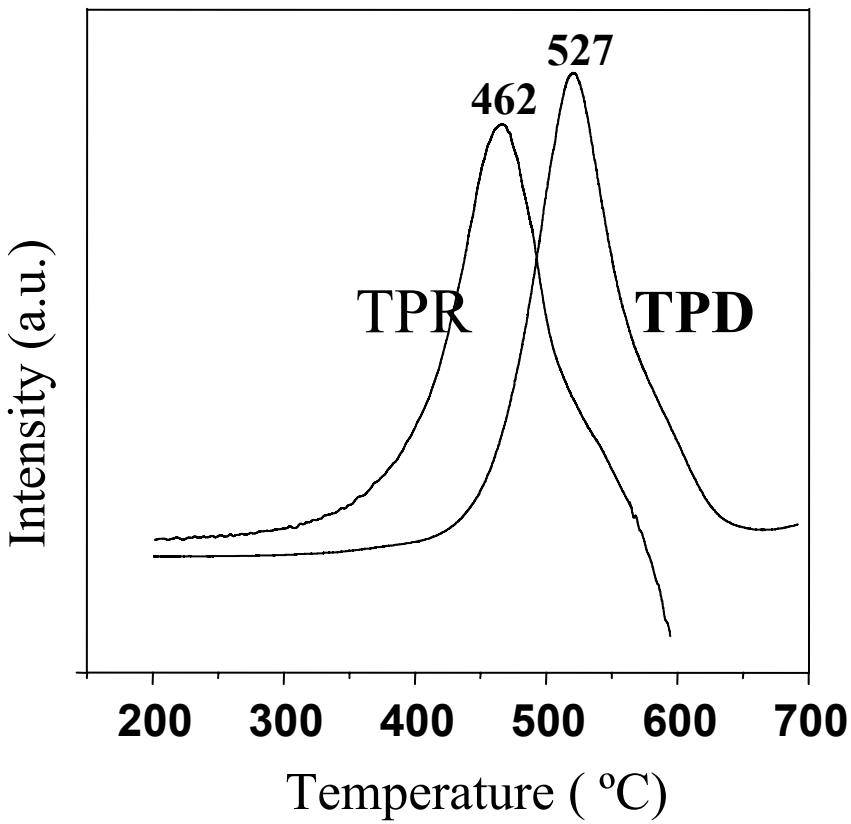
$LiNH_2 + 2LiH \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow Li_3N + 2H_2$ 10.5wt%

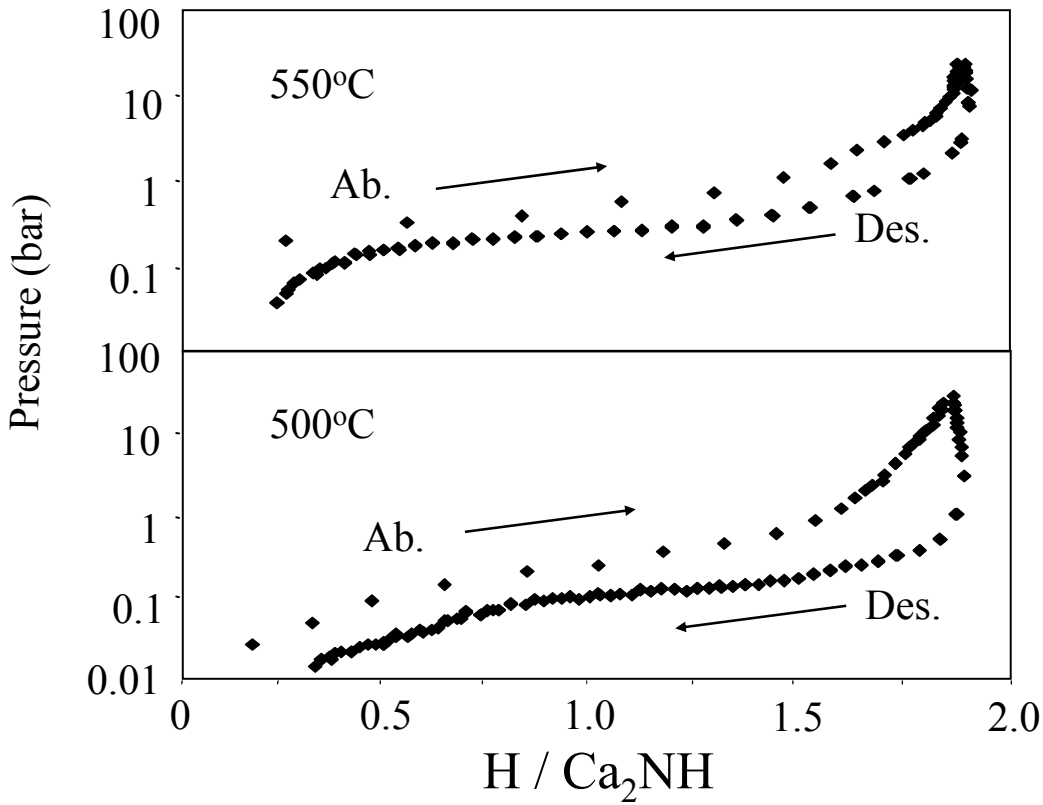




-- Chen P, Xiong ZT, Tan KL et al, Nature 2002, 420, 302-304

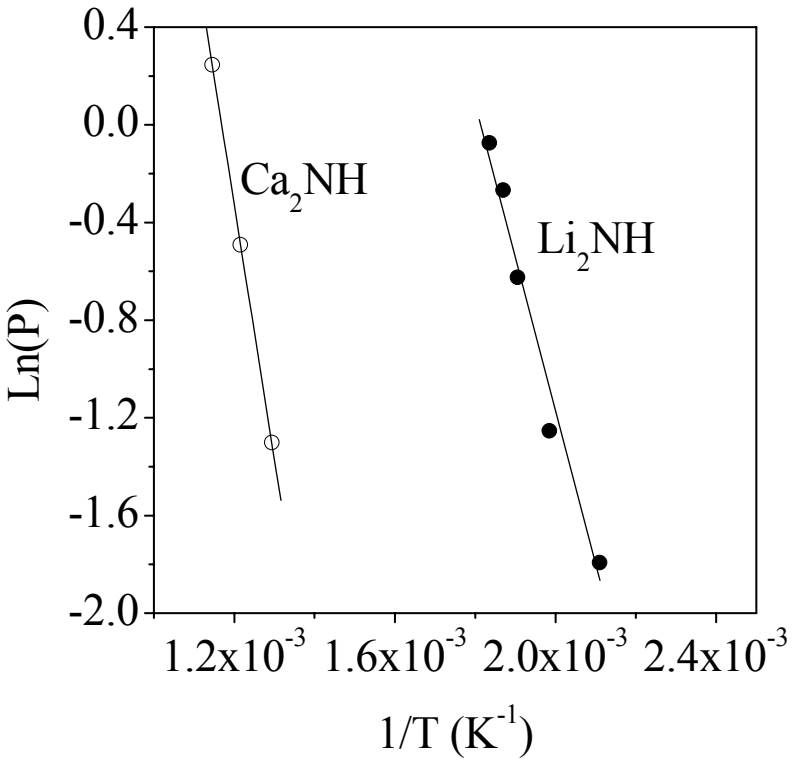
$CaNH + CaH_2 \leftrightarrow Ca_2NH + H_2$ > 2 wt%





