

# Hydrogen Storage in Metal-N-H Complexes

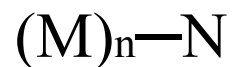
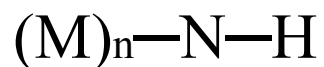
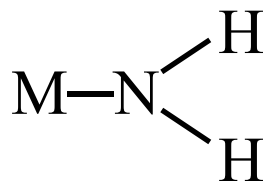
Ping CHEN, Zhitao XIONG, Guotao WU, Jianjiang HU  
Physics Department, Science Faculty



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# Systems under Investigations

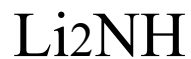


Amide

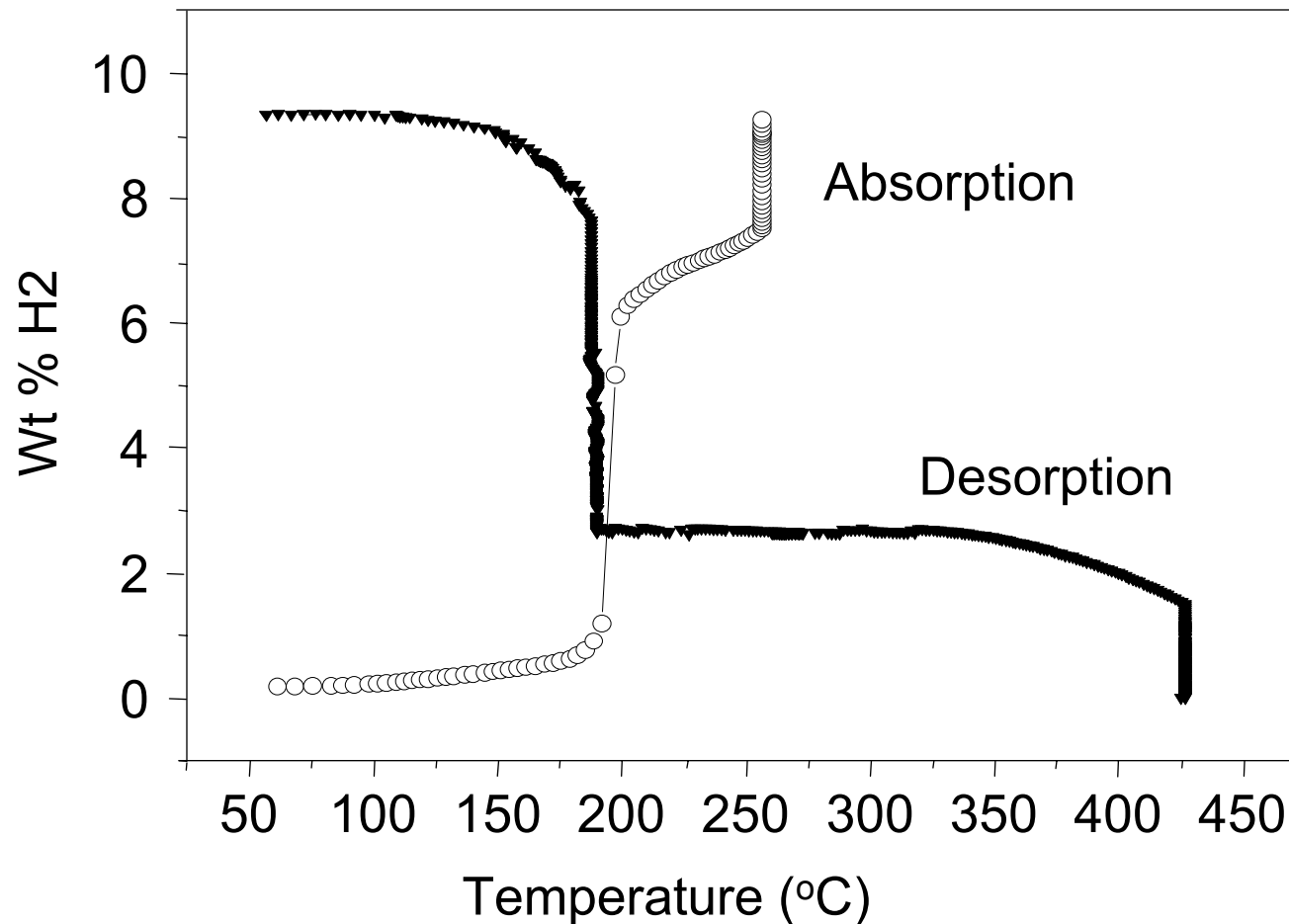
Imide

Nitride

Nitride Hydride

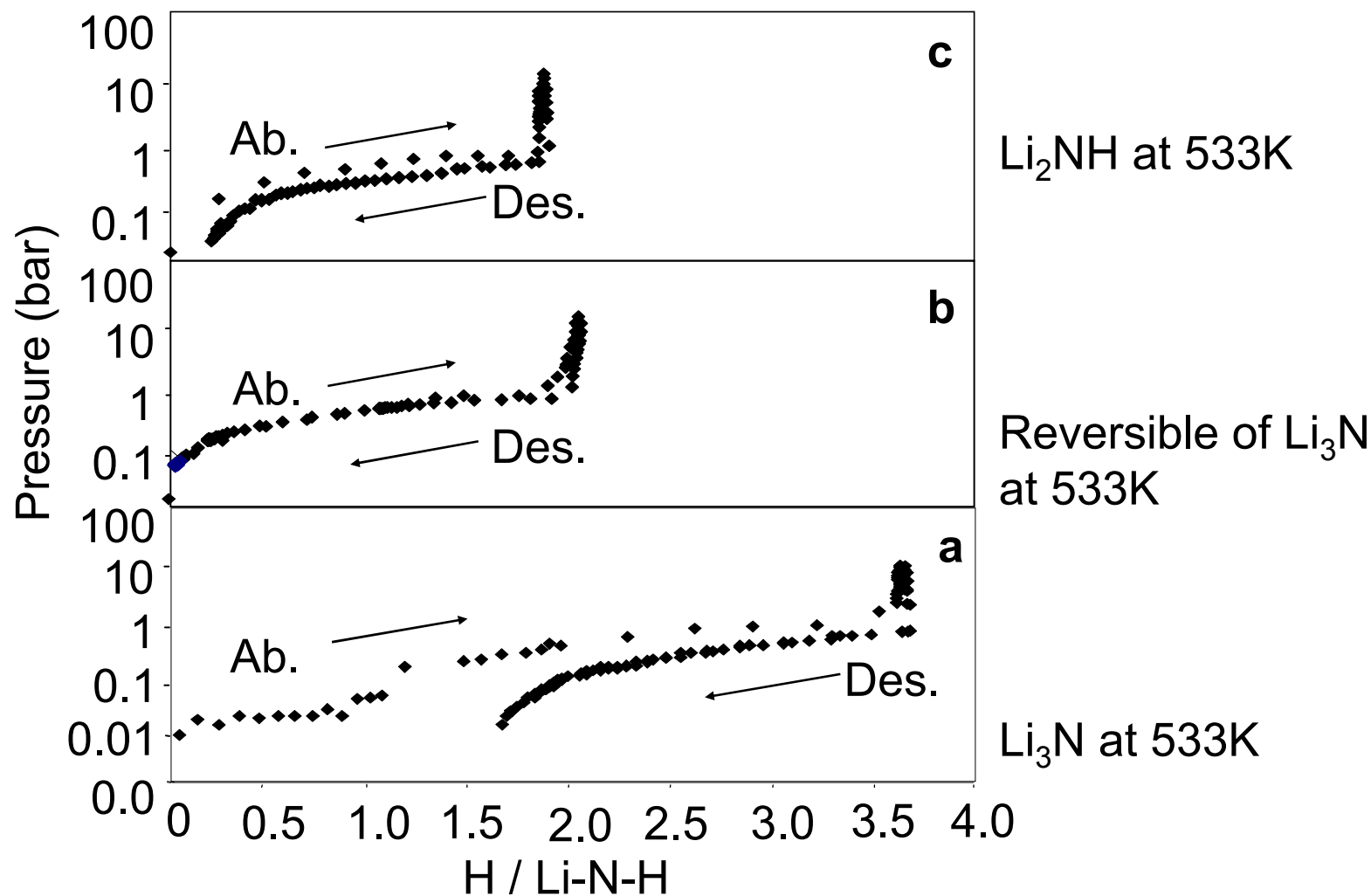


# TPR & TPD of Li<sub>3</sub>N sample



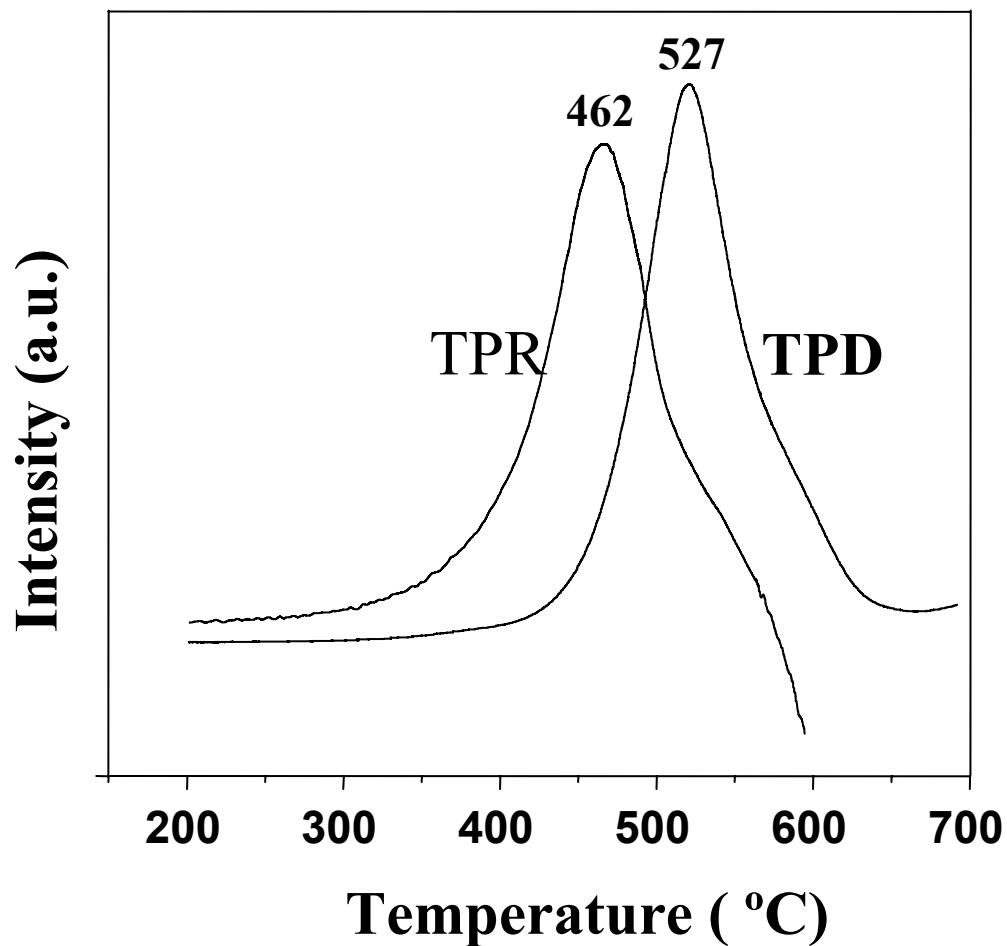
-- Chen P, Xiong ZT, Tan KL et al, Nature 2002, 420, 302-304

