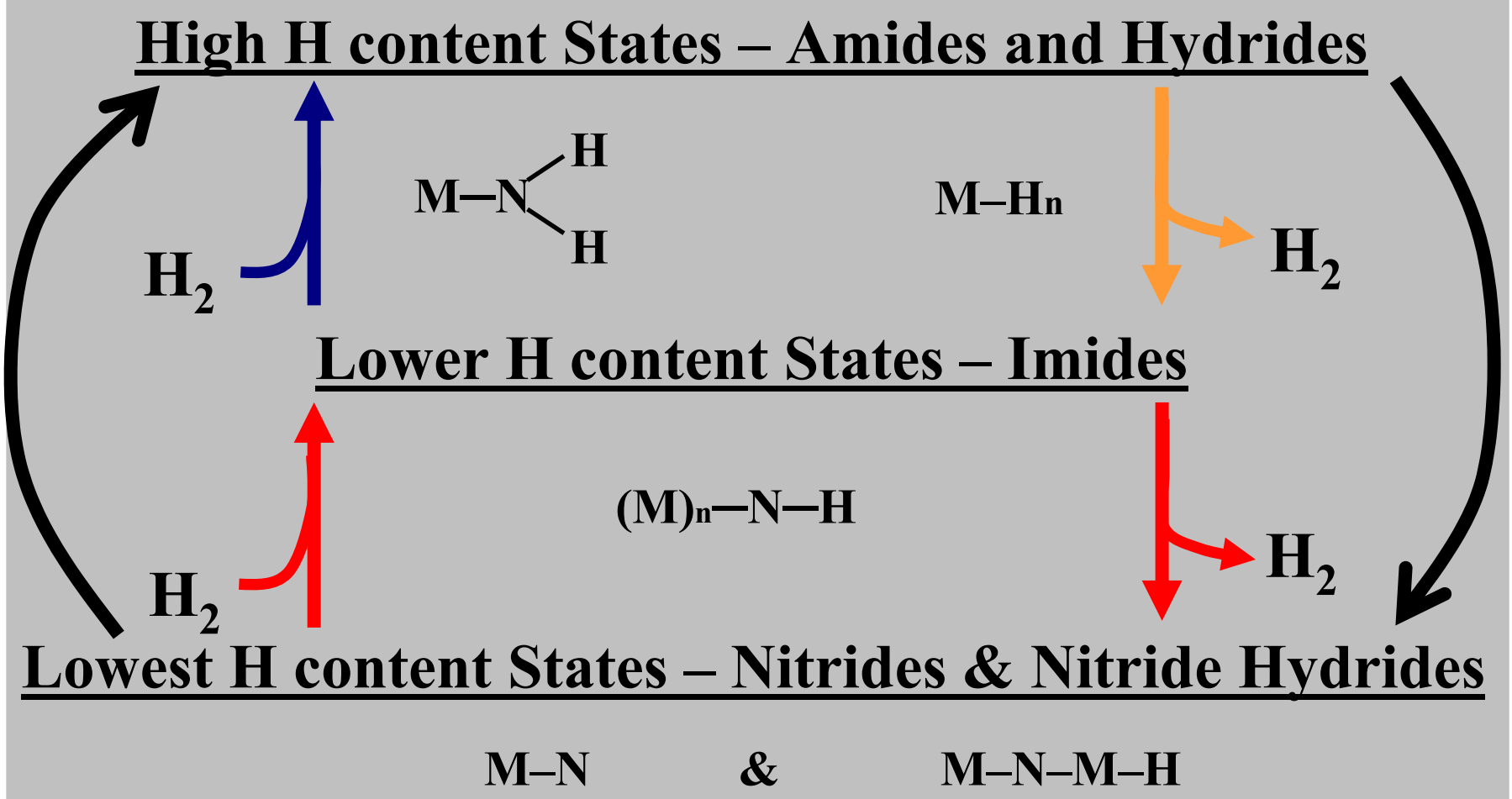
Metal-N-H for Hydrogen Storage

Ping CHEN*, Zhitao XIONG, Guotao WU, Yongfeng LIU, Jianjiang HU, Chaw Keong Yong

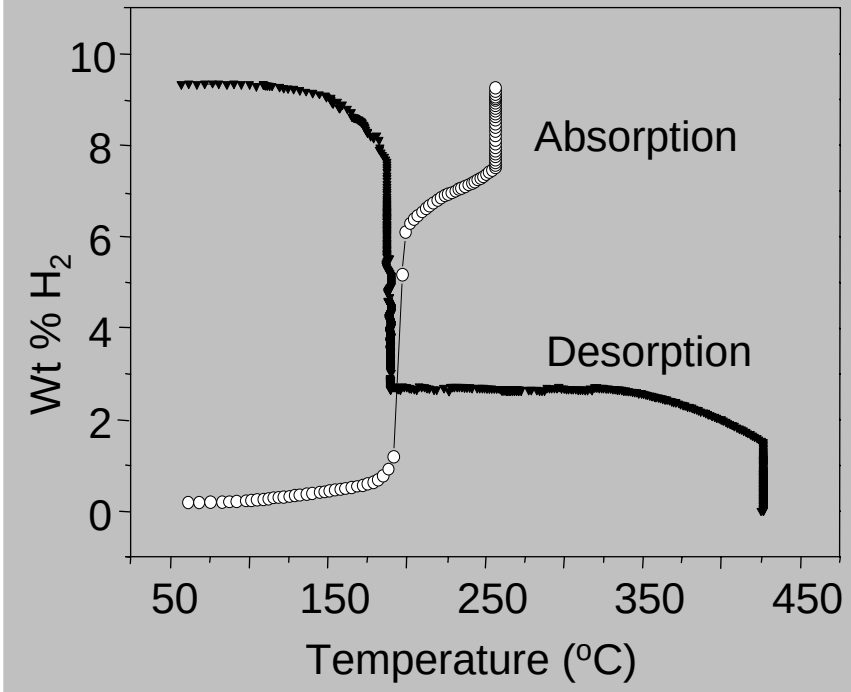
Department of Chemistry & Department of Physics

National University of Singapore, Singapore 117542

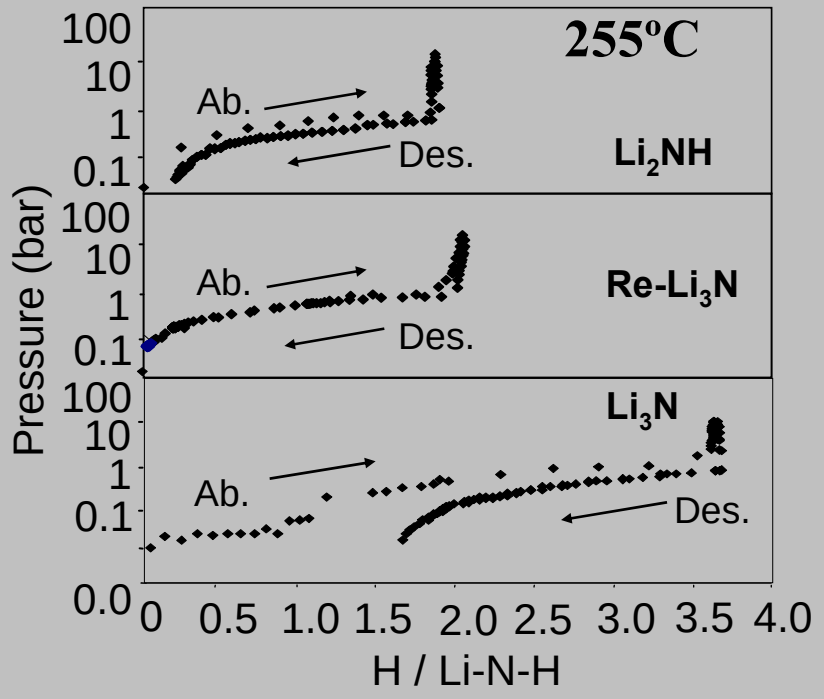
Material Scope



$LiNH_2 + 2LiH \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow Li_3N + 2H_2$