-- Xiong ZT, Chen P, Tan KL et al, J. Mater. Chem. 2003, 13, 1767

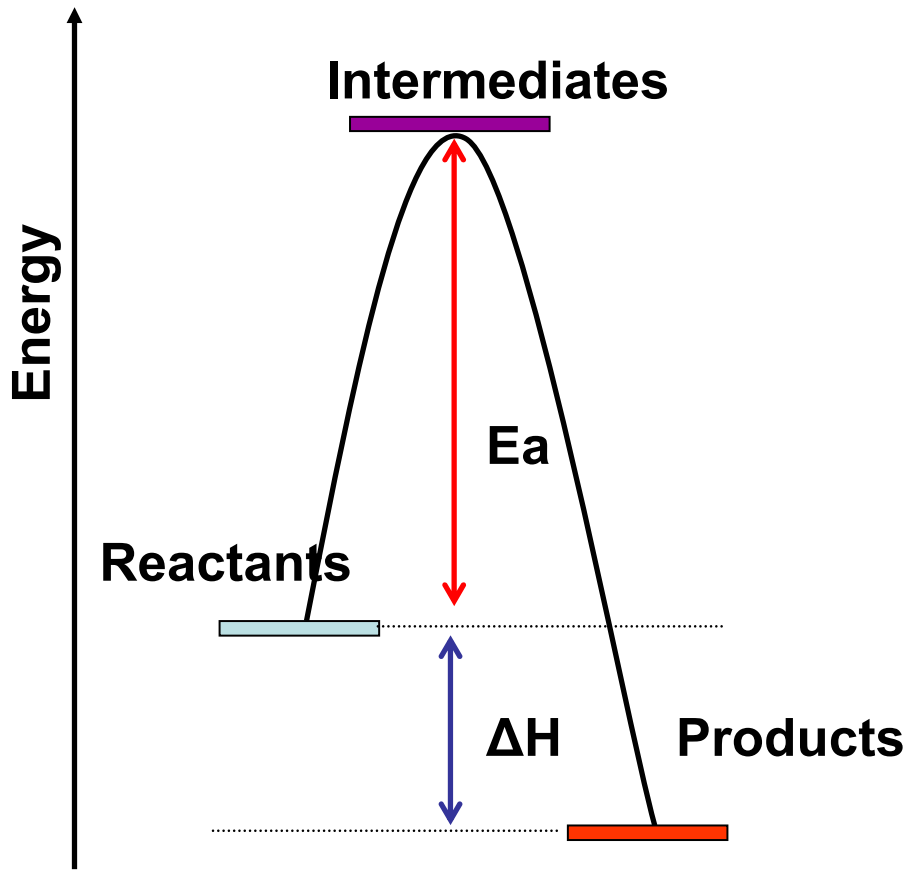
Thermodynamic parameters



Li2NH ΔH = -66.1 kJ/mol

Ca2NH ΔH = -88.7 kJ/mol

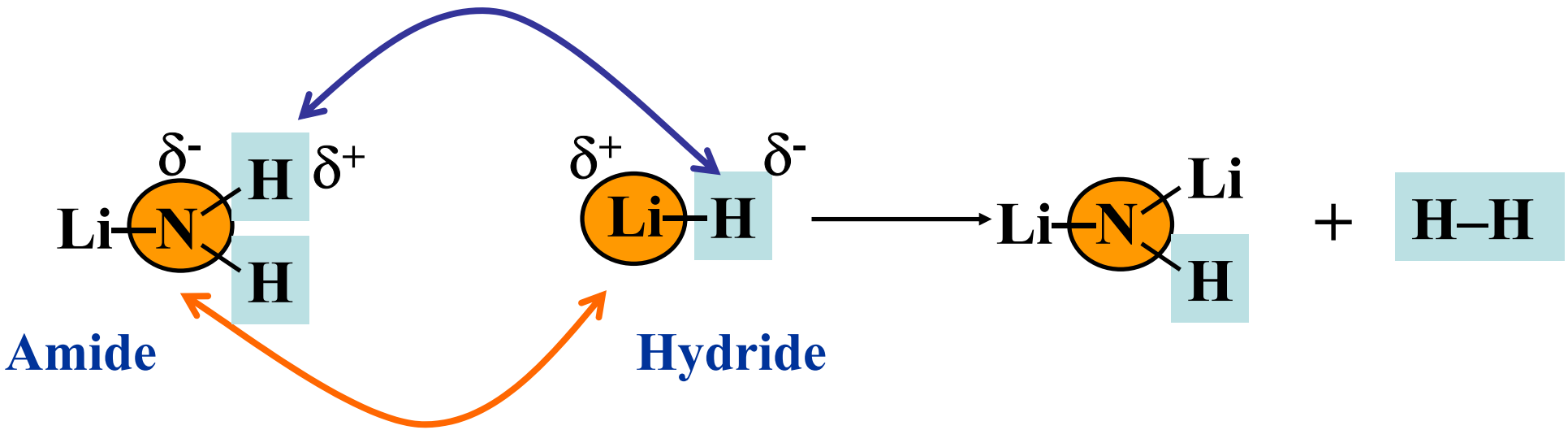
$$M\text{-}N\text{-}H_n + H_2 \leftrightarrow M\text{-}N\text{-}H_{n+2}$$



ΔH, ΔS – determine the reaction Temp.

Tuning the Thermodynamic Parameters

III. Mechanistic Interpretations



$$H^+ + H^- \rightarrow H_2 \qquad \Delta H = -17.37\ eV$$

The abnormally high potential for the combination of H^+ and H^- to H_2, and the Columbic attraction between N and M are likely to be the driving forces!

If the interaction above is universal, variety of reactions can be taken place between different amides and hydrides with hydrogen release.

IV. Approach for Material Development

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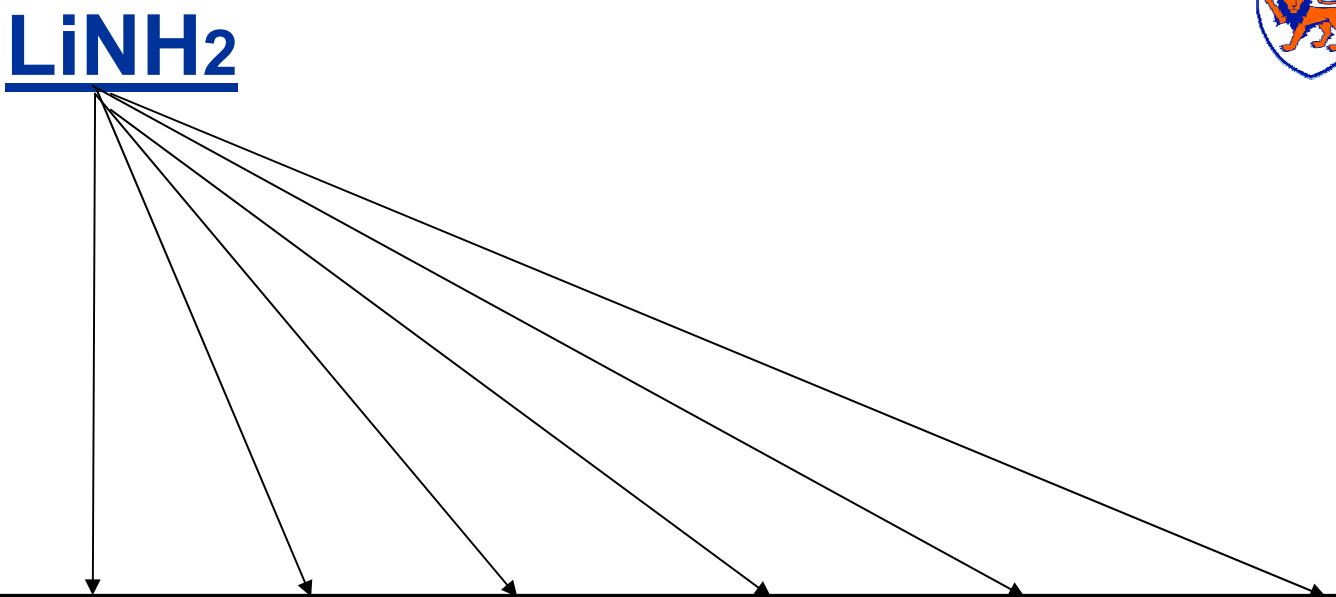
Changing amide or hydride - Resources

Binary Amides		Ternary Amides
Available	Self-made	Self-made
$LiNH_2$	$Mg(NH_2)_2$	$Li_3Na(NH_2)_4$
$NaNH_2$	$Ca(NH_2)_2$	$Na_2Mg(NH_2)_4$
KNH_2		$NaCa(NH_2)_3$ etc.