# P-C-T Curves of Li-N-H



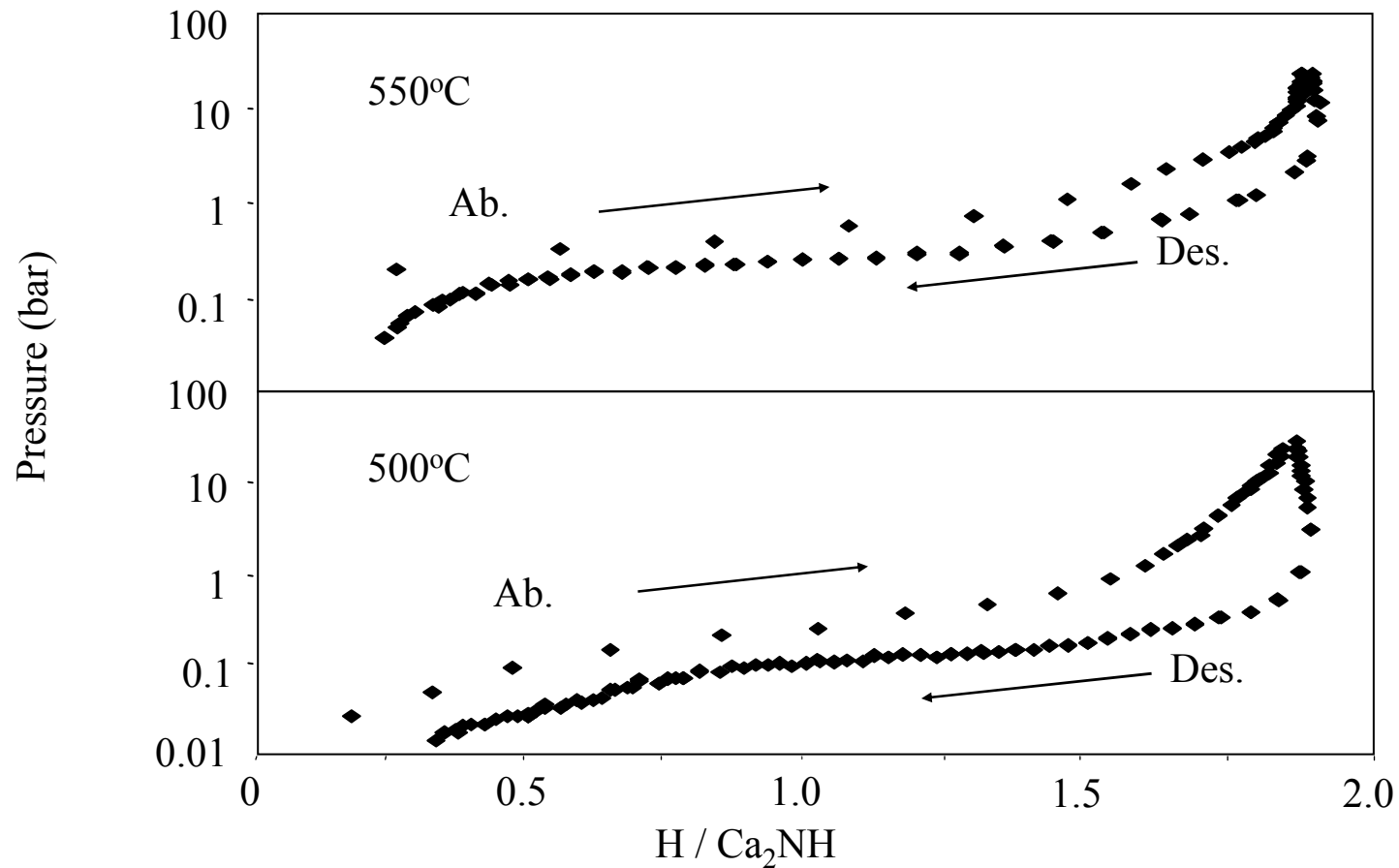
-- Chen P, Xiong ZT, Tan KL et al, Nature 2002, 420, 302-304

# TPR & TPD of $\text{Ca}_2\text{NH}$ sample



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

# P-C-T curves of $\text{Ca}_2\text{NH}$



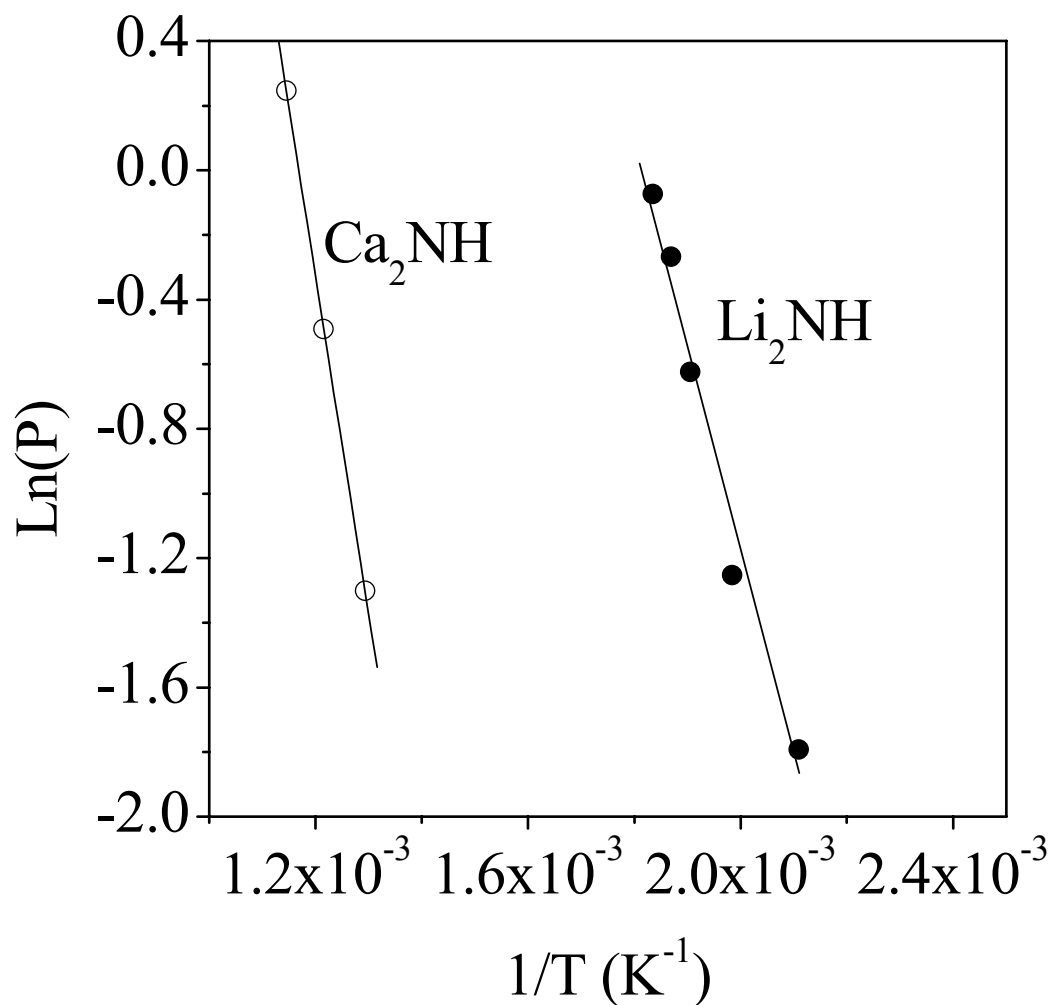
-- Chen P, Xiong ZT, Tan KL et al, Nature 2002, 420, 302-304

# Reactions

Material	Reaction	Capacity	Temperature
Li <sub>3</sub> N	$\text{Li}_3\text{N} + 2\text{H}_2 \rightarrow \text{LiNH}_2 + 2\text{LiH}$	11.4wt%	323-673K
Li <sub>2</sub> NH	$\text{Li}_2\text{NH} + \text{H}_2 \rightarrow \text{LiNH}_2 + \text{LiH}$	7.0wt%	323-673K
Ca <sub>2</sub> NH	$\text{Ca}_2\text{NH} + \text{H}_2 \rightarrow \text{CaNH} + \text{CaH}_2$	2.1wt%	723-973K