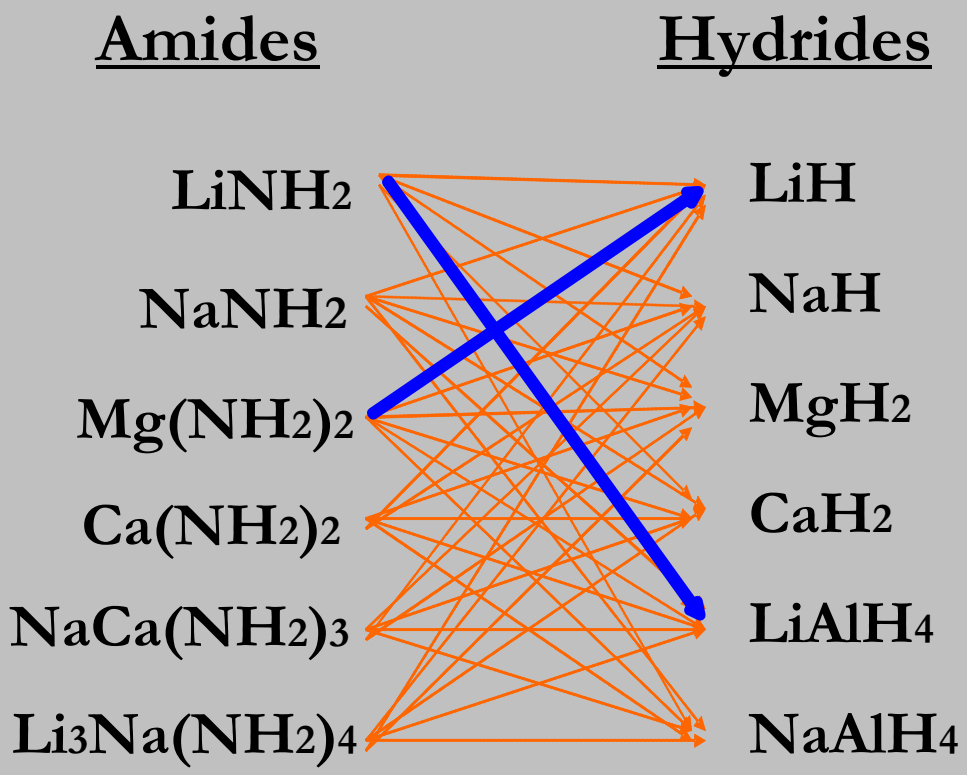
TG results of a Li_3N sample



P-C-T curves of Li_3N and Li_2NH

*– Chen P, Xiong ZT, Luo JZ et al, Nature **2002**, 420, 302-304*

Starting Chemicals and Potential Systems



Li-Mg-N-H

$$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2 \quad 5.5wt\%$$

I. **Hydrogenation & dehydrogenation**

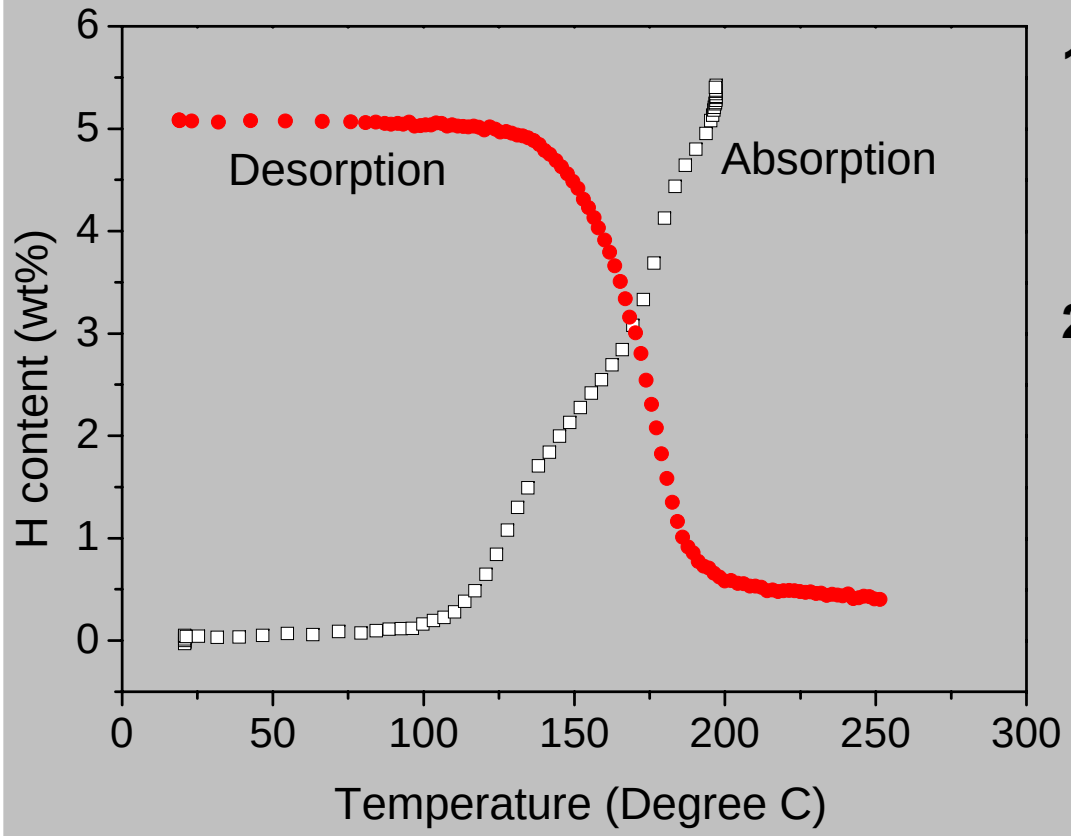
II. **Thermodynamics**

III. **Mechanistic interpretation**

Ref:

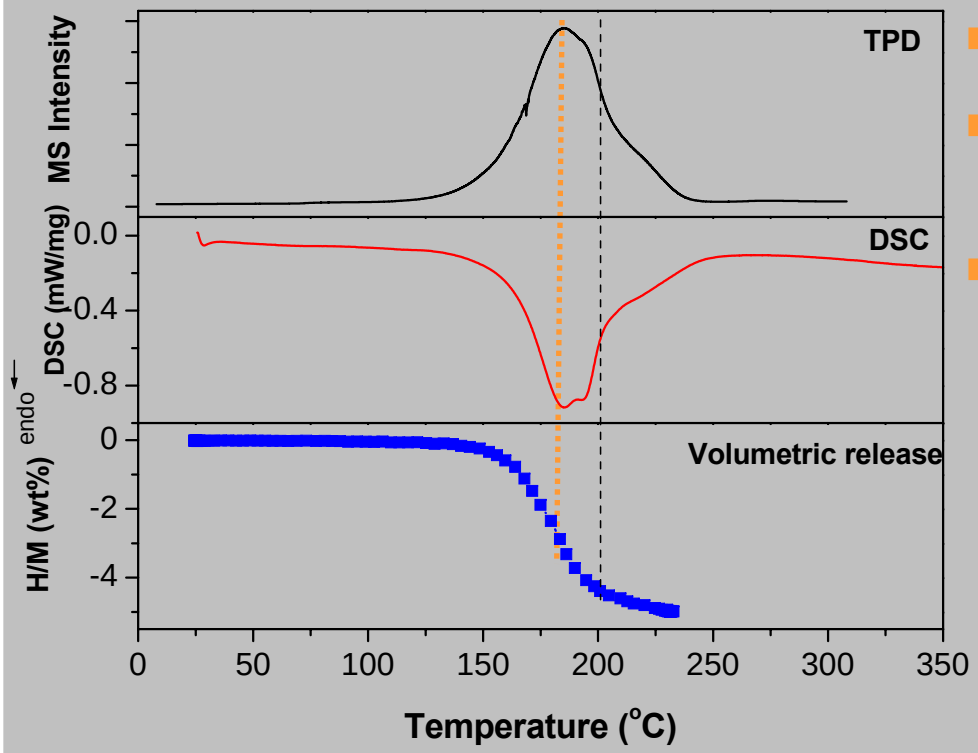
- *Chen P et al. Oral presentation at MRS Fall Meeting 2003 (Boston).*
- *Xiong ZT, Wu GT, Hu JJ, et al. Adv Mater 2004; 16:1522.*
- *Luo WF. J Alloy Compd 2004; 381:284.*
- *Leng HY, Ichikawa T, Hino S, et al. J Phys Chem B 2004; 108:8763.*
- *Nakamori Y, Orimo S. J Alloy Compd 2004; 370:271.*
- *Xiong ZT, Hu JJ, Wu GT, et al. J Alloy Compd 2005; 398:235.*

I. Hydrogenation & Dehydrogenation



1. **~ 4H atoms detach from the starting chemicals, i. e., more than 5.0wt% reversible storage capacity;**
2. **Temperature range 100 – 250 °C;**
3. **Slow hydrogenation.**

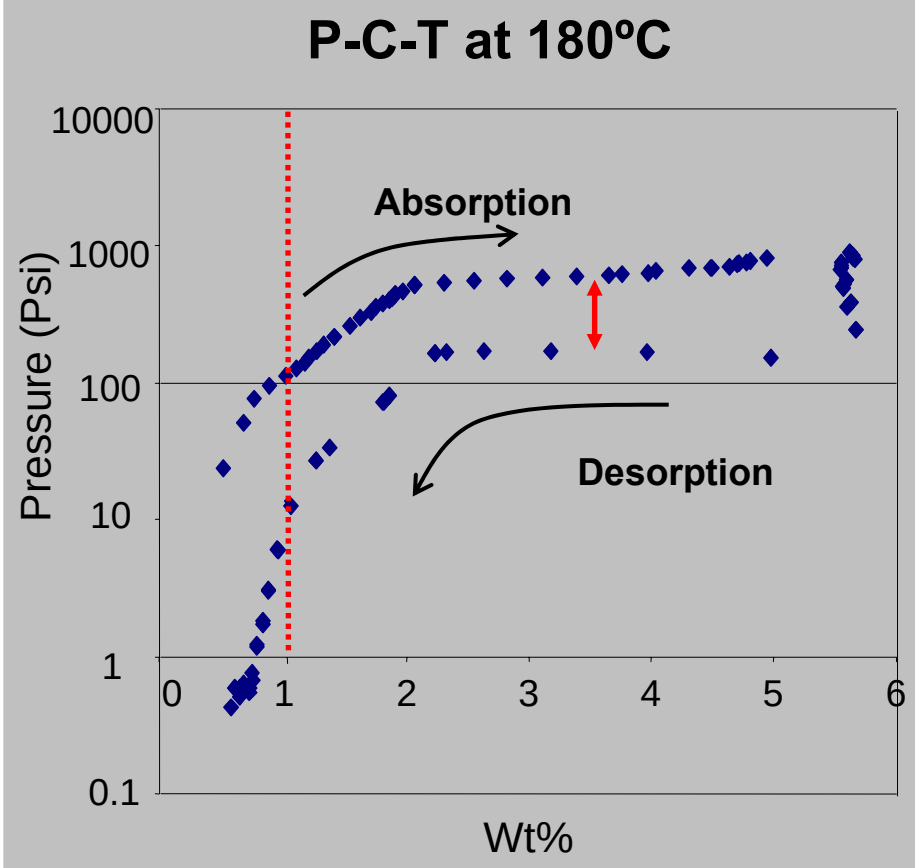
II. Thermodynamics



- Mild endothermic process.
- The overall heat of desorption is ~44 kJ/mol-H_2.
- Multi-step process