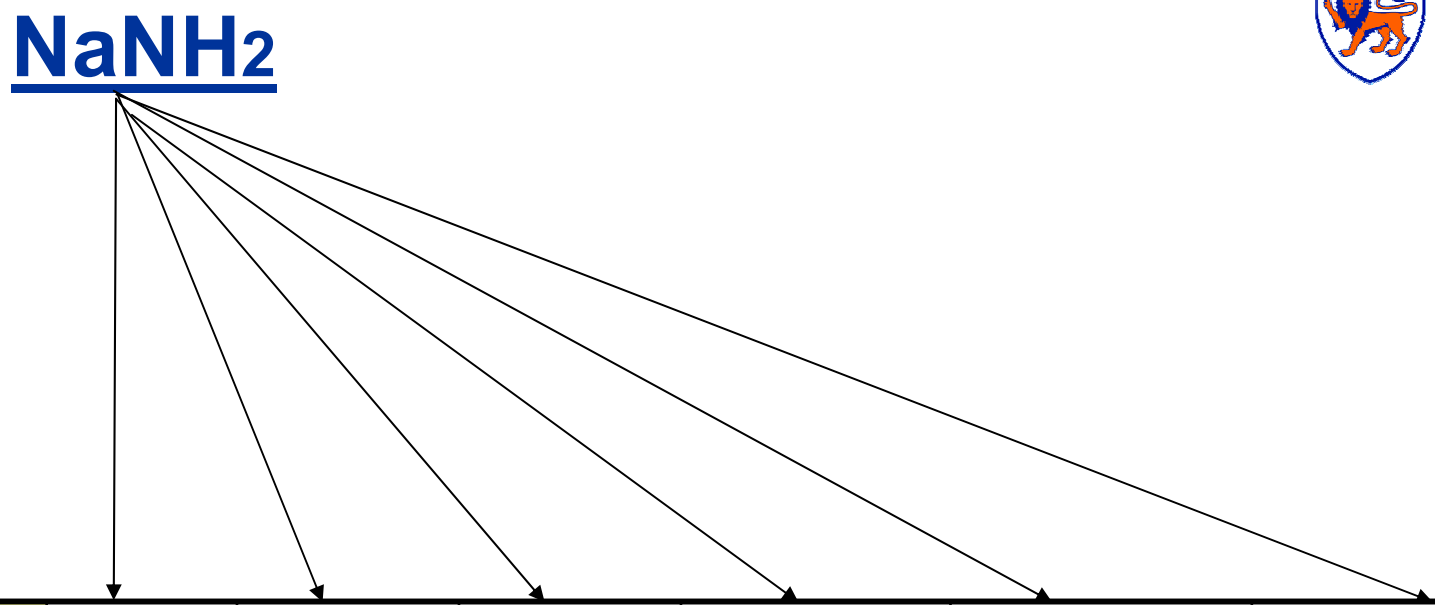
Binary Hydrides		Complex Hydrides
LiH	MgH_2	$LiAlH_4$
NaH	CaH_2	$NaAlH_4$
KH	AlH_3	$LiBH_4$
	TiH_2	Na_3AlH_6
		$LiNa_2AlH_6$



Performance	LiH	NaH	CaH_2	MgH_2	$LiAlH_4$	$NaAlH_4$
H_2 Desorption	Y	Y	Y	Y	Y	Y
Reversibility	Y	?	Y	Y	Y	N
Enthalpy	___*	___	___	__	_	?

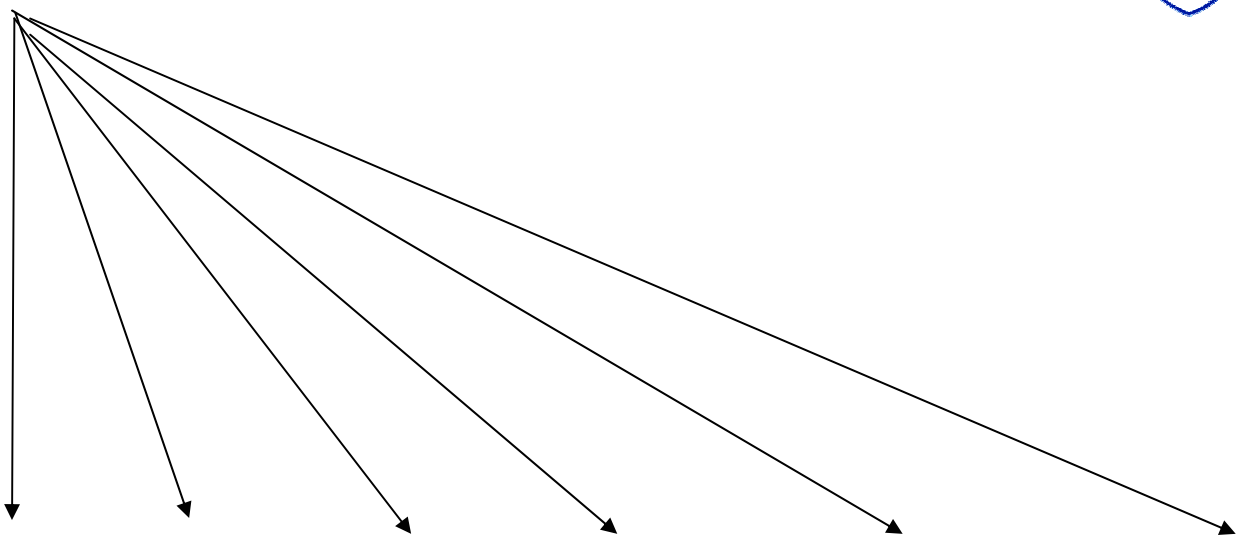
* The longer the bar, the heavier the endothermic nature.

? Uncertain, need more investigations

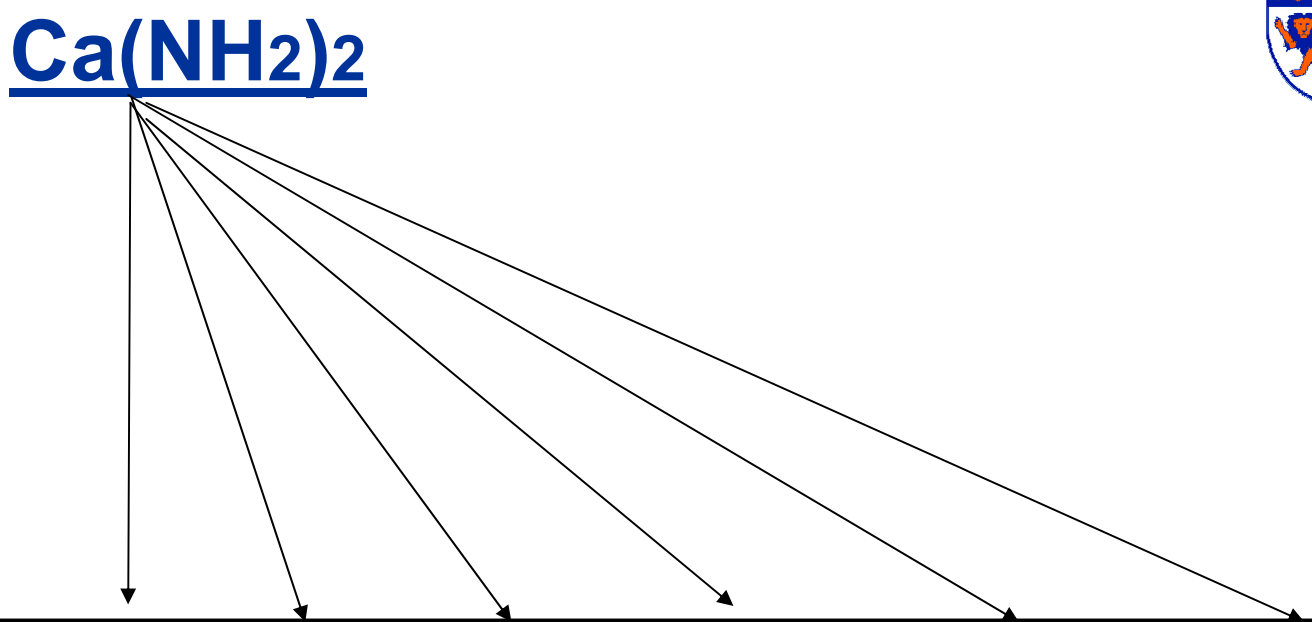


Performance	LiH	NaH	CaH_2	MgH_2	$LiAlH_4$	$NaAlH_4$
H_2 Desorption	Y	?	Y	Y	Y	Y
Reversibility	Y	?	?	Y	N	?
Enthalpy	___	?	_	___	++	_