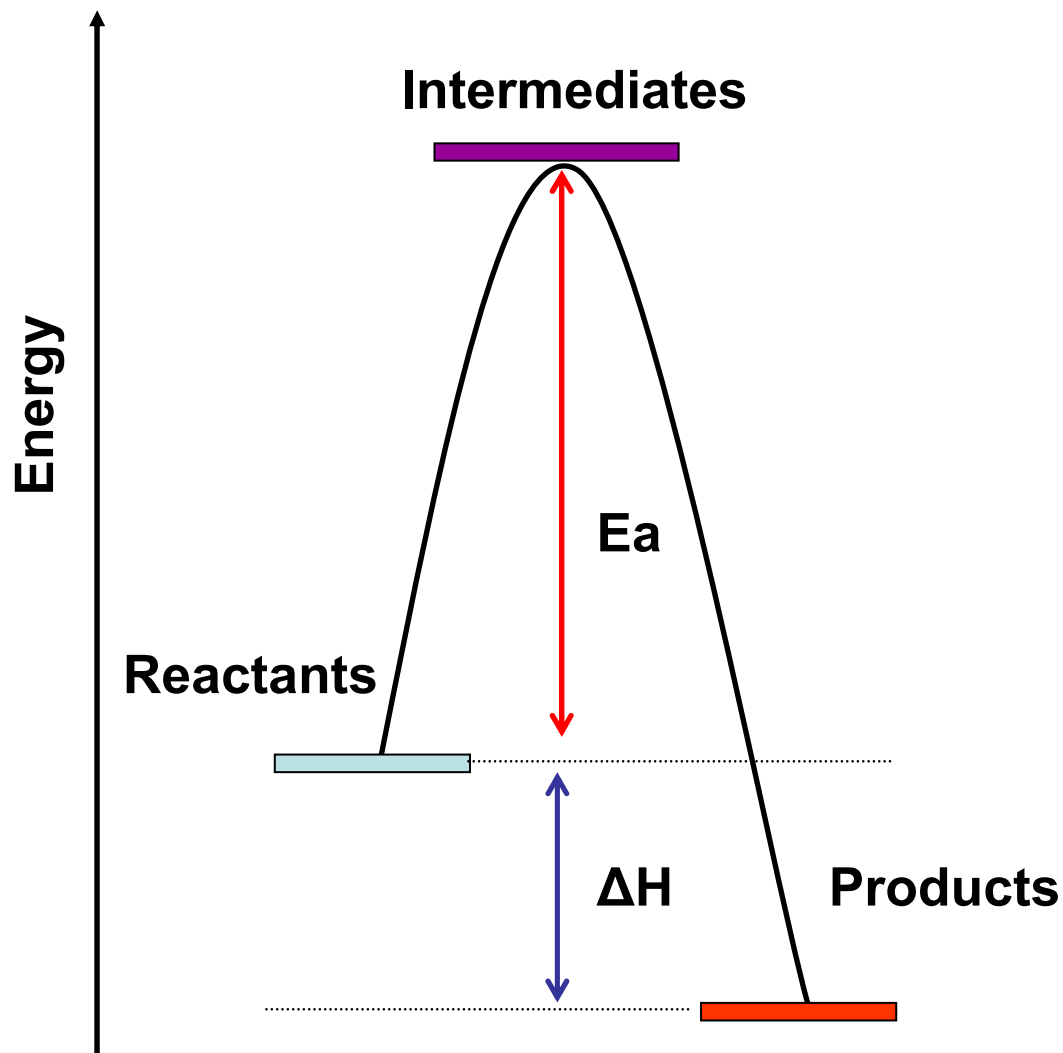
# Thermodynamic parameters – van't Hoff plot



$$\Delta H = -66.1 \text{ kJ/mol } \text{Li}_2\text{NH}$$

$$\Delta H = -88.7 \text{ kJ/mol } \text{Ca}_2\text{NH}$$

# Tuning the Thermodynamic Parameters



$$\Delta G^0 = -RT \ln K_p = RT \ln P_{\text{H}_2}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

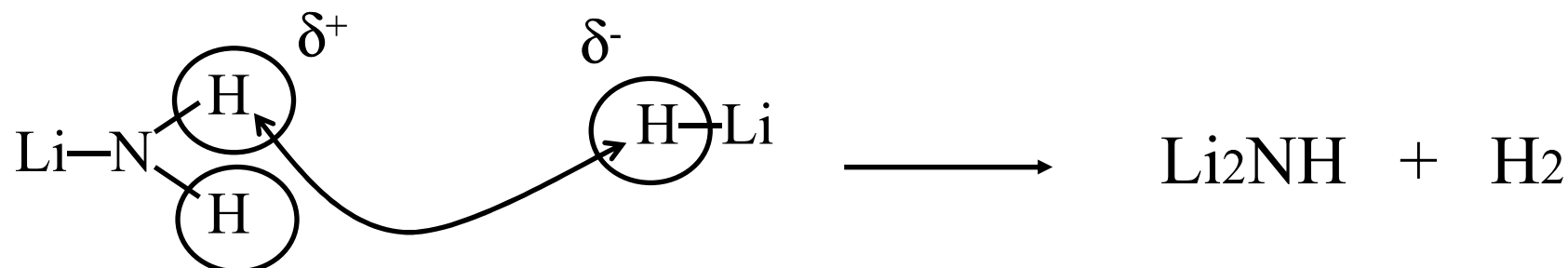
$$\Delta S \cong S_{\text{H}_2}$$

At  $P_{\text{H}_2} = 1.0 \text{ bar}$ ,  $\Delta G^0 = 0$ , thus,

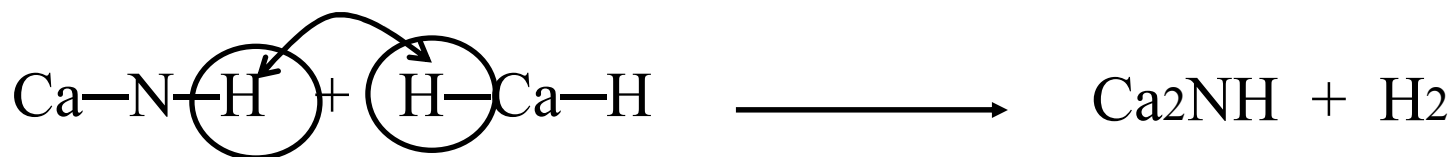
$$T = \Delta H^0 / S_{\text{H}_2}$$

$\Delta H$  – determine the reaction temperature

# Mechanism – Interaction between amide & hydrides

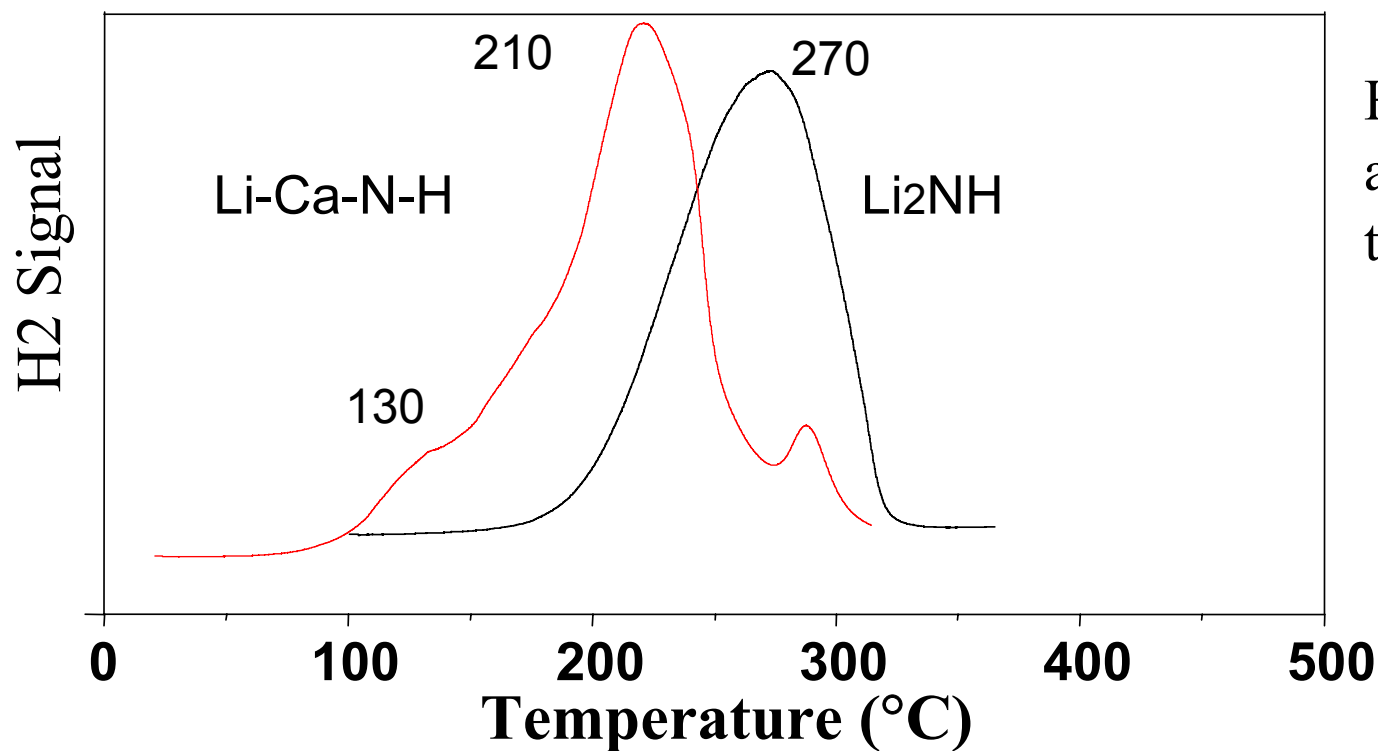


**H atoms attached to N normally possess positive charges, however, H in ionic hydrides have negative one. The strong chemical potential for the combination of H<sup>+</sup> and H<sup>-</sup> is one of the important driving forces!**