-- Xiong ZT, Hu JJ, Wu GT, Chen P, Luo WF, Gross K, Wang J, J Alloy Comp, ***2005****, 398, 235.*

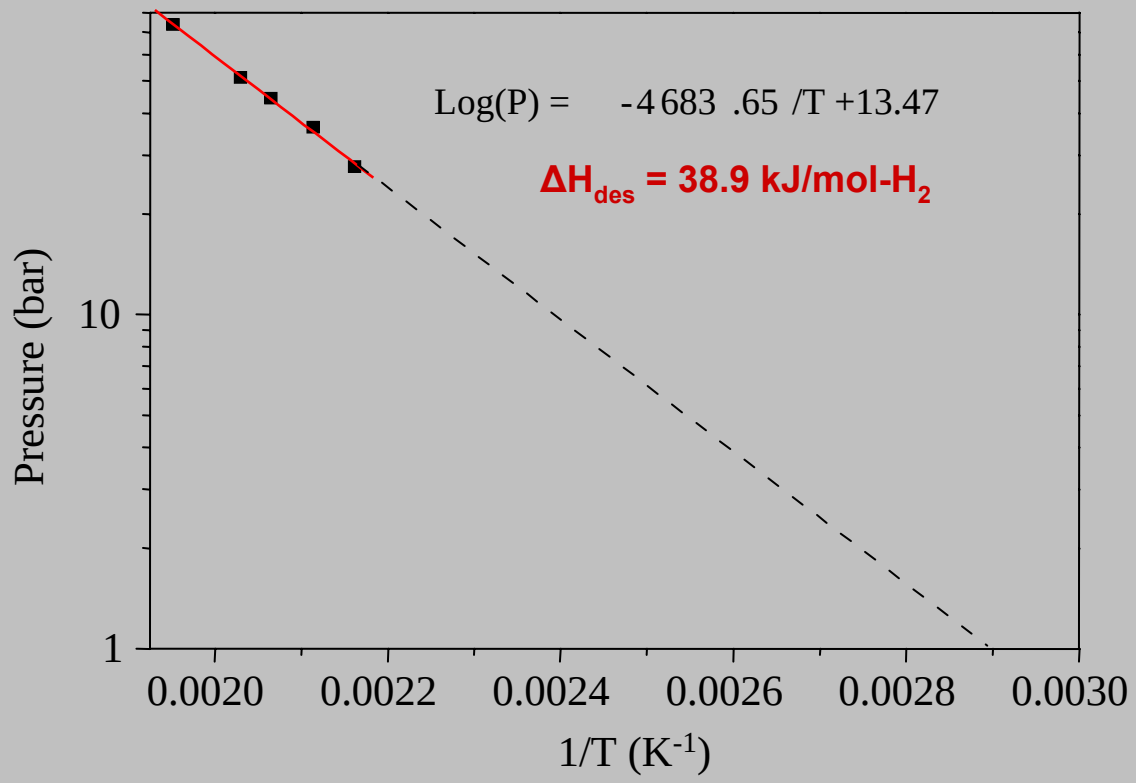
II. Cont'd



- **Relatively high desorption plateau pressure, i. e., at 180ºC, the plateau pressure is above 20 bars.**
- **Certain hysteresis exists.**
- **Multi-step reaction with different thermodynamics.**
- **Slow when approaching equilibrium.**

*–Xiong ZT, Wu GT, Hu JJ, Chen P, Adv Mater, **2004**, 16, 1522.*
–Luo WF. J Alloy Compd 2004; 381:284.

II. Cont'd Van't Hoff plot



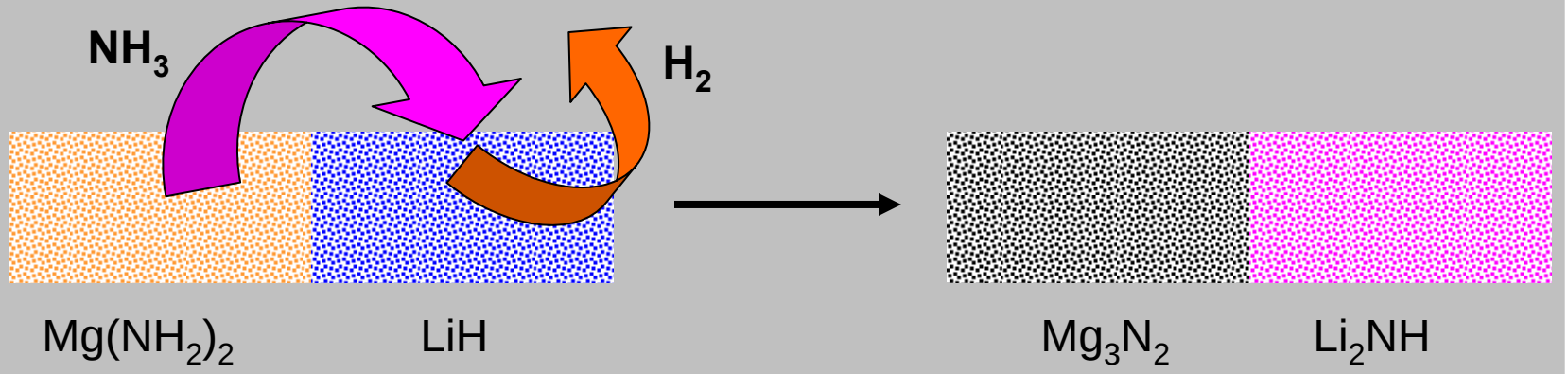
Hydrogen desorption equilibrium pressure at 90ºC is ~ 1.0 bar, close to the PEM fuel Cell operation temperature. However, kinetic barrier is high.

-- Xiong ZT, Hu JJ, Wu GT, Chen P, Luo WF, Gross K, Wang J, J Alloy Comp, ***2005****, 398, 235.*

III. Mechanistic Interpretation

Proposal I – NH_3 mediated mechanism

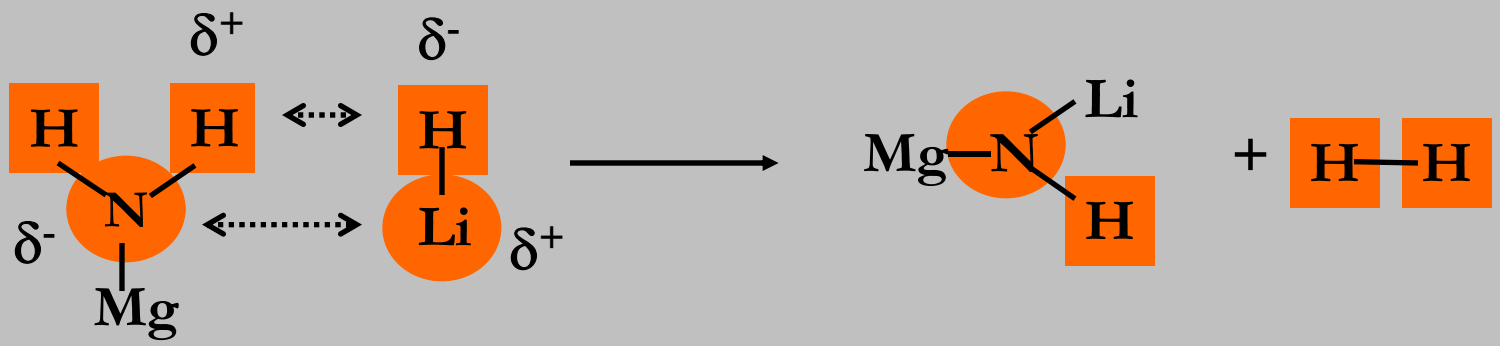
Step I	$Mg(NH_2)_2 \rightarrow 1/3\ Mg_3N_2 + 4/3NH_3$	Slow
Step II	$NH_3 + LiH \rightarrow LiNH_2 + H_2$	Fast
Step III	$LiNH_2 \rightarrow Li_2NH + NH_3$	Slow



- Leng H. Y., Ichikawa T., Hino S., Nakagawa T., Fujii, H., J Phys Chem B, ***2005****, 109, 10744-10748.*