$Mg(NH_2)_2$



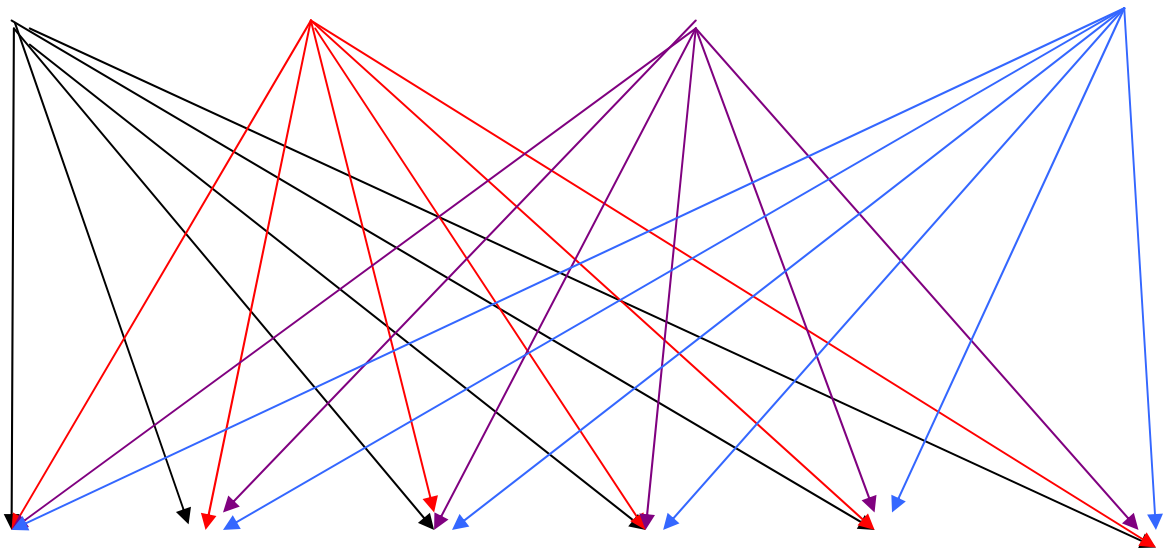
Performance	LiH	NaH	CaH_2	MgH_2	$LiAlH_4$	$NaAlH_4$
H_2 Desorption	Y	Y	Y	Y	Y	Y
Reversibility	Y	Y	?	?	?	?
Enthalpy	—	——	–	–	–	–



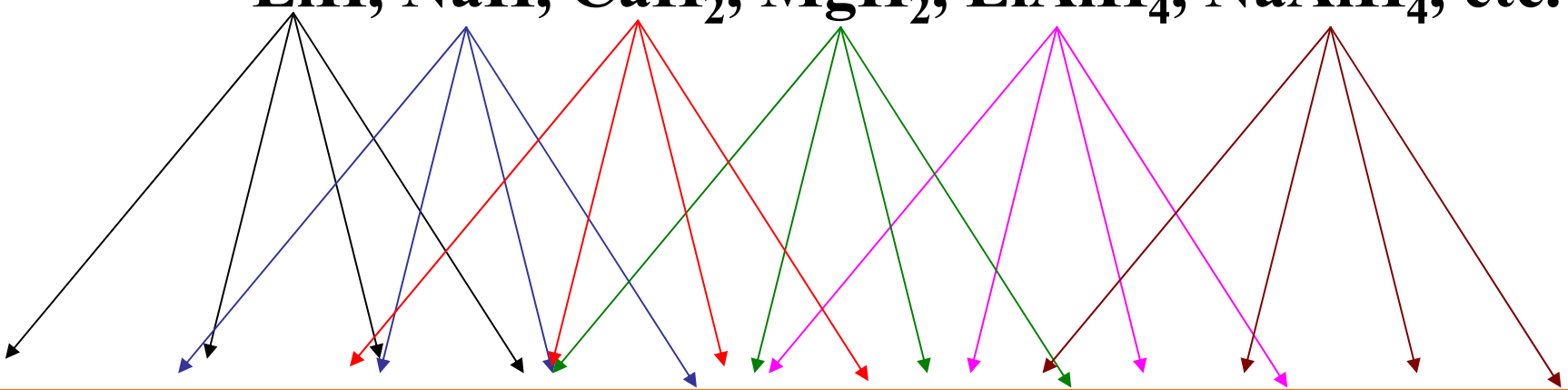
Performance	LiH	NaH	CaH_2	MgH_2	$LiAlH_4$	$NaAlH_4$
H_2 Desorption	Y	Y	Y	Y	Y	Y
Reversibility	Y	?	Y	?	?	?
Enthalpy	___	_	+ & _	_	_	_

Multinary Systems

$Li_3Na(NH_2)_4$, $Na_2Mg(NH_2)_4$, $NaCa(NH_2)_3$, $LiAl(NH_2)_4$



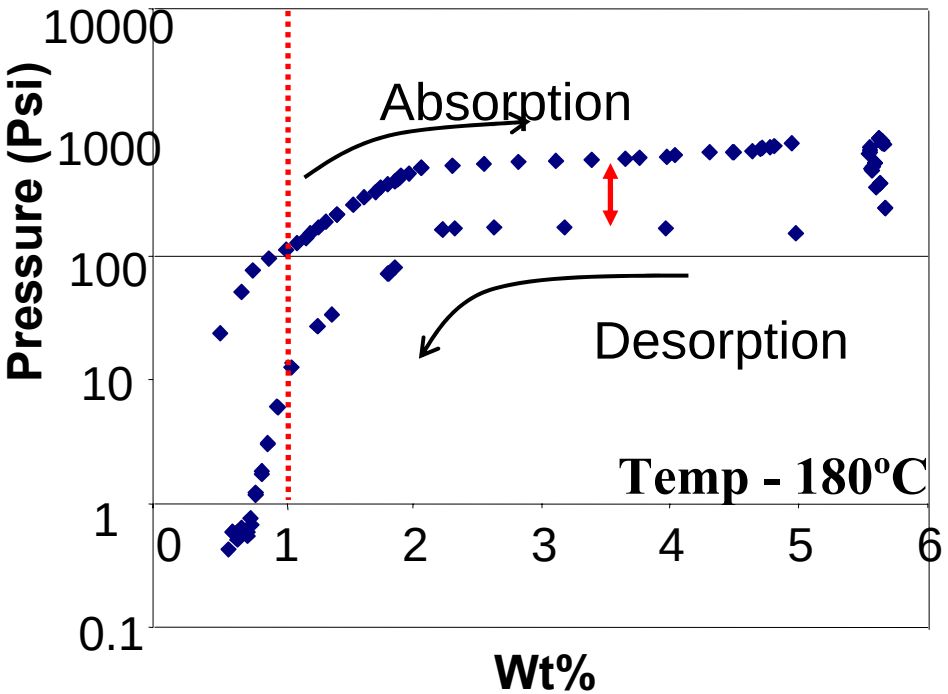
LiH, NaH, CaH_2, MgH_2, $LiAlH_4$, $NaAlH_4$, etc.