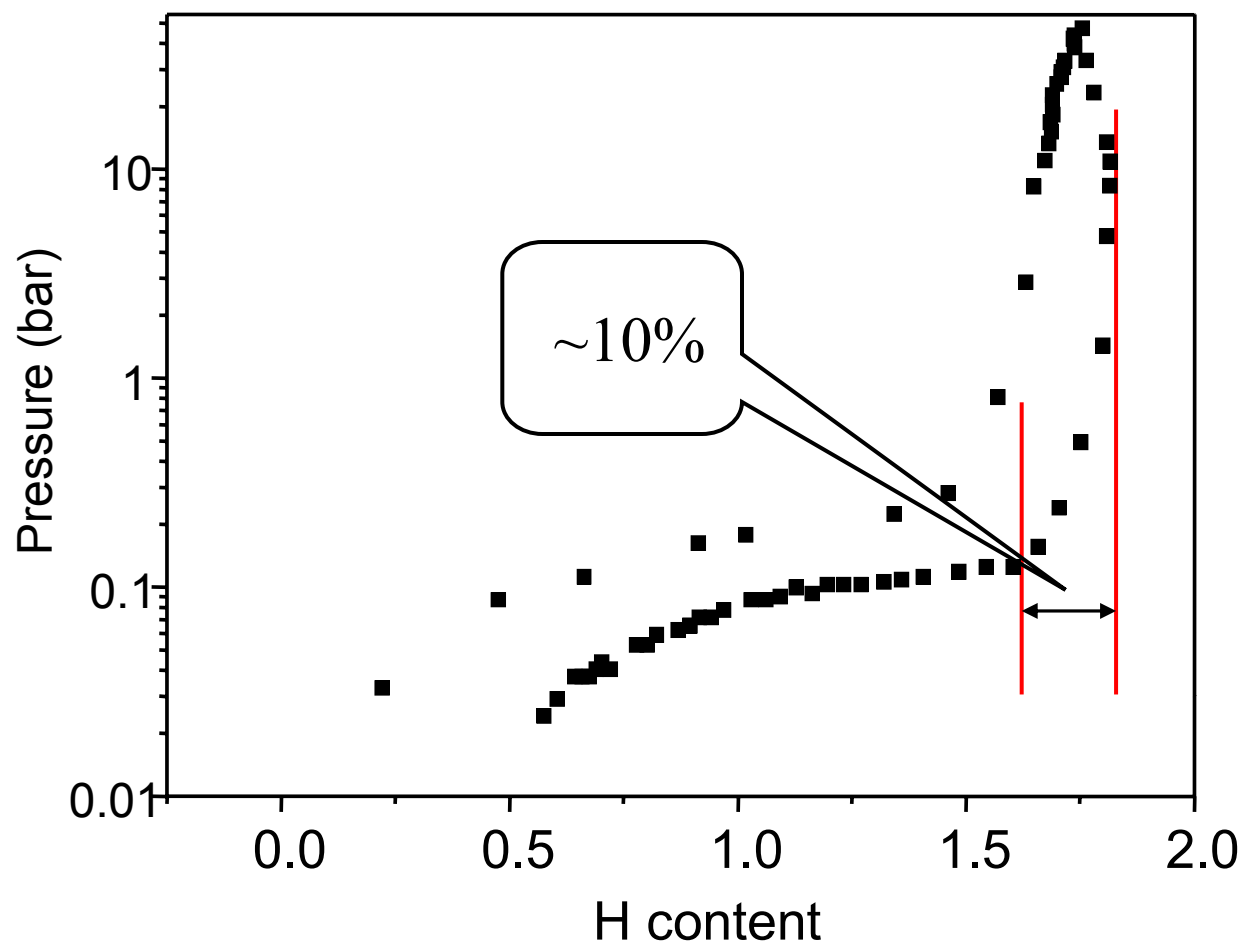
**By changing amide or hydride, new reactions and new materials may be discovered.**

### Li-based ternary imide I – Li-Ca-N-H



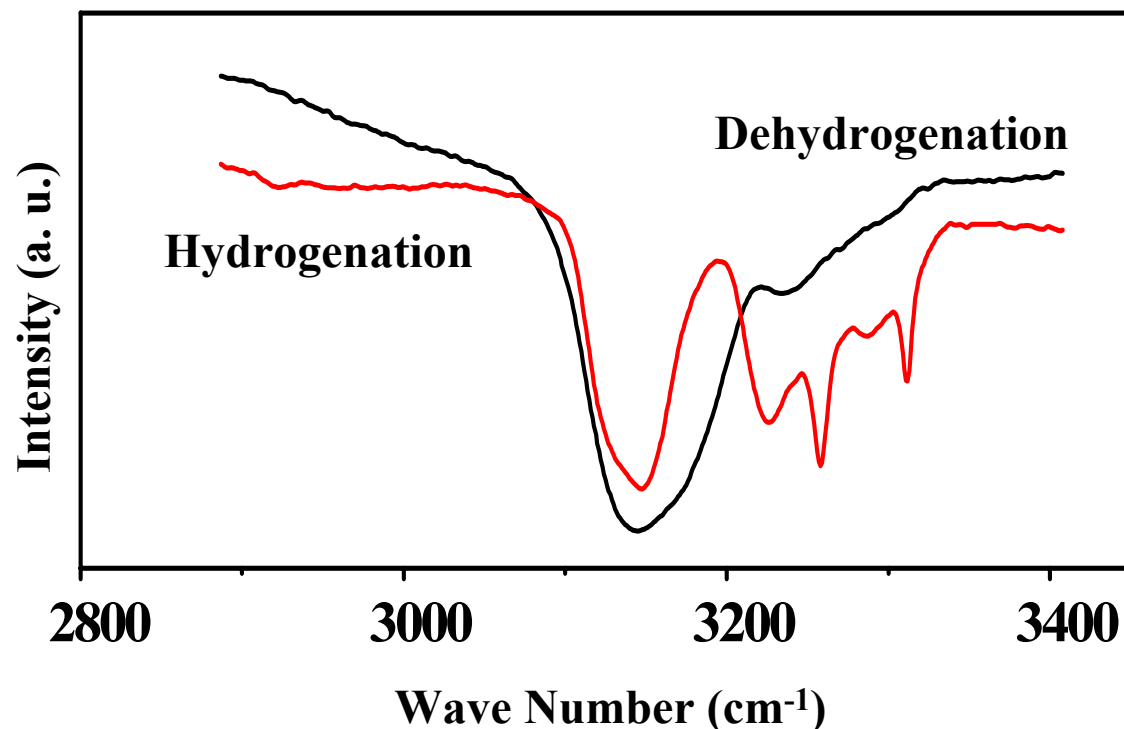
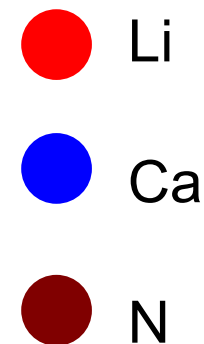
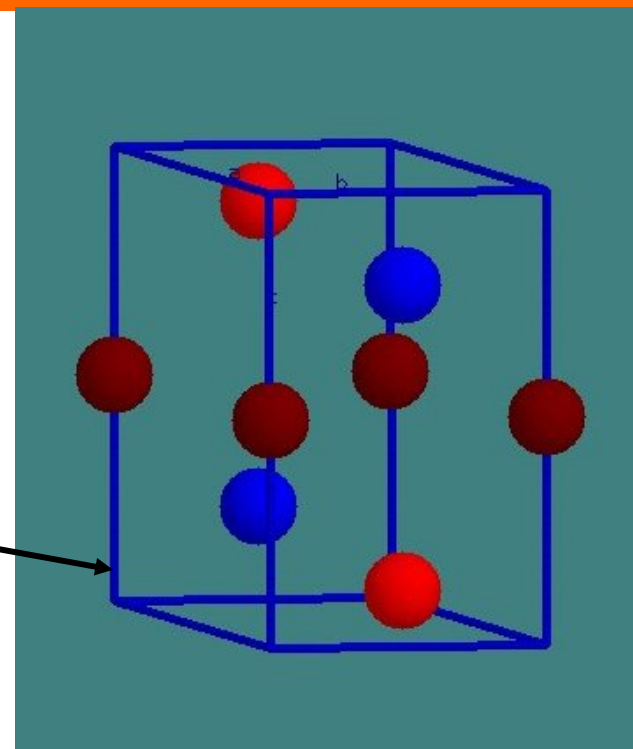
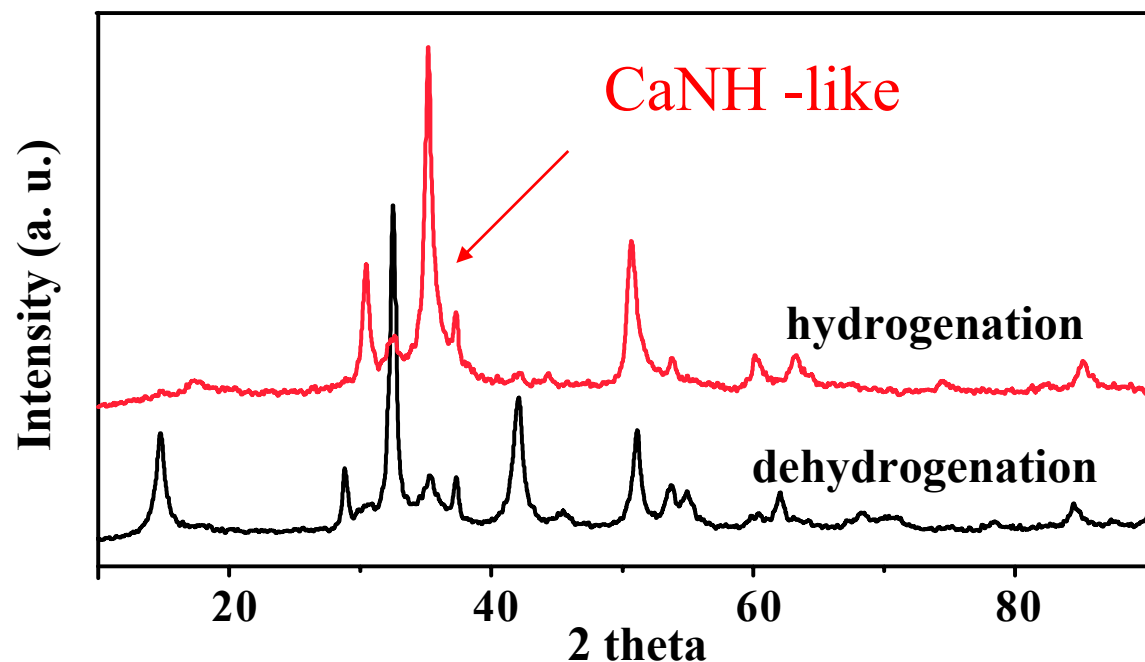
Hydrogen desorption occurs at lower temperature for the ternary system.

### Li-Ca-N-H – P-C-T curve at 220°C



Less than 2 hydrogen atoms can be reversibly stored by one ternary complex of Li-Ca-N-H, which is ~ 2.0 wt% of the starting material.