III – cont'd

Proposal II – Direct interaction between amide and hydride



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

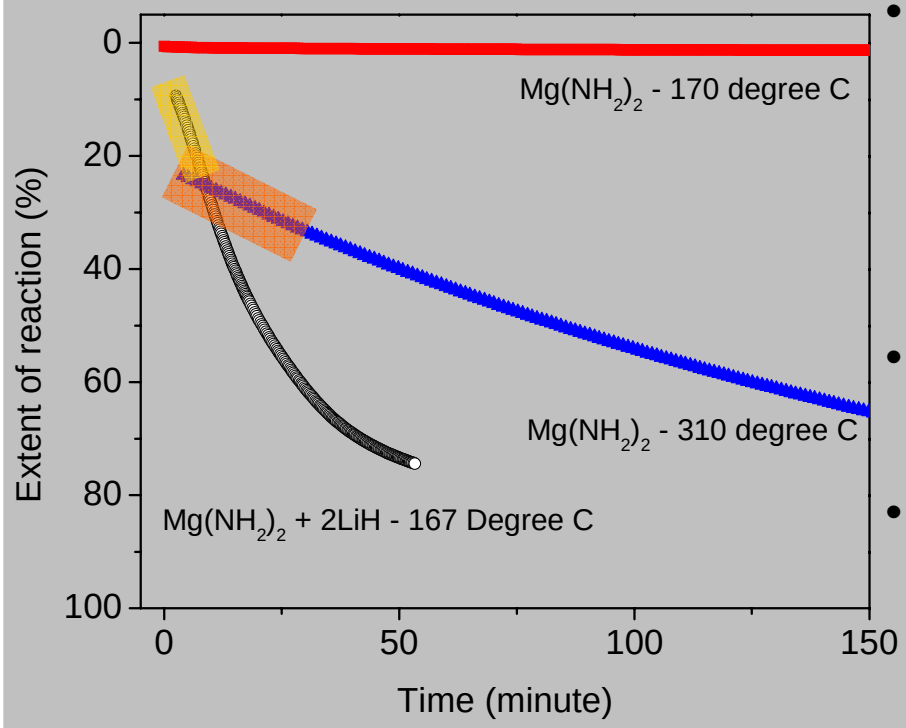
$$N^{\delta-} + Li^{\delta+} \rightarrow N{\rightarrow}Li$$

The coulombic attraction between $H^{\delta+}$ and $H^{\delta-}$ may induce a dihydrogen bond between amide and hydride to form a transition state, which favors the formation of imide and H_2.

*- Chen, P.; Xiong, Z. T.; Luo, J.Z.; Lin, J.Y.; Tan, K.L. J. Phys. Chem. B **2003**, 107, 10967*

III. Cont'd Isothermal Kinetic Investigations

$Mg(NH_2)_2 + 2LiH \rightarrow Li_2Mg(NH)_2 + 2H_2$ & $Mg(NH_2)_2 \rightarrow MgNH + NH_3$

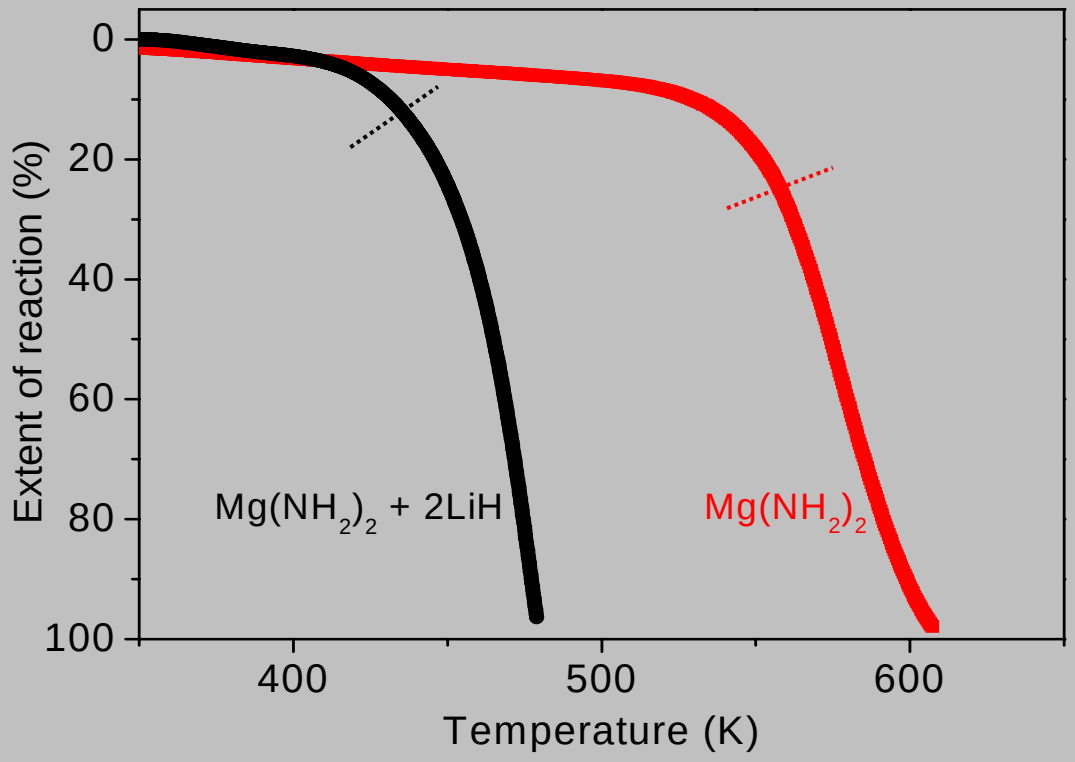


- Hydrogen desorption from the amide and hydride mixture is much faster than ammonia generation from the thermal decomposition of amide alone.
- Linear growth was observed in both reactions at the initial stage.
- The linear relationship keeps till reaction extent reaches ~ 25% for $Mg(NH_2)_2$-2LiH and ~ 40% for thermal decomposition of $Mg(NH_2)_2$.

- Chen P., Xiong ZT. ; Yang LF., Wu GT., Luo WF., J. Phys Chem B, 110 (29), 2006, 14221.

III. Cont'd Non-isothermal Investigations

$$r = d\alpha/dt = k(T) = Ae^{-Ea/RT}$$

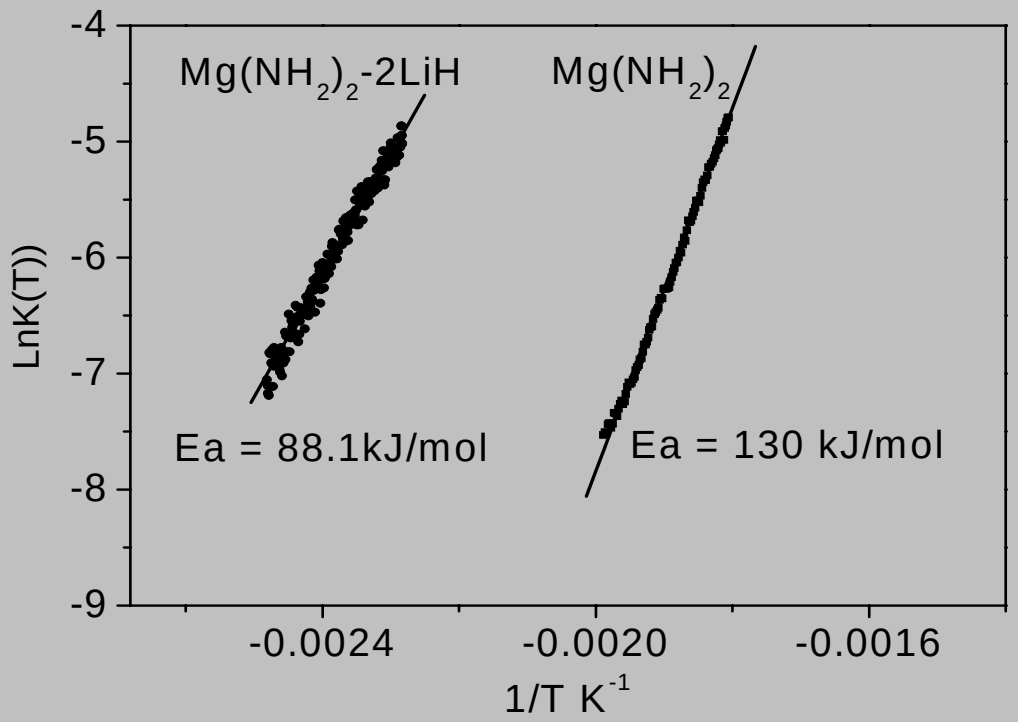


Conditions:

- **Sample loading: ~ 100mg**
- **Temperature ramping rate: 0.5K/min.**
- **Pressure: 10^{-5} mbar**

- Chen P., Xiong ZT. ; Yang LF., Wu GT., Luo WF., J. Phys Chem B, 110 (29), 2006, 14221.