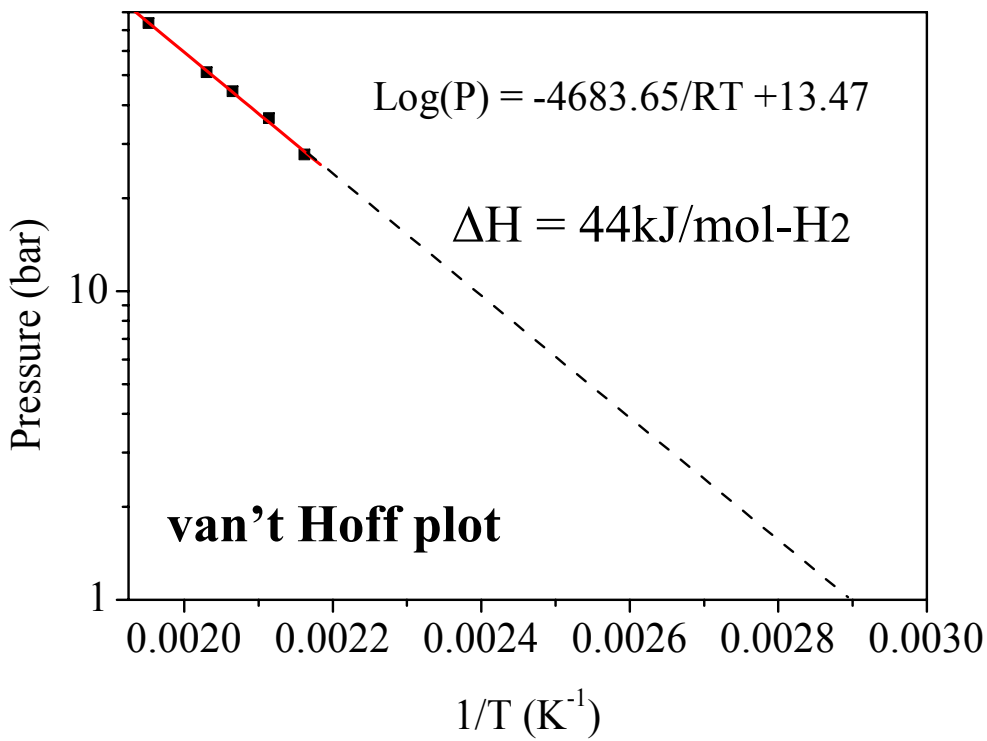


V. Case of Study

- **Li-Mg-N-H**
- **Mg-Ca-N-H**
- **Li-Na-Al-N-H**
- **Li-Mg-Ca-N-H**

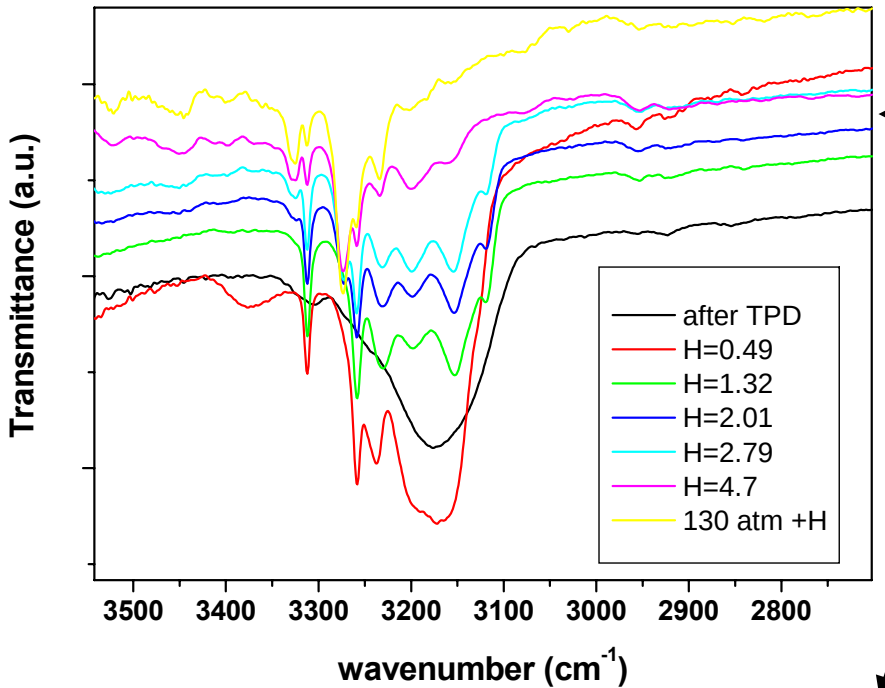
$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2MgN_2H_2 + 2H_2$ 5.88wt%