## II. Ternary Systems Li-Ca-N-H

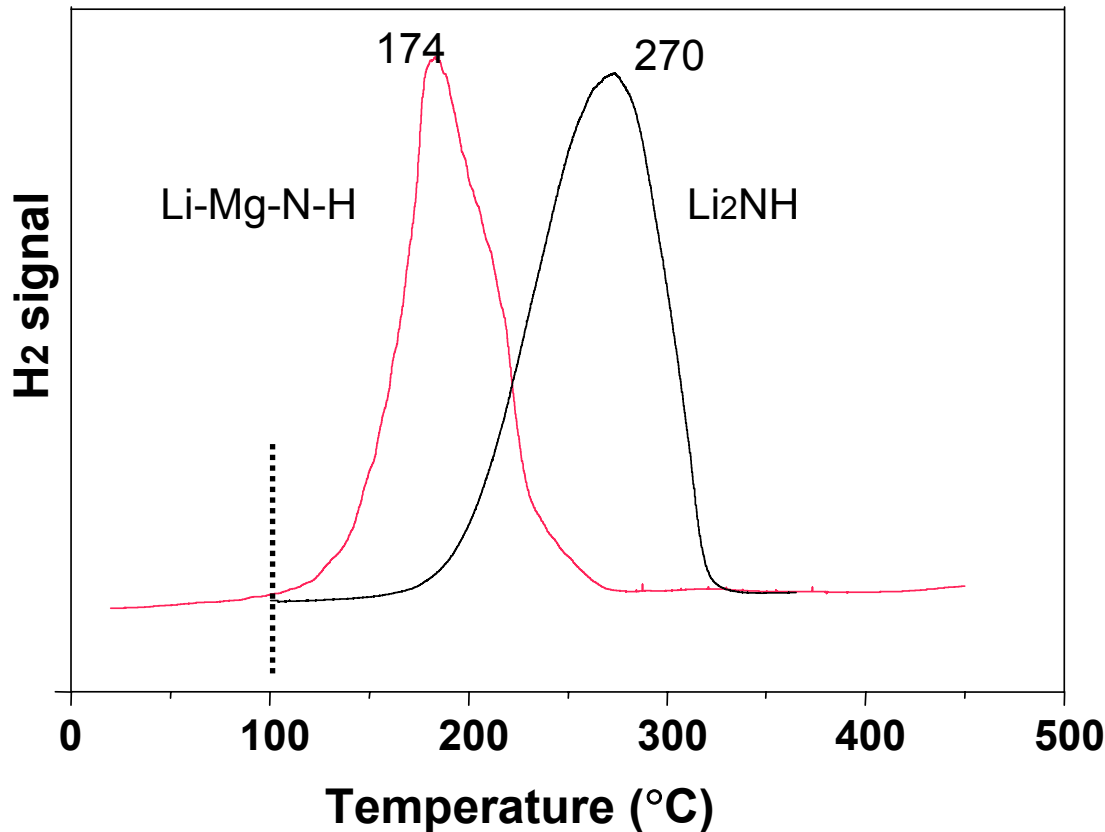


Space Group No.: 164  
Short Hermann-Mauguin  
Symbol: P- 3 M 1  
Schoenflies Symbol: D3d3

Anti-La<sub>2</sub>O<sub>3</sub> Structure

a = 3.56000 Å  
b = 3.56000 Å  
c = 5.93560 Å

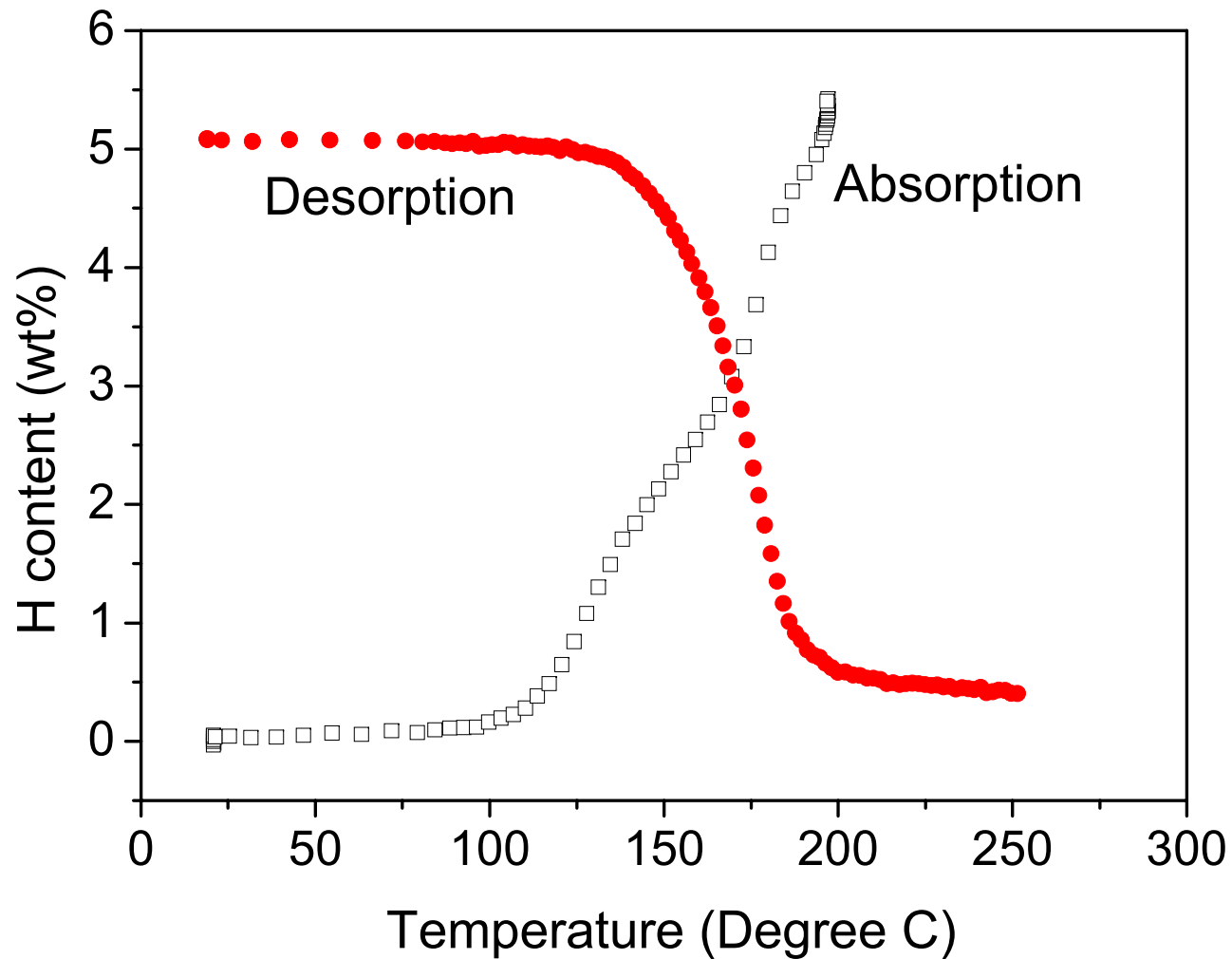
Li-based ternary imides II – Li-Mg-N-H



Hydrogen desorption profiles of Li-Mg-N-H and Li<sub>2</sub>NH. Drastic temperature decrease in hydrogen desorption was achieved in ternary systems.

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

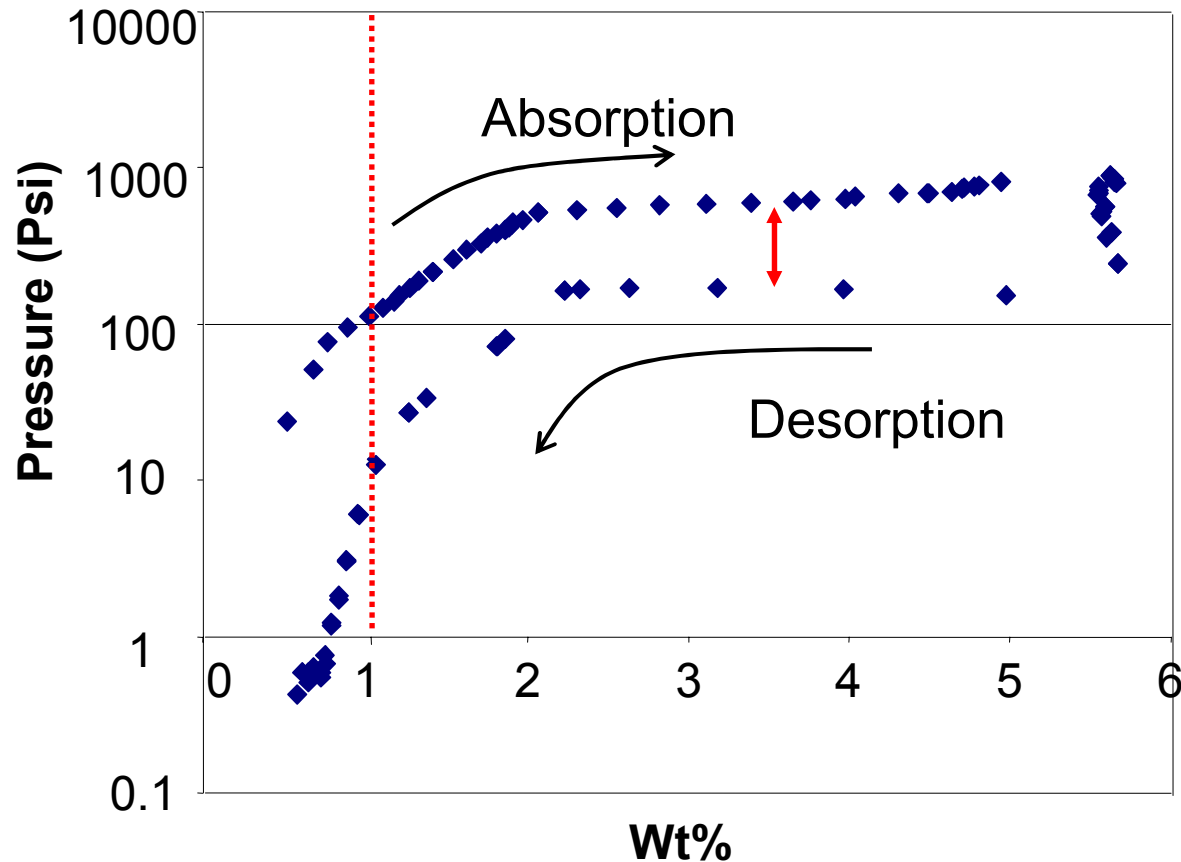
# Volumetric Release & Soak



-- Xiong ZT, Hu JJ, Wu GT, Chen P, Luo W, Gross K, Wang J, *J Alloy Comp*, in press