III. Cont'd Non-isothermal Investigations



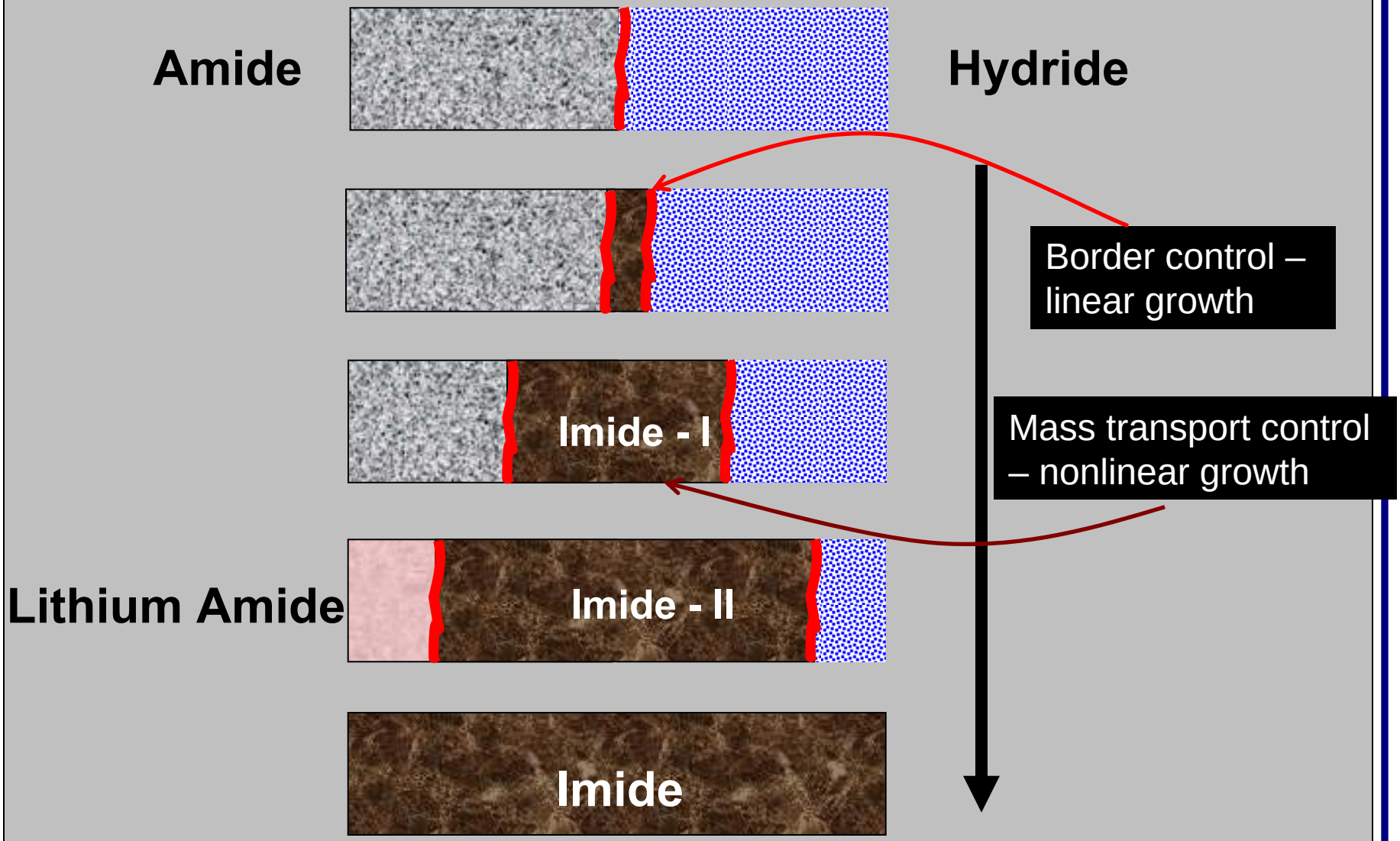
$k_{H2} = 2.01X10^{6}e^{-88100/RT}$

$k_{NH3} = 1.34X10^{8}e^{-130000/RT}$

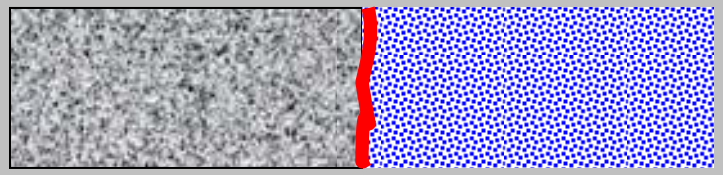
The rate of decomposition of $Mg(NH_2)_2$ is too slow to match that of the H_2 desorption at temperature below 300°C, indicating it is unlikely to be an elementary reaction in the hydrogen desorption from $Mg(NH_2)_2$-LiH mixture.

- Chen P., Xiong ZT. ; Yang LF., Wu GT., Luo WF., J. Phys Chem B, 110 (29), 2006, 14221.

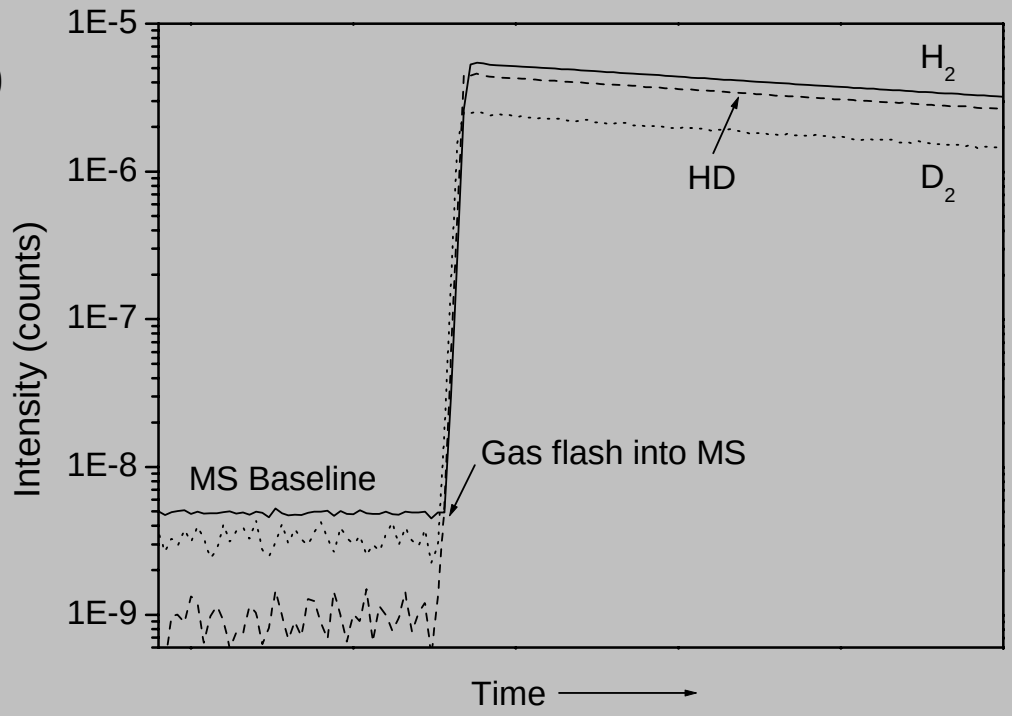
Scheme -Proposed



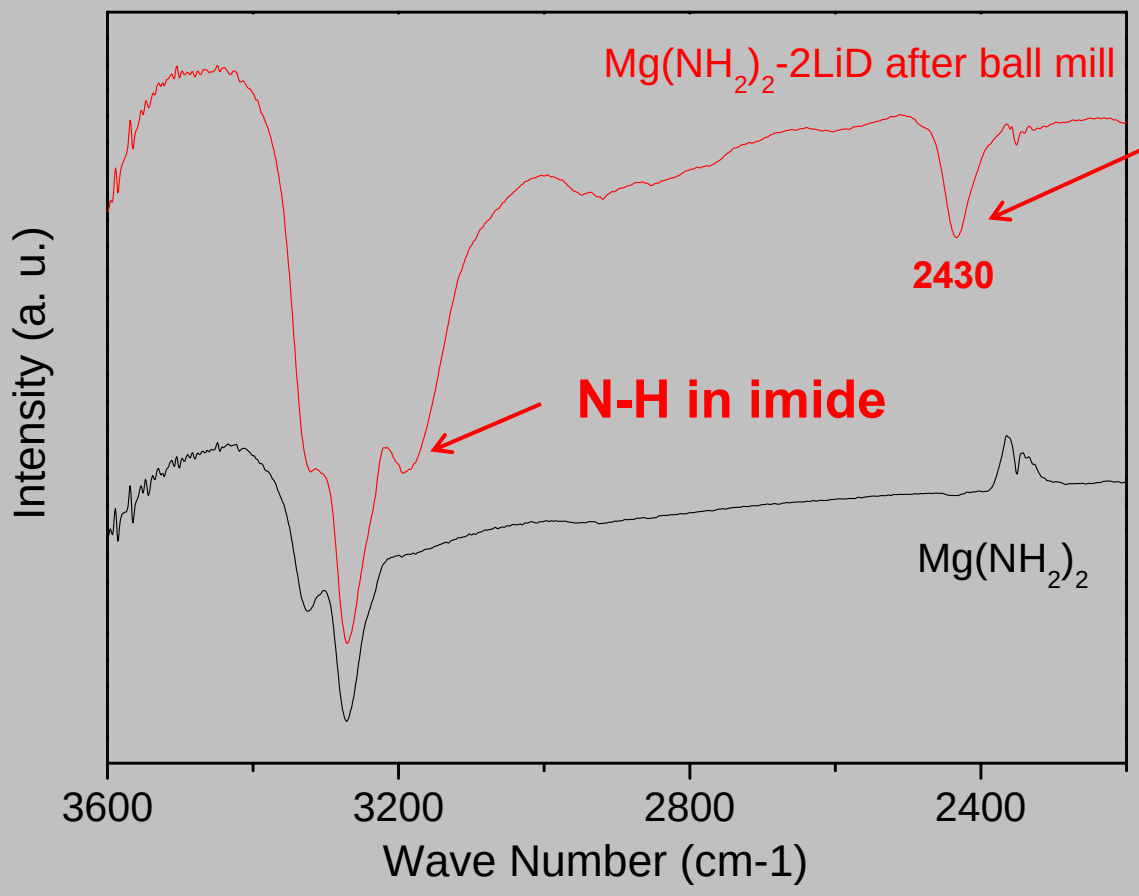
III. Cont'd Isotopic Investigations

$Mg(NH_2)_2$  LiD

Ball mill $Mg(NH_2)_2$ and LiD for 10 hours and analyse the gaseous product(s).