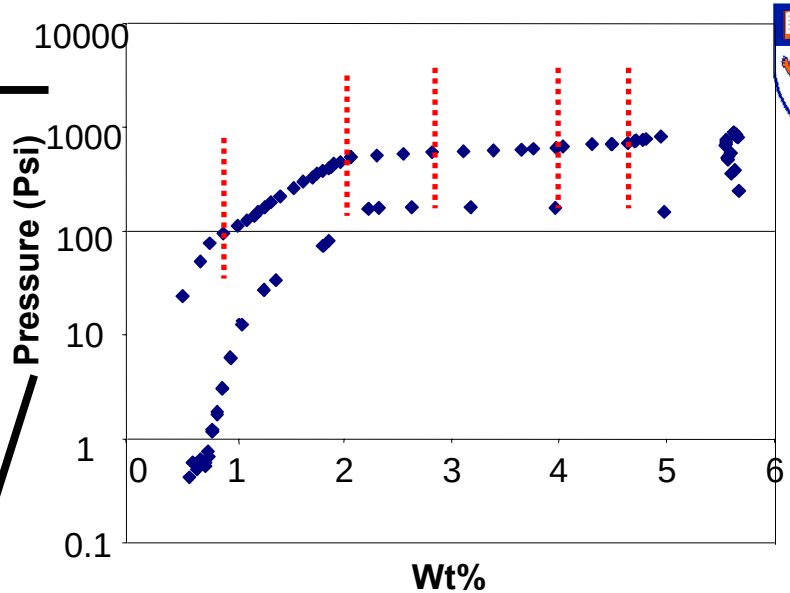


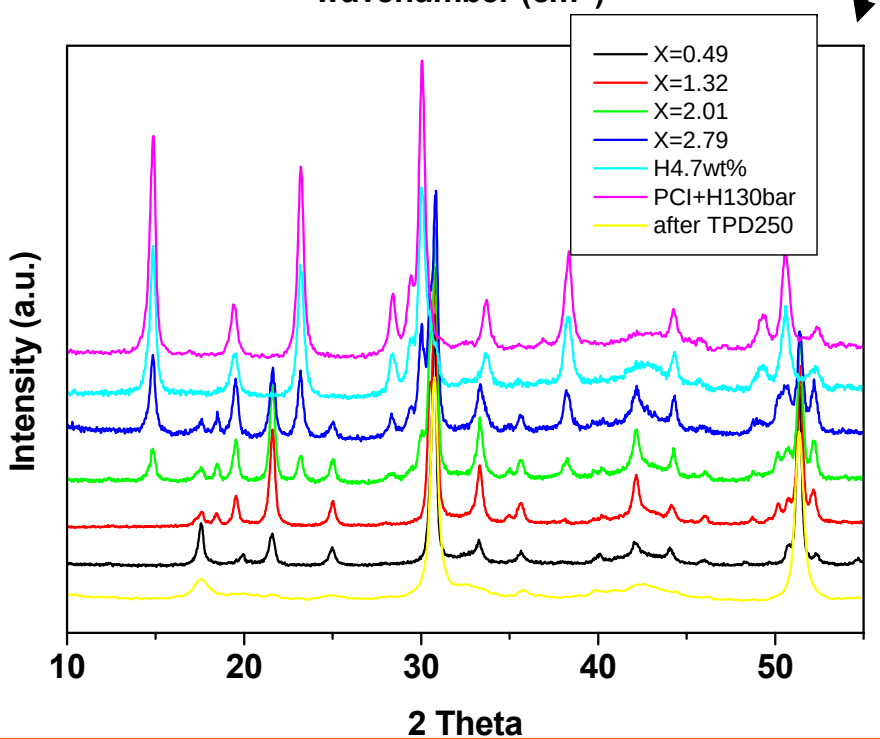


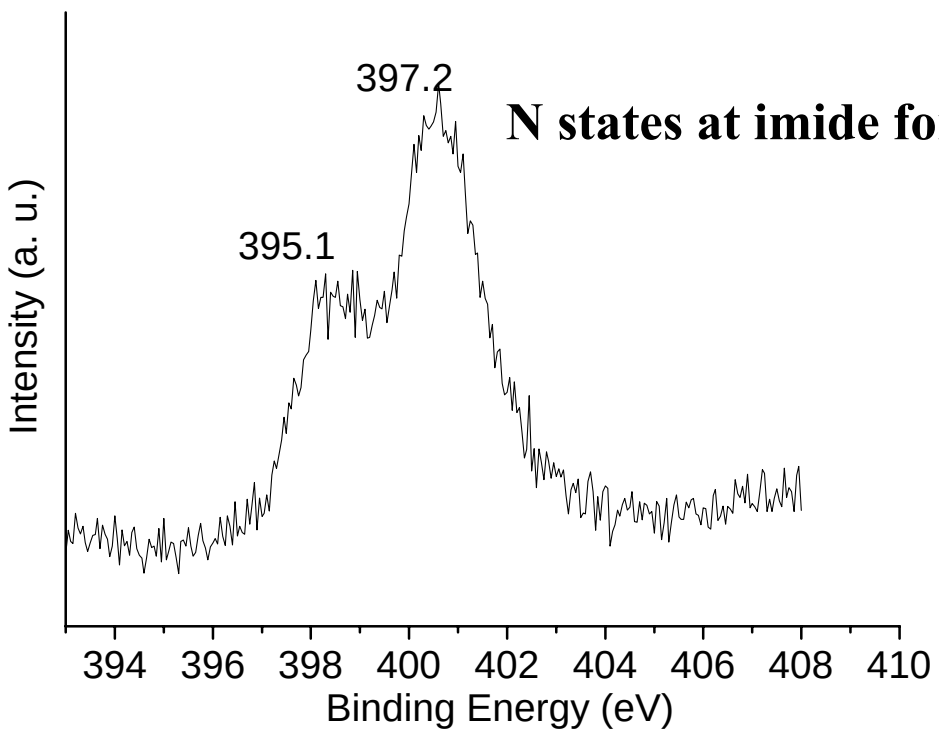
Thermodynamic analysis shows the operation temperature could be below 363K.

-- Xiong ZT, Wu GT, Hu JJ, Chen P, Adv Mater, 2004, 16, 1522-1525

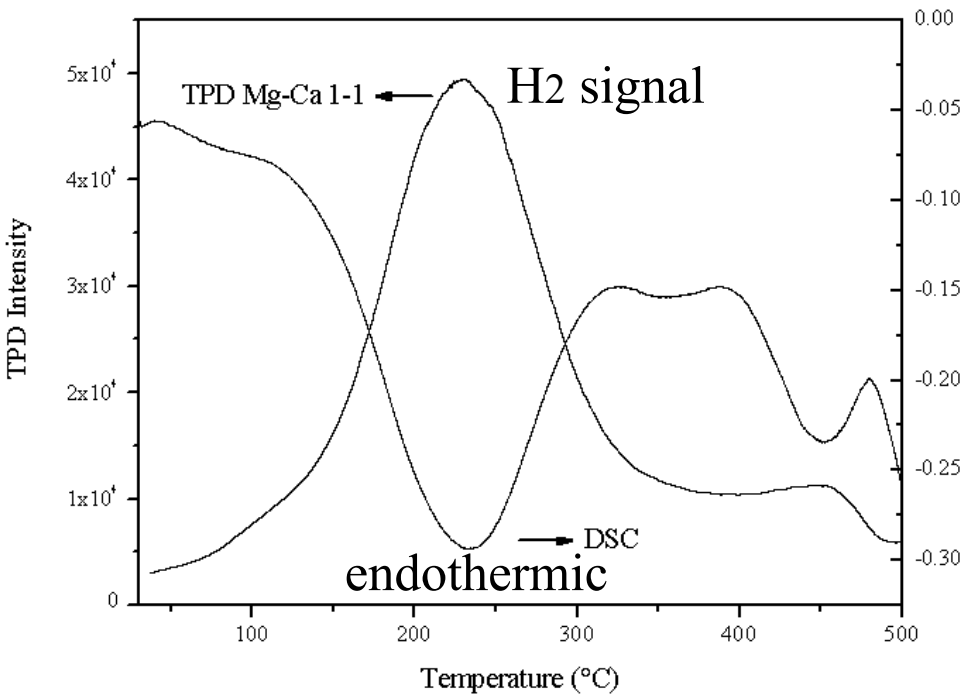

Transmittance (a.u.)
wavenumber (cm-1)
3500 3400 3300 3200 3100 3000 2900 2800
after TPD
H=0.49
H=1.32
H=2.01
H=2.79
H=4.7
130 atm +H

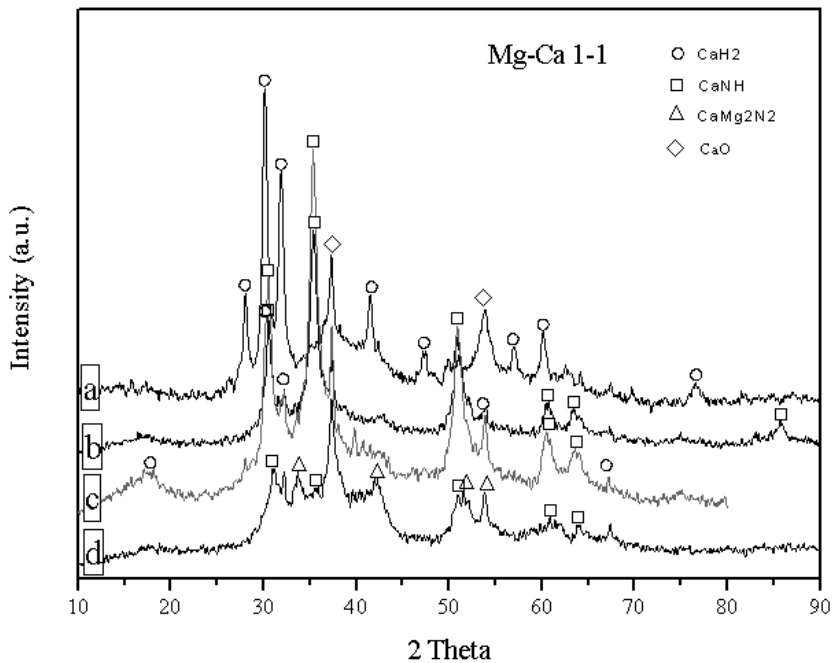

Pressure (Psi)
10000
1000
100
10
1
0.1
0 1 2 3 4 5 6
Wt%


Intensity (a.u.)
2 Theta
10 20 30 40 50
X=0.49
X=1.32
X=2.01
X=2.79
H4.7wt%
PCI+H130bar
after TPD250


Intensity (a. u.)
Binding Energy (eV)
394 396 398 400 402 404 406 408 410
397.2
395.1
N states at imide form