## Li-Mg-N-H – P-C-T at 180°C

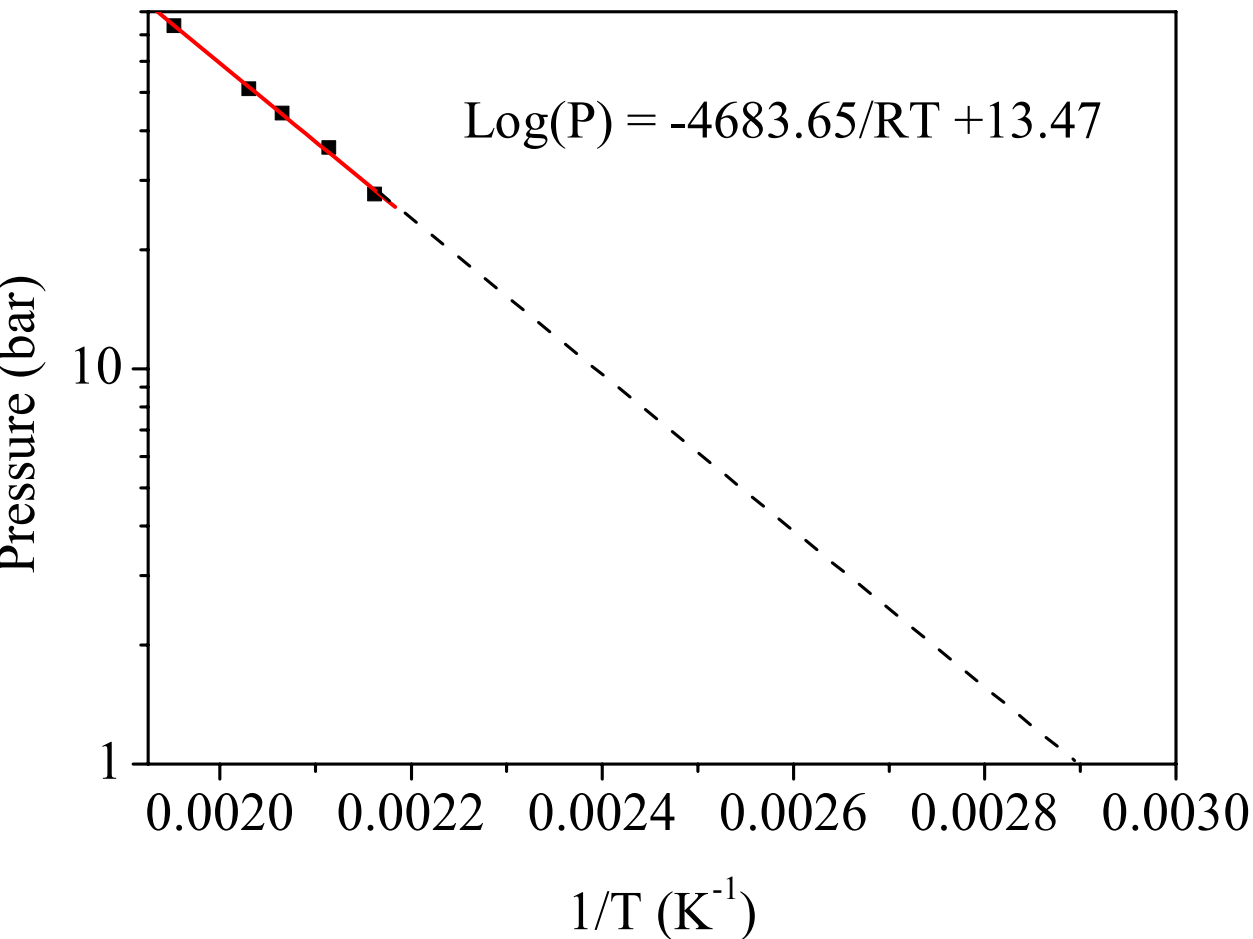


P-C-T measurement shows ~ 5.5wt% of storage achieved at temperature around 180°C or below. The desorption pressure is pretty high, i. e., at 180°C, the plateau pressure is above 20 bars.

Certain hysteresis exists.

# Li-Mg-N-H - Thermodynamic Analysis

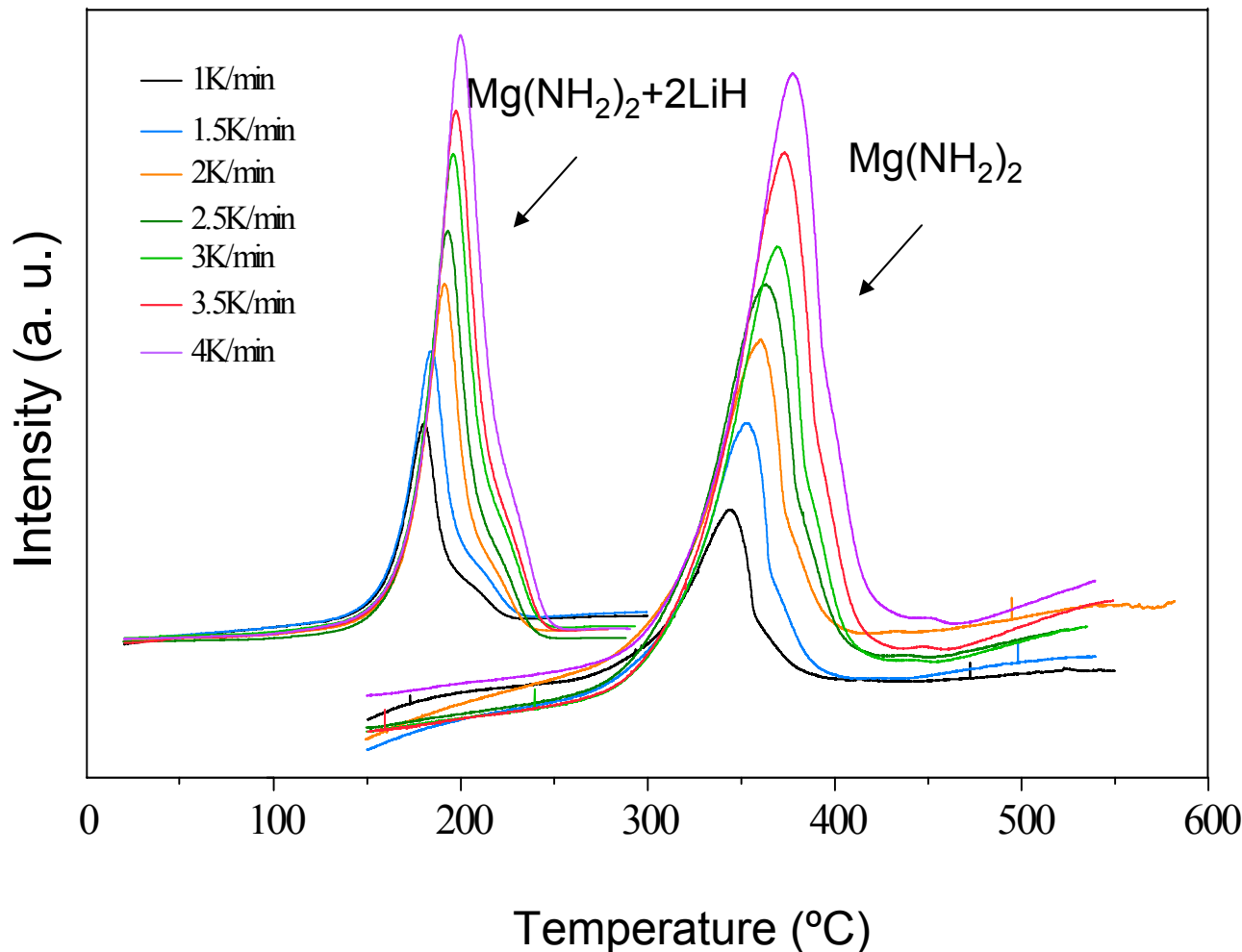
## Van't Hoff plot



$$\Delta H_{\text{des}} = 38.9 \text{ kJ/mol-H}_2$$

Theoretically, hydrogen desorption equilibrium pressure at 90°C is 1.0 bar, close to the PEM fuel Cell operation temperature.

# Li-Mg-N-H - Kinetic Analysis



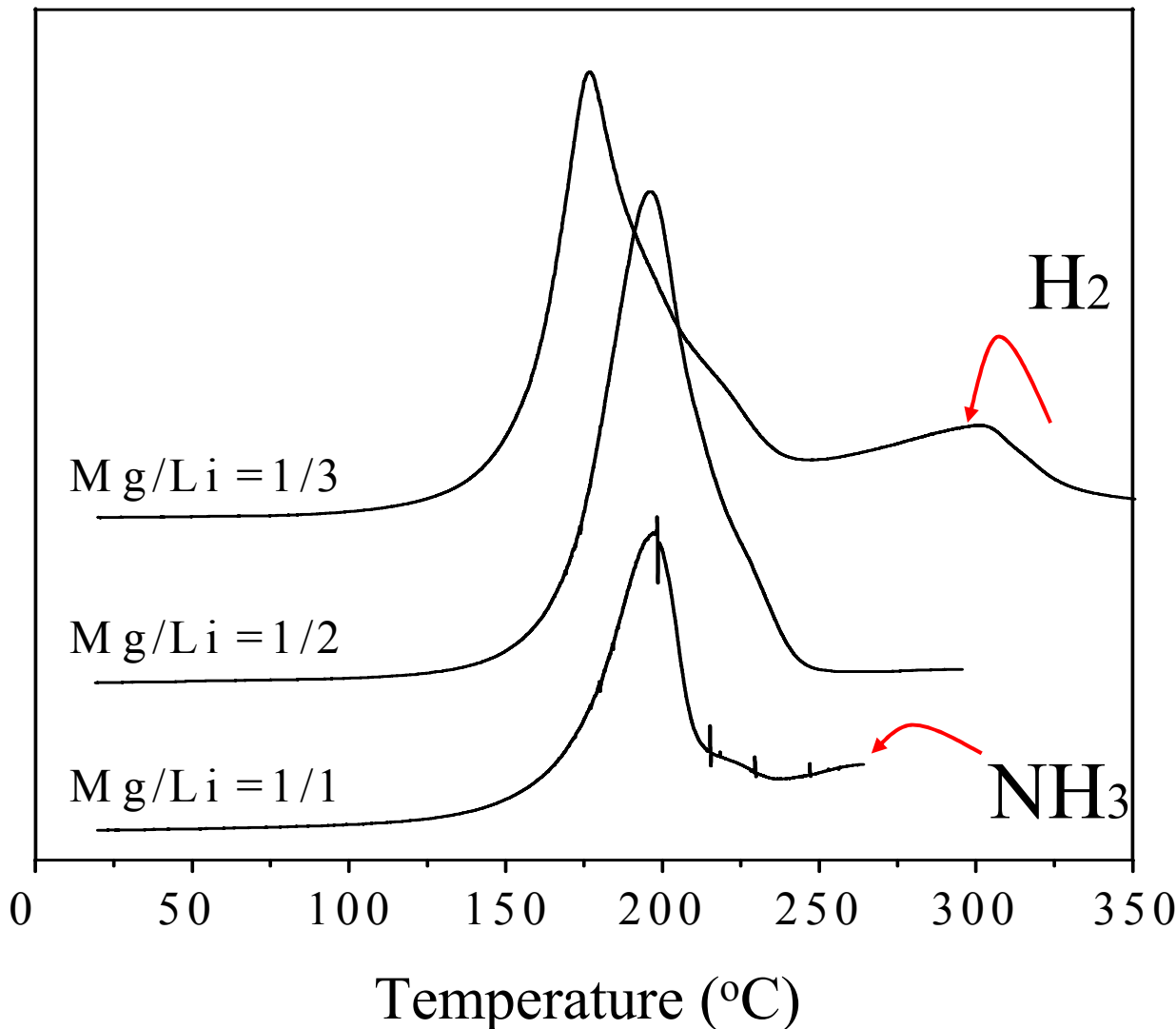
Kissinger's plot  

$$d[\ln(\beta/T_m^2)]/d(1/T_m) = -E_a/R$$

Activation energy for hydrogen release from  $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$  is:  $E_a = 102 \text{ kJ/mol-H}_2$ .