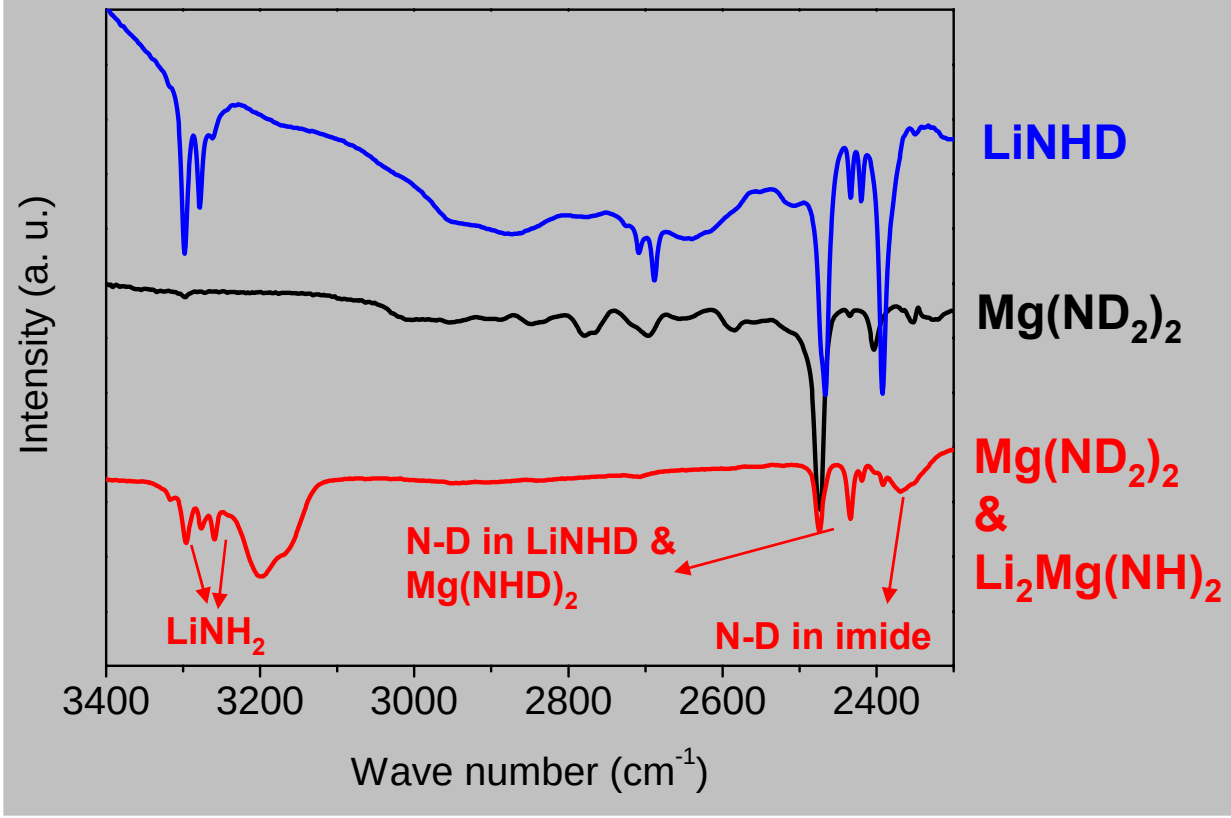
III. Cont'd Amide - Hydride Interface

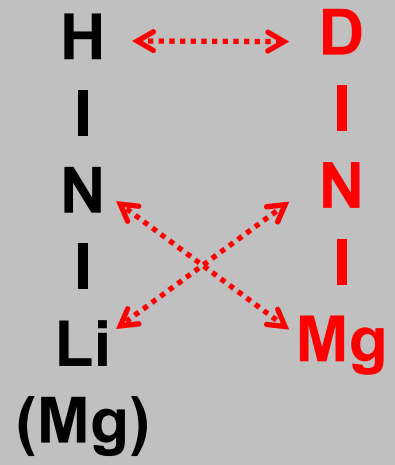


H ⇢ D
I I
N ⇢ Li
I
Mg

III. Cont'd Amide - Imide Interface

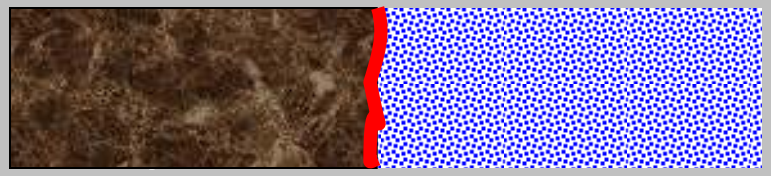
$Mg(ND_2)_2$  $Li_2Mg(NH)_2$



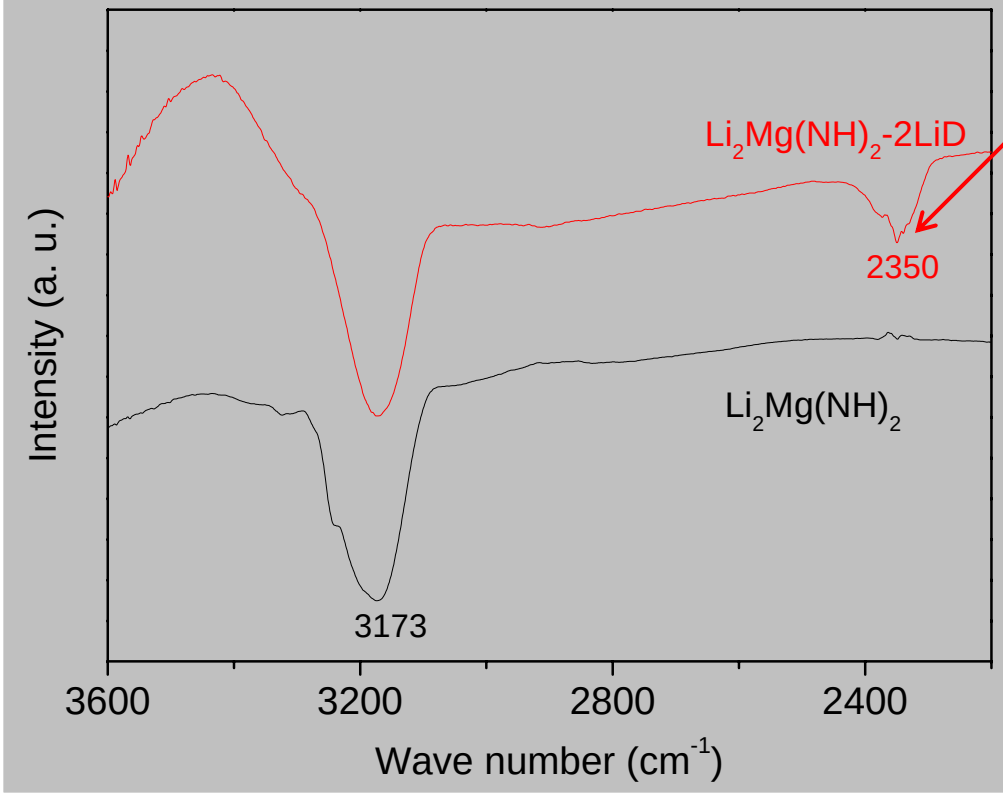


III. Cont'd Imide - Hydride Interface

$Li_2Mg(NH)_2$



LiD



N-D in imide

H ⇢ D
I I
N ⇢ Li
I
Mg
(Li)

Comparatively difficult

III. Cont'd

- Hydrogen desorption from the mixture of $Mg(NH_2)_2$-2LiH undergoes a step-wised reaction.
- Thermodynamic analysis shows that ~ 3.5wt% of hydrogen can be desorbed at 1.0bar equilibrium pressure at ~ 90°C.
- Thermal decomposition of $Mg(NH_2)_2$ may not be a necessary elementary step in the amide-hydride reaction.
- Kinetic barrier comes from the phase boundary reactions and mass transport.
- Transition states of amide-hydride, amide-imide and imide-hydride may form during the reaction.