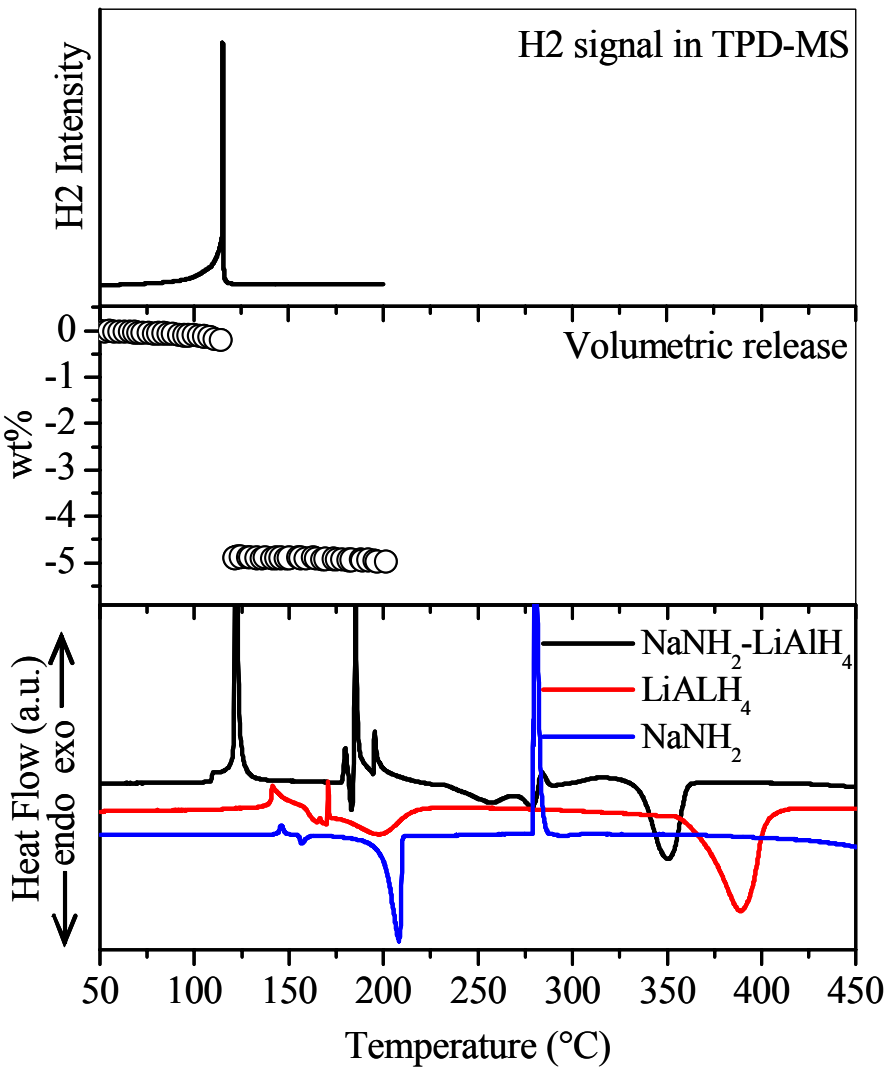
Mg-Ca-N-H – $Mg(NH_2)_2 + CaH_2$ > 4wt%

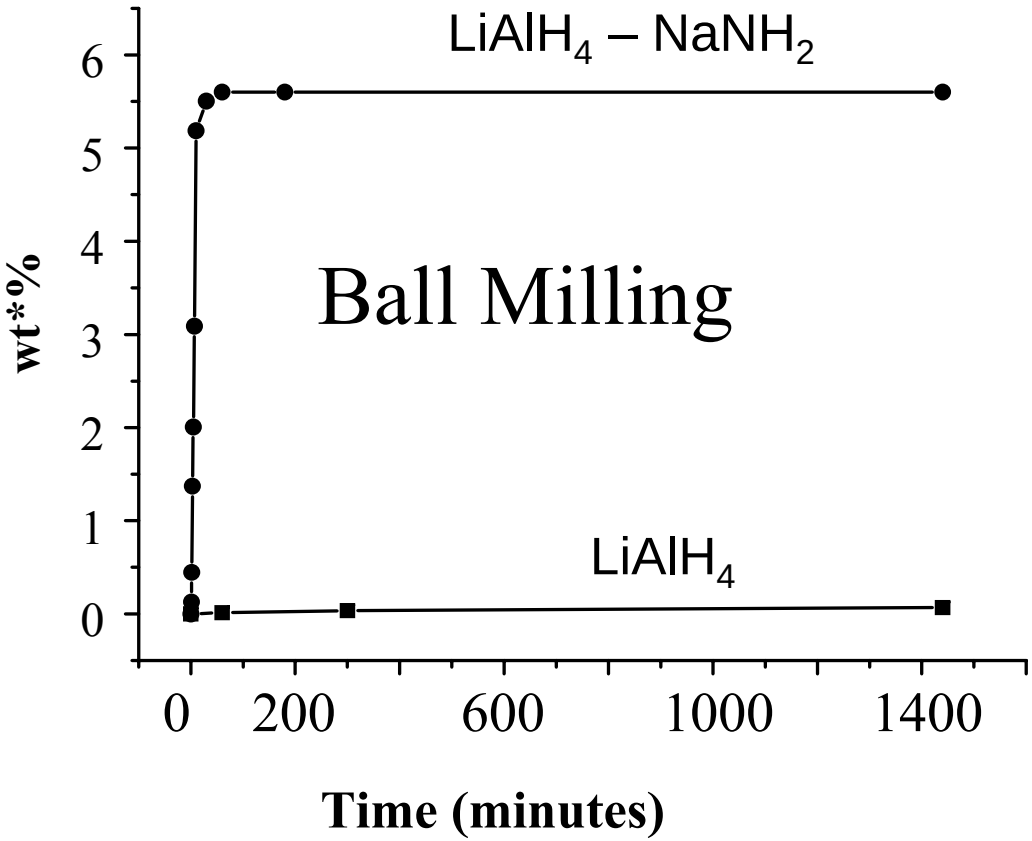


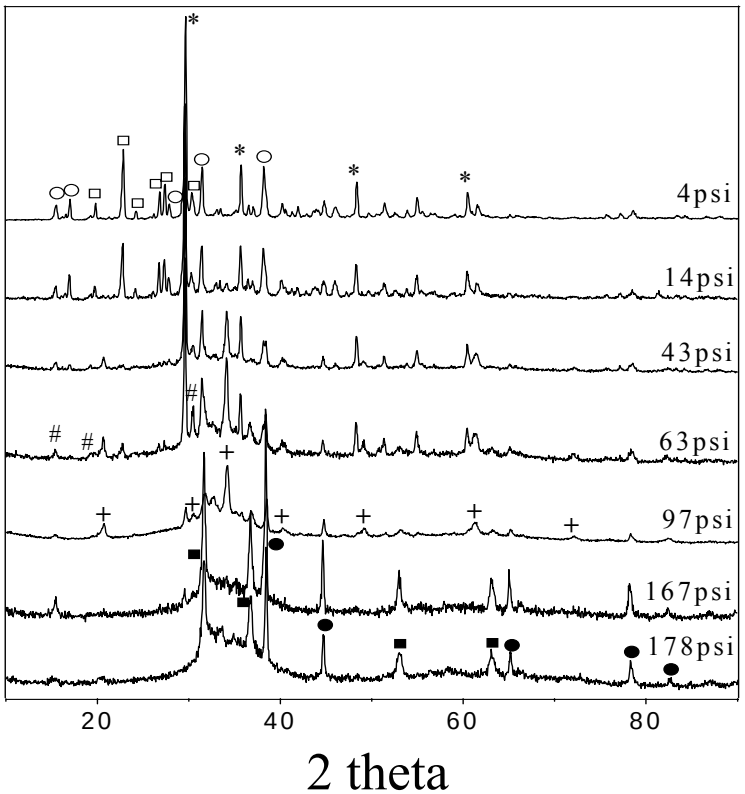


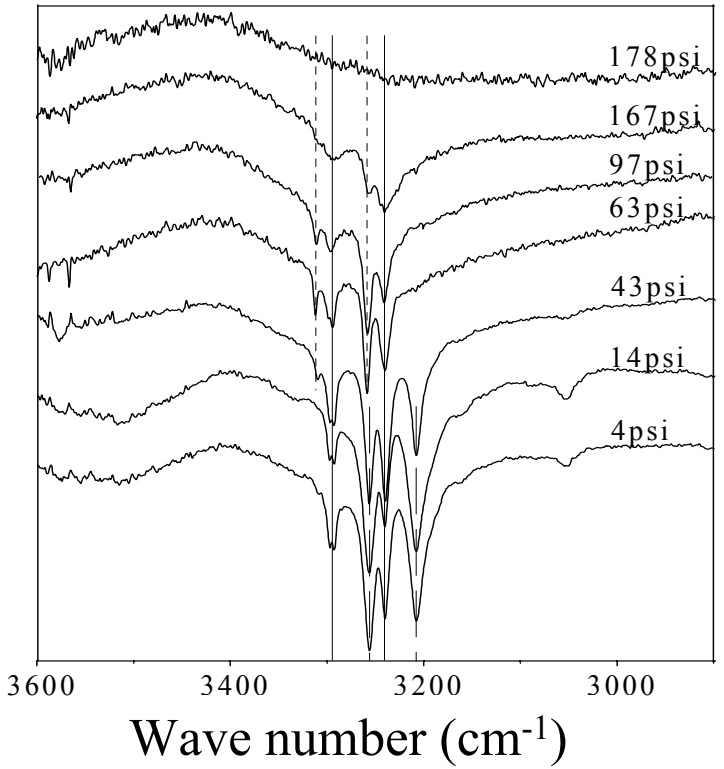
It is a mild endothermic process. However, reversibility is hard to achieve. The kinetic part should be investigated intensively.