For the decomposition of  $\text{Mg}(\text{NH}_2)_2$ , it is  $\sim 130 \text{ kJ/mol}$

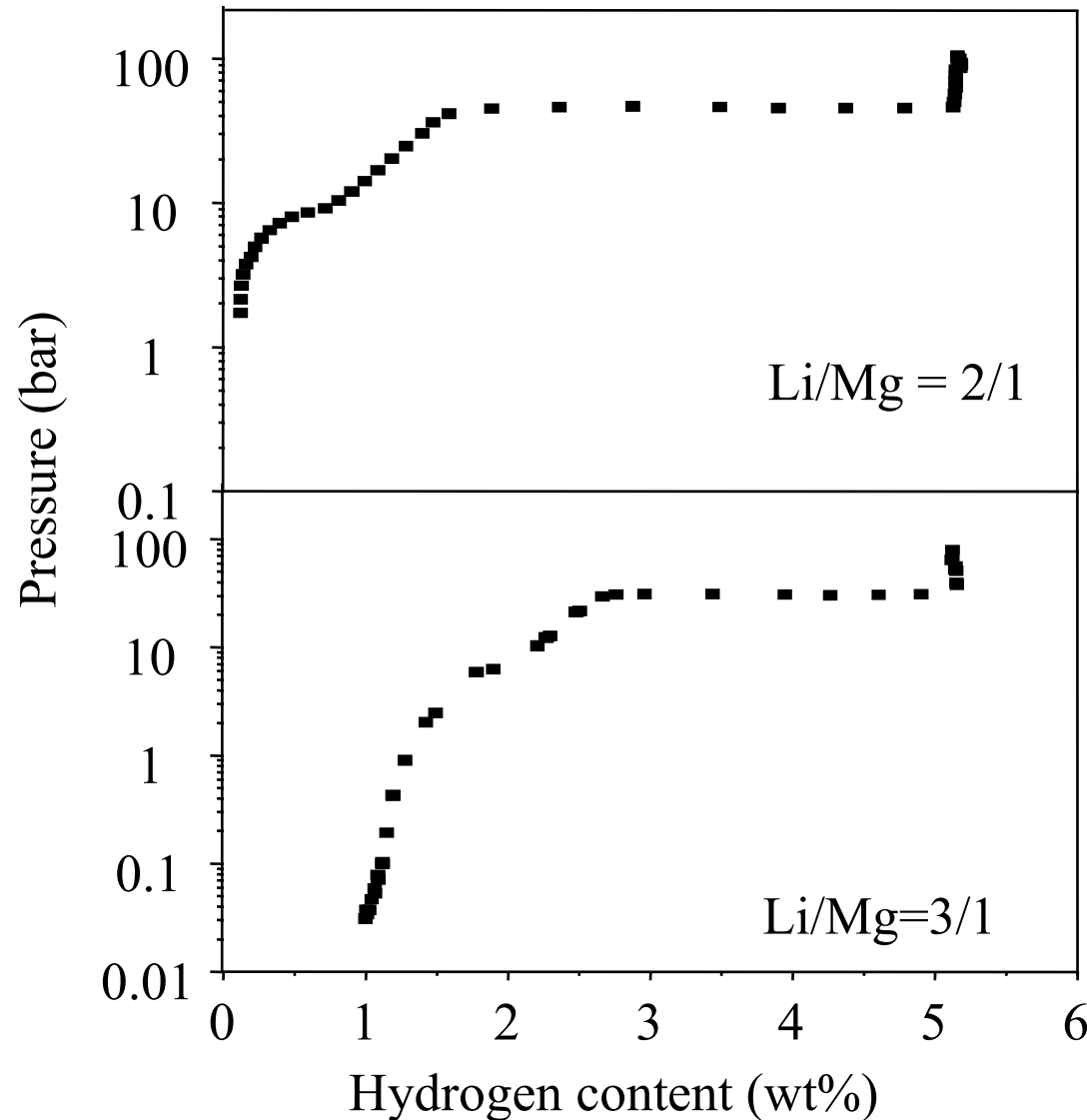
# Compositional Changes



Decrease in LiH content will lead to the release of ammonia at temperature around 200°C.

Increase Li content further stabilizes N content in the complex and may also leads to the increase in total amount of H<sub>2</sub> desorbed. However, part of the hydrogen could be only released at higher temperatures.

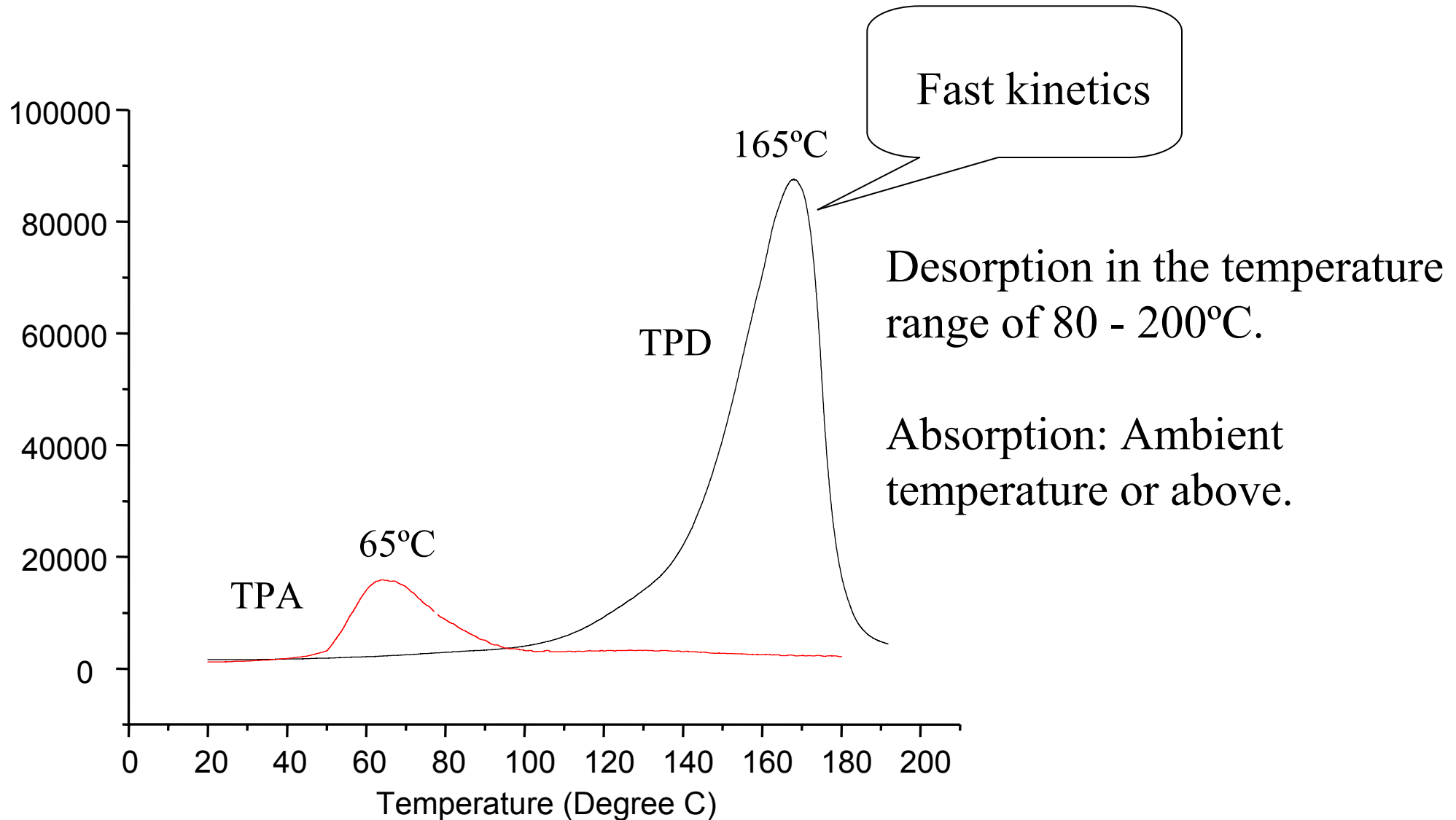
# P-C-T Measurements – 220 °C



Clearly, Li-Mg-N-H with Li/Mg=2/1 gives more usable hydrogen at lower temperature than that of Li/Mg=3/1, wherein part of the hydrogen retains in the complex until higher temperatures.