- Kinetic improvement
- Thermodynamic alteration

Li-Al-N-H

$$LiAlH_4 + 2\,LiNH_2 \rightarrow Li_3AlN_2 + 4H_2 \quad 9.5\ wt.\%$$

I. Hydrogen desorption during ball milling

II. Reversible Hydrogen

Refs:

– P. Chen, *2005 APS March Meeting*, March 21–25, 2005; Los Angeles, CA

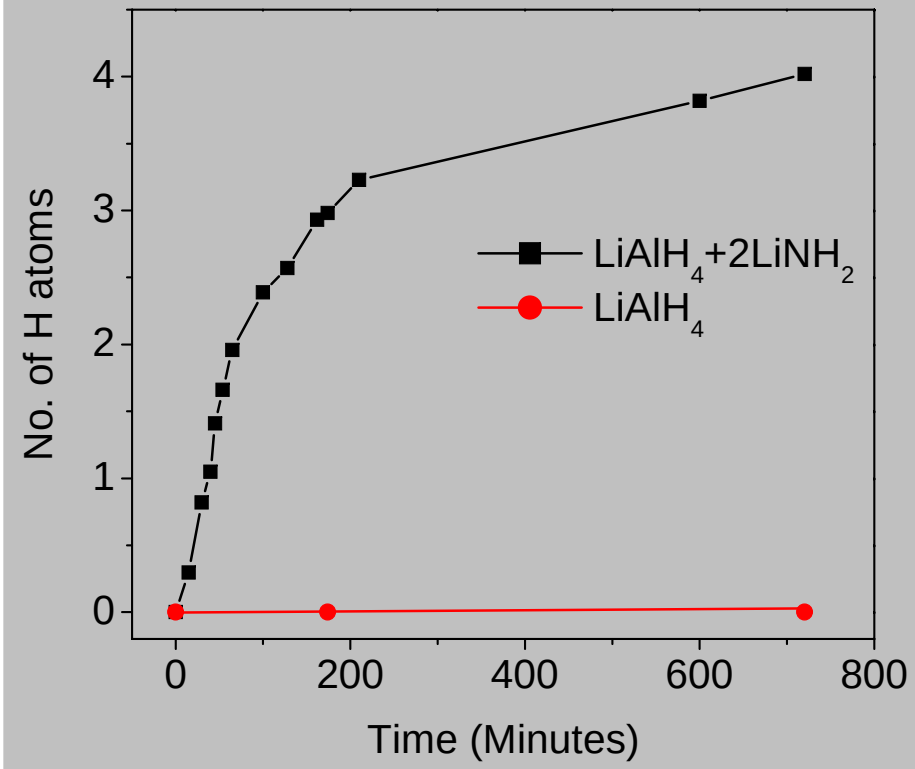
– Z.T. Xiong, G.T. Wu, J.J. Hu and P. Chen, *J. Power Sources,* Available online 15 May 2006

– Y. Nakamori, A. Ninomiya, G. Kitahara, M. Aoki, T. Noritake, K. Miwa, Y. Kojima and S. Orimo, *J. Power Sources* 2006, 155, 447.

– L. Jun and Z.Z. Fang, *J. Phys. Chem. B* 2005, 109, 20830.

I. Hydrogen Desorption during Ball Milling

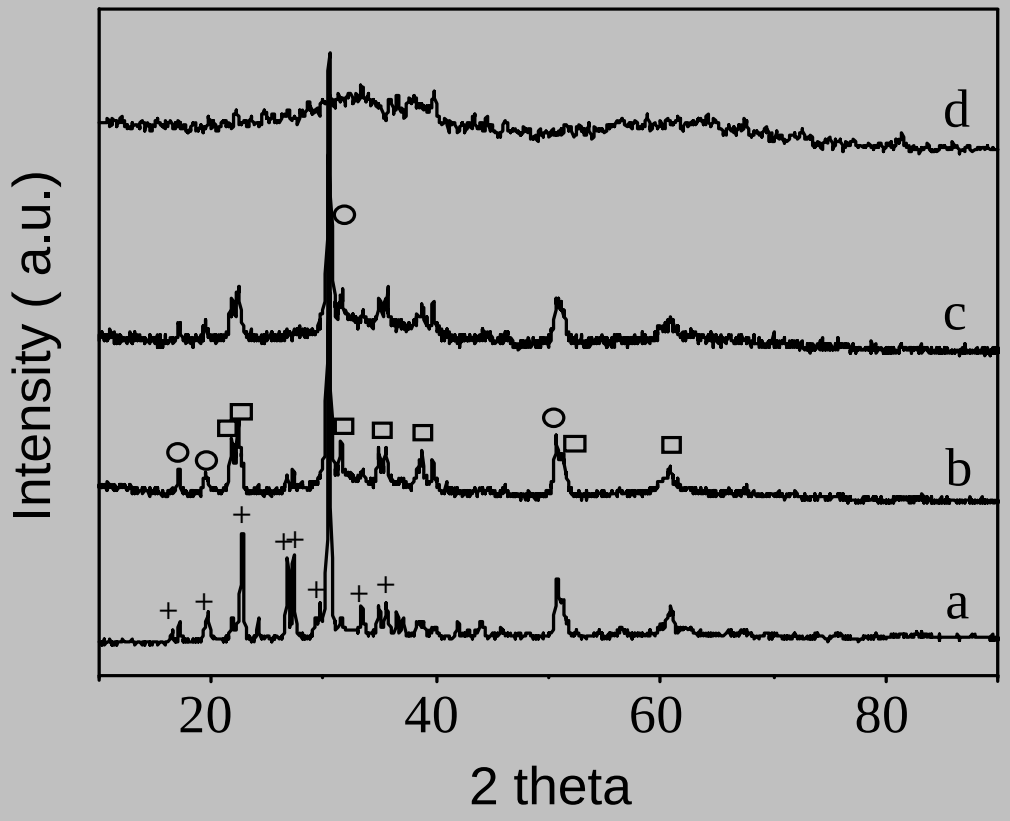
$$LiAlH_4 + 2\,LiNH_2 \rightarrow [Li_3AlN_2H_4] + 2\,H_2 \quad 4.7\ wt.\ \%$$



- ~ 4H atoms detached from the starting chemicals.
- Little H_2 desorption from $LiAlH_4$ when ball milled alone.
- $LiNH_2$ is unlikely to be a catalyst.

– Chen P et al, APS March meeting, LA, 2005.
– Xiong ZT, Wu GT, Hu JJ, Liu YF, Chen P et al, submitted.

I. cont'd Structural Changes



+ - $LiAlH_4$, o – $LiNH_2$. □ - Li_3AlH_6

- Li_3AlH_6 appears shortly after the ball milling.
- No metallic Al was detected.
- Final amorphous structure.

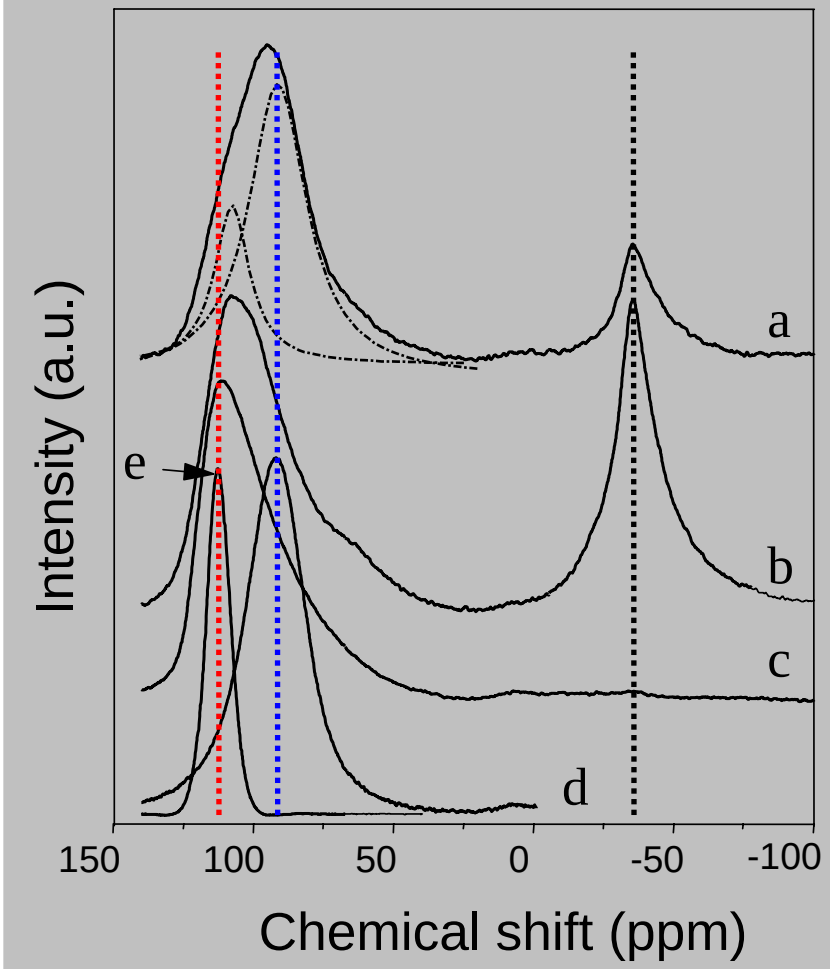
a - $LiAlH_4$ + 2 $LiNH_2$

b - ~ 1 H atom detached.

c - ~ 2 H atoms detached.

d - ~ 4 H atoms detached.