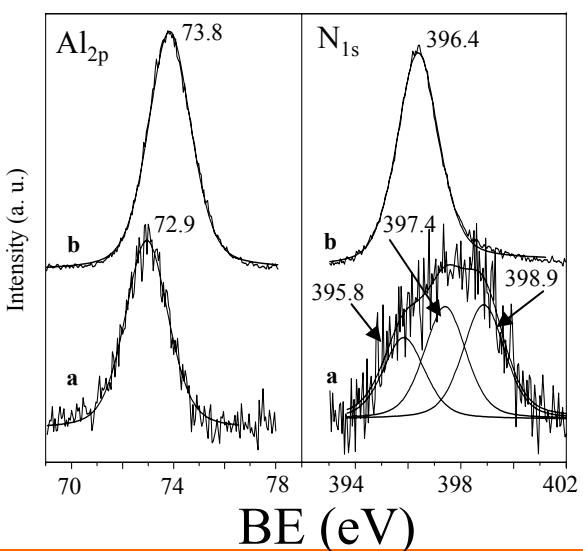
Na-Li-Al-N-H – $NaNH_2 + LiAlH_4$ > 5wt%











XRD, FTIR and XPS investigations reveal stepwise phase changes and the development of a new ternary Li-Al-N-H compound. Three N states were identified.

$$NaNH_2 + LiAlH_4$$

$$\downarrow$$

$$NaAlH_4 + Li_3Na(NH_2)_4 + NaNH_2$$

$$\downarrow \quad -H_2$$

$$Li_3Na(NH_2)_4 + LiNa_2AlH_6 + LiNH_2 + Al$$

$$\downarrow \quad -H_2$$

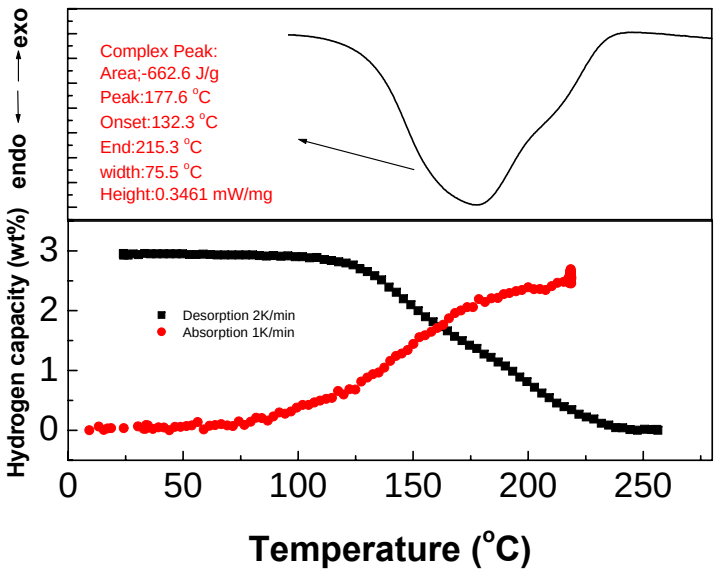
$$NaH + Al + LiAl_{0.43}NH_{0.7}$$

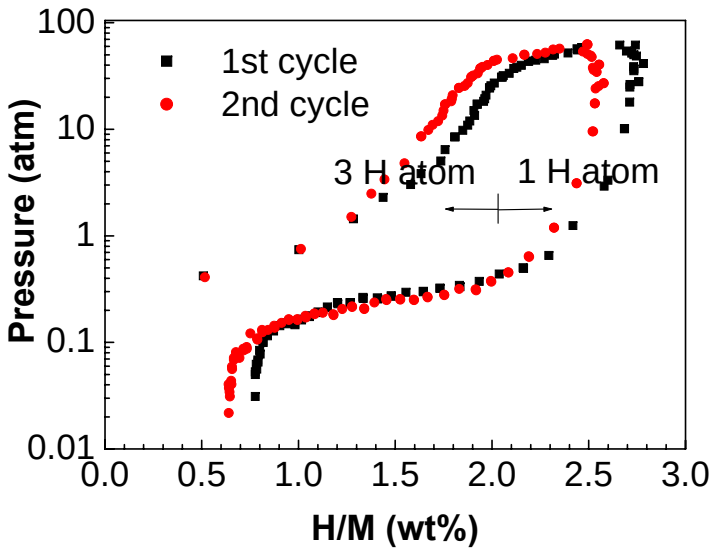
Overall:

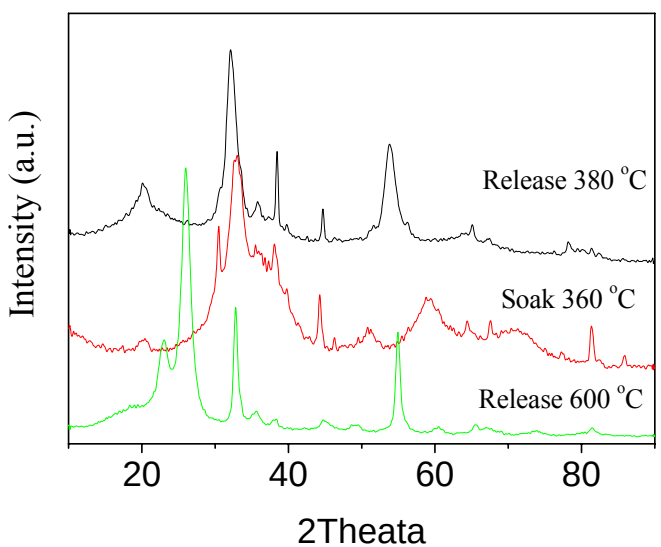
$$NaNH_2 + LiAlH_4 \rightarrow NaH + 0.57Al + LiAl_{0.43}NH_{0.7} + 4.3\ H$$

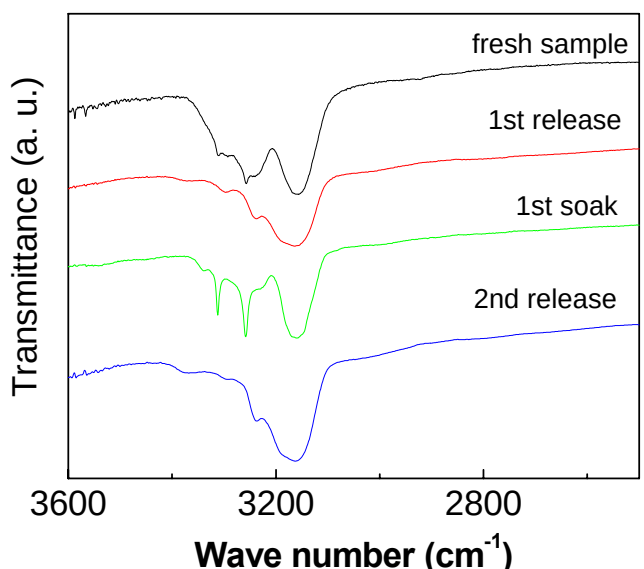
It is a highly exothermic reaction, irreversible.

Li-Mg-Ca-N-H


Complex Peak:
Area;-662.6 J/g
Peak:177.6 °C
Onset:132.3 °C
End:215.3 °C
width:75.5 °C
Height:0.3461 mW/mg
endo ⟶ ⟵exo
Hydrogen capacity (wt%)
Desorption 2K/min
Absorption 1K/min
Temperature (°C)


1st cycle
2nd cycle
3 H atom
1 H atom
Pressure (atm)
H/M (wt%)


Release 380 °C
Soak 360 °C
Release 600 °C
Intensity (a.u.)
2Theata


fresh sample
1st release
1st soak
2nd release
Transmittance (a. u.)
Wave number (cm-1)

In summary, reversible hydrogen storage has been confirmed in the following systems –

A. Li3N
B. Li2NH
C. Ca3N2
D. Ca2NH
E. Li-Mg-N-H with different molar ratio of Li/Mg/N
F. Li-Ca-N-H with different molar ratio of Li/Ca/N
G. Mg-Na-N-H with different molar ratio of Mg/Na/N
H. Mg-Ca-N-H with given Mg/Ca/N molar ratio
I. Li-Al-N-H with given Li/Al molar ratio
J. Other multinary systems etc

More are expected

V. Challenges

- **Controlling & Tuning the thermodynamic parameters**
- **Identifying new structures**
- **Understanding reaction mechanism – Reduce the kinetic barrier**
- **Chemical Instability – Competing chemical routes exist, exp. direct decomposition of reactants. Sensitive to moisture, CO_2, O_2 etc.**
- **Lifetime – phase segregation, which induces the slow kinetics.**
- **Material Synthesis and storage.**

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Collaborators

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Professor Gert Wolf (TU Bergakademie Freiberg)

Team members

Dr. Zhiato Xiong, Dr. Guotao Wu, Dr. Jianjiang Hu, Dr. Yongfeng Liu (NUS)