I. cont'd Chemical Environments of Al



– Li_3AlH_6 developed first then consumed;

– Al-N bonding was established right after ball milling $LiAlH_4$ and $LiNH_2$;

– Most of Al atoms are in $[AlN_4]$ environment after BM.

a - ~ 1.0 H detached from the starting chemicals;

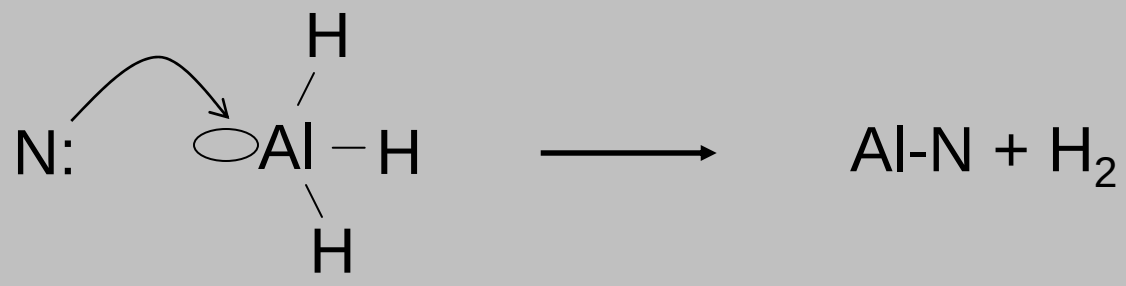
b - ~ 2.0 H detached;

c- ~ 4.0 H detached;

d – $LiAlH_4$

e – AlN

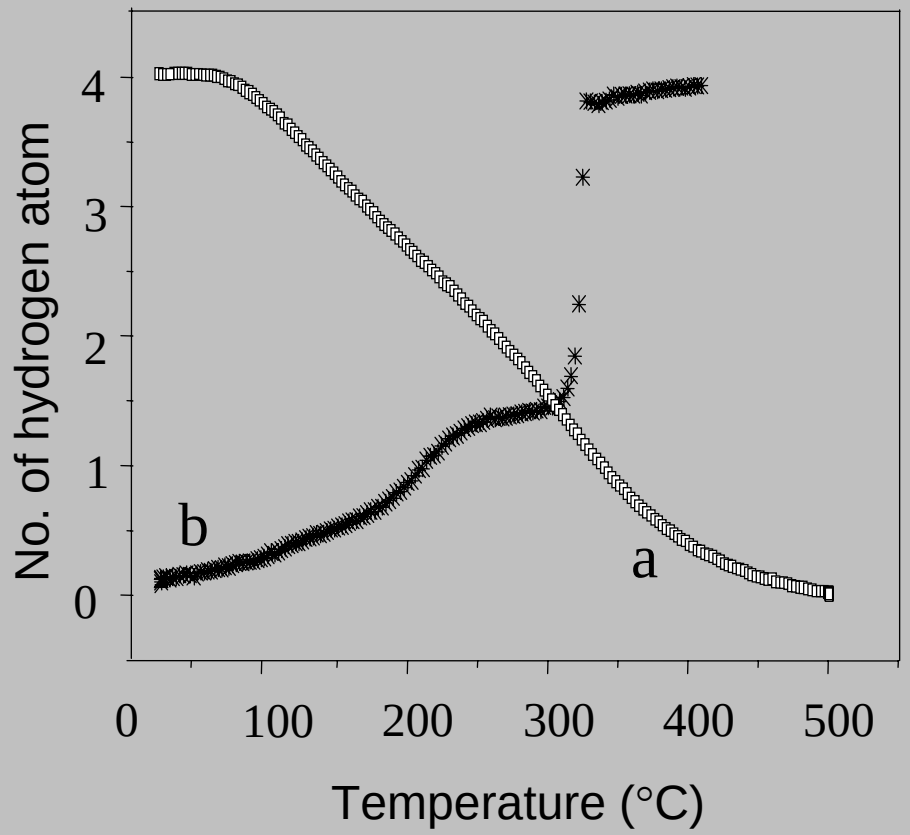
I. cont'd



- **Dehydrogenation is of exothermic nature – enthalpy of AlN**
- **Meta-stable solid product - [$Li_3AlN_2H_4$] = $LiNH_2$ + 2LiH + AlN**

II. Reversible Hydrogen

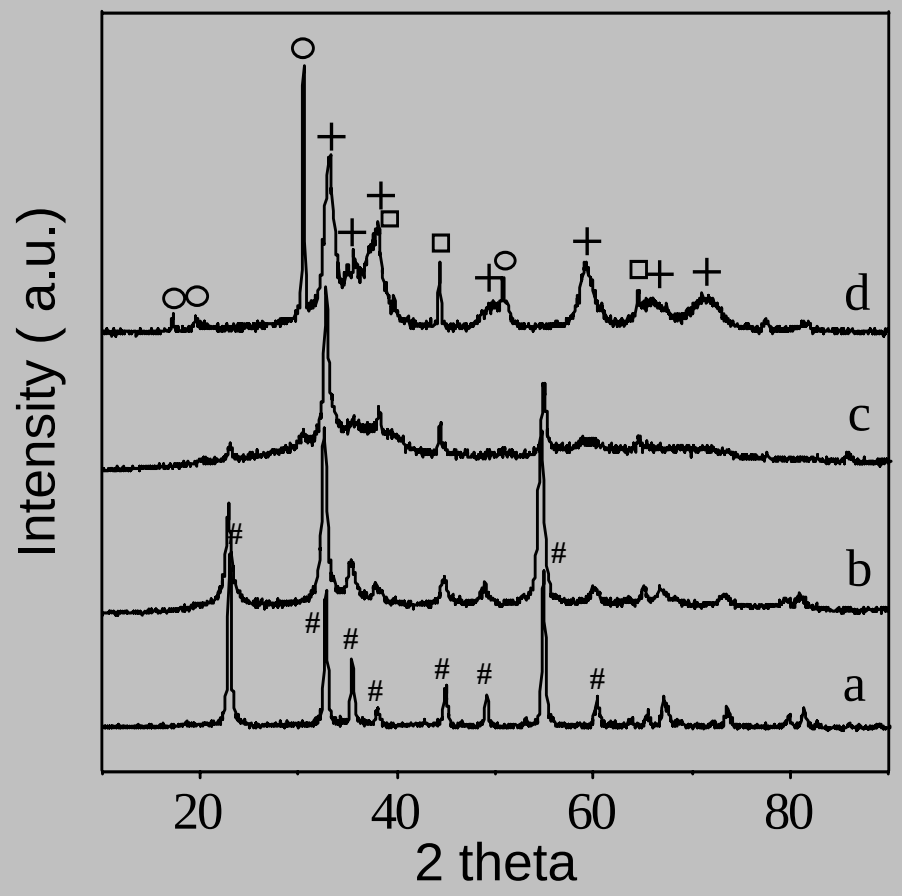
$$[Li_3AlN_2H_4] \leftrightarrow Li_3AlN_2 + 2H_2 \quad 5\ wt.\%$$



a – Volumetric release.

b – volumetric soak.

II. Cont'd $Li_3AlN_2 + 2H_2 \leftrightarrow LiNH_2 + 2LiH + AlN$



d – Fully hydrogenated

c – Hydrogenated to 280°C

b – Hydrogenated to 220°C

a – Li_3AlN_2

- Li_3AlN_2, o – $LiNH_2$, + - AlN, □ - LiH

II. Cont'd Ternary Nitride

- $LiNH_2 + 2LiH + AlN \leftrightarrow Li_3AlN_2 + 2H_2$

$\Delta = 50.1$ kJ/mol-H_2

- $LiNH_2 + 2LiH \leftrightarrow Li_3N + 2H_2$

$\Delta = 80.5$ kJ/mol-H_2

- $Li_3N + AlN \leftrightarrow Li_3AlN_2$

$\Delta H = -30.4$ kJ/mol

Features of M-N-H Systems

- High Hydrogen Content, above 10wt.%
- Endothermic or exothermic, tunable
- Broad material scope
- New chemicals & chemistry

- Critical Mass transportation
- Multi-stepped process
- Ammonia likely co-produced

- Fundamental research, both experimental & simulating

Acknowledgements

Team members

- Dr. Zhiato Xiong, Dr. Guotao Wu, Dr. Jianjiang Hu, Dr. Yongfeng Liu, Mr. Chaw-Keong Yong, Mr. Chee-koon Ng, Mr. How-Kwong Wong, Mr. Kok-Wen Ho

Financial Supports

- Agency of Science, Technology and Research (A*STAR), Singapore.
- Sandia National Laboratories, USA
- General Motors R&D Center, USA

Collaborators

- Dr. Xue Junmin, A/P Chowdari BVR, Professor Xu Guoqin, NUS
- Dr. Liu Tao, Dr. Yang Ping, Professor Andrew Wee, SSLS.
- Dr. Weifang Luo, Dr. Karl Gross, Dr. James Wang, Sandia National Laboratories, USA
- Professor Gert Wolf (TU Bergakademie Freiberg)
- Dr. Fred Pinkerton and Dr. Scott Jorgensen, GM