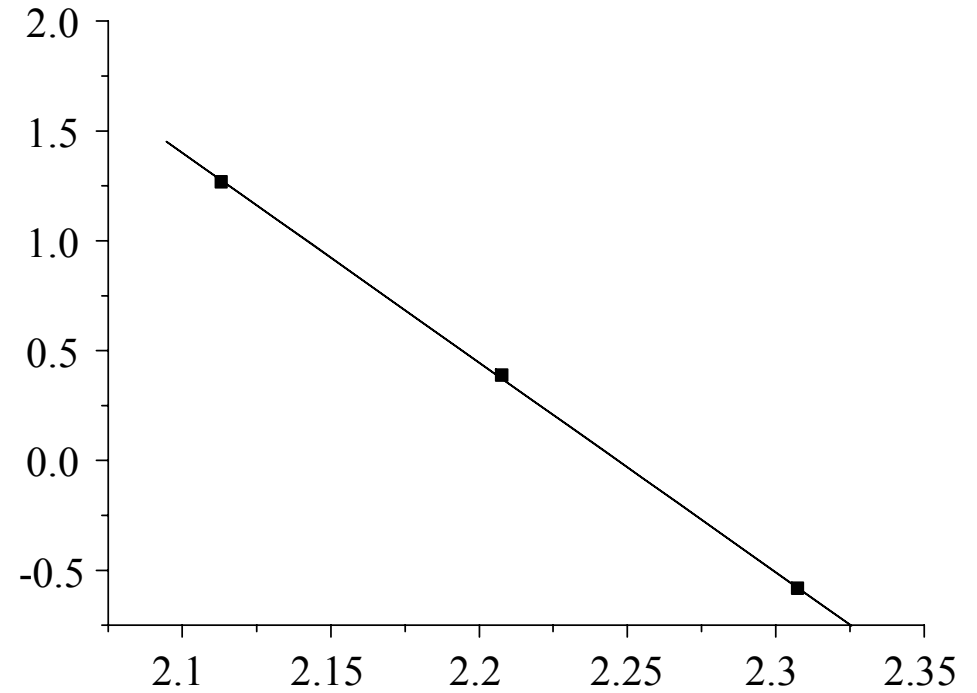
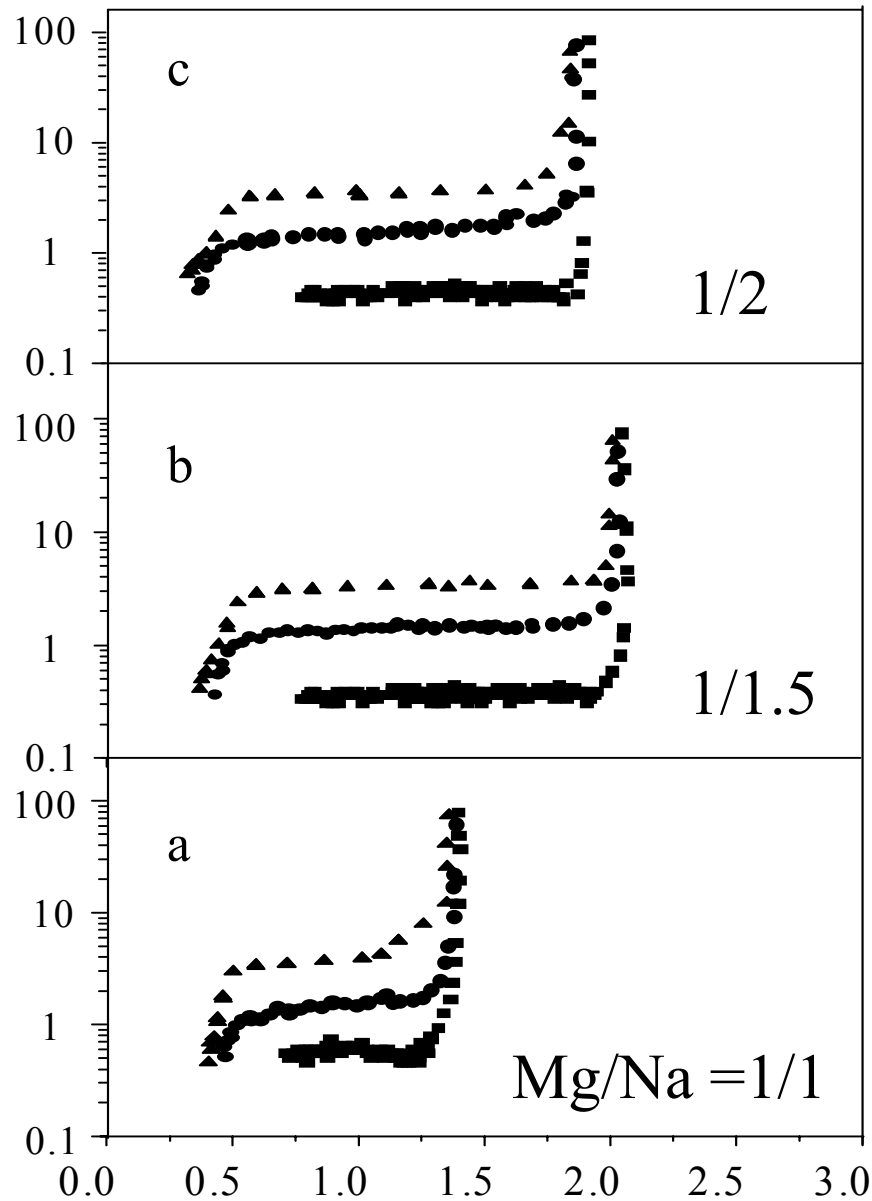
## Ammonia Control

- **There are competing processes involved, i.e., Desorption of H<sub>2</sub> and direct decomposition of NH containing compounds to NH<sub>3</sub>.**
- **Generally, desorption of H<sub>2</sub> is favored at lower temperatures.**
- **To avoid ammonia, we can either lower down the operation temperature or increase hydride content in the reactant.**



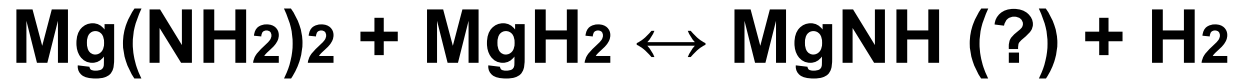
-- Xiong ZT, Hu JJ, Wu GT, Chen P., *J Alloy Comp*, published on line

# P-C-T and van't Hoff plot



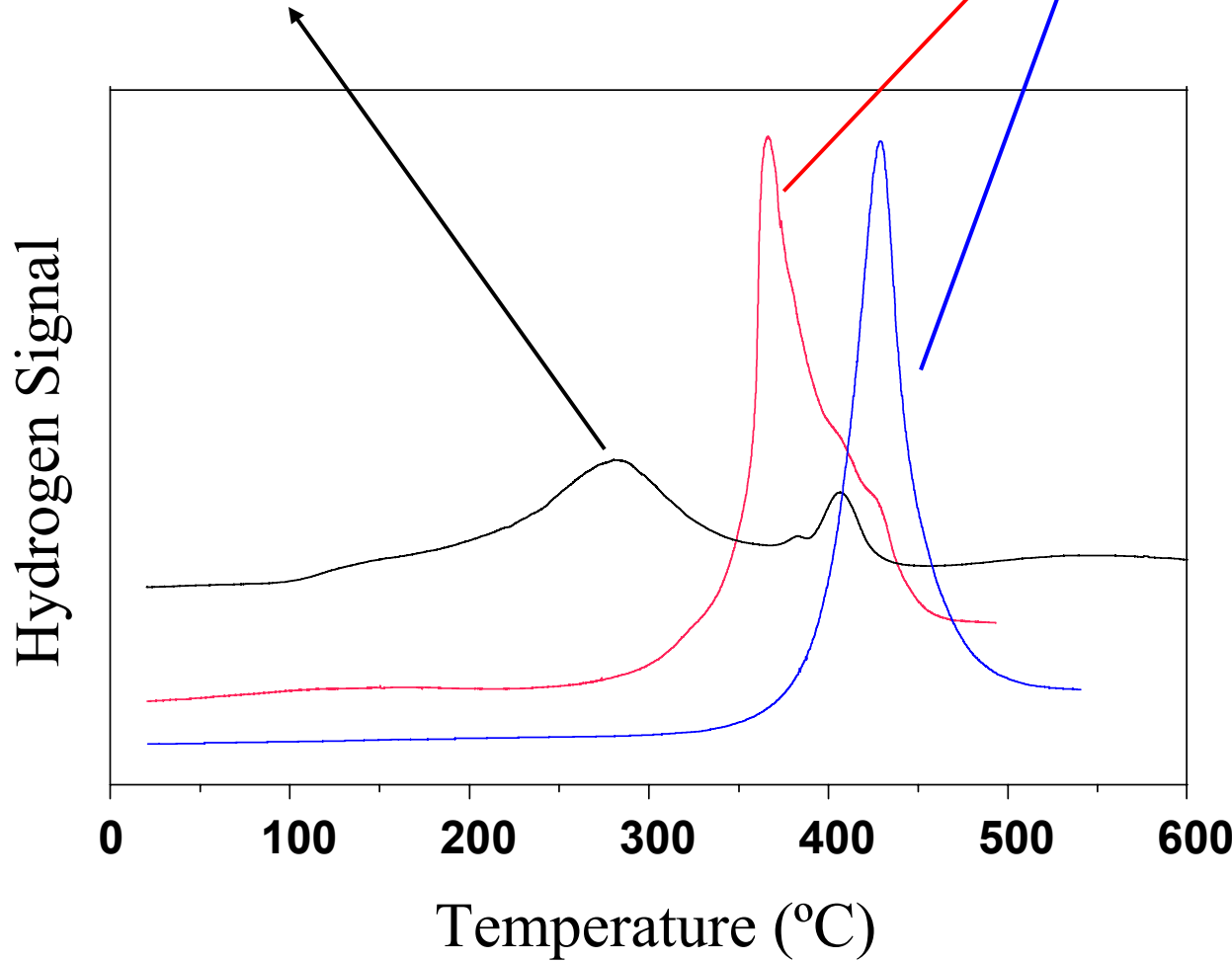
$$\Delta H = 19 \text{ kCal/mol-H}_2$$





Synthesized sample

Starting materials



**More than 2.0 wt % of hydrogen was released at room temperature or below. Hard to recharge.**

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

- A.  $\text{Li}_3\text{N}$**
- B.  $\text{Li}_2\text{NH}$**
- C.  $\text{Ca}_3\text{N}_2$**
- D.  $\text{Ca}_2\text{NH}$**
- 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. Li-Al-N-H with molar ratio of Li/Al = 3/1**
- H. Mg-Na-N-H with different molar ratio of Mg/Na/N**
- I. Mg-Ca-N-H etc..**

- **Chemical Instability – Competing chemical routes exist, exp. direct decomposition of reactants. Sensitive to moisture, CO<sub>2</sub>, O<sub>2</sub> etc.**
- **Operation Temperature.**
- **Lifetime – sample segregation, which induces the slow kinetics.**
- **Material Synthesis and storage.**
- **Thermodynamic data.**

- **Plenty systems for exploration : Nitride, Imide, Nitride hydrides etc., binary, ternary or Multinary.**
- **Huge room for optimization: Catalyst, Additive, Crystal dimension, Morphology etc..**
- **New Chemistry – New chemicals, New reactions.**

# Acknowledgements

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## Collaboration

Institute of Applied Energy (Japan)

## Collaborators

Dr. Weifang Luo, Dr. Karl Gross, Dr. James Wang (SNL)

Professor Gert Wolf (TU Bergakademie Freiberg)

# References

1. P. Chen, Z. Xiong, et.al. *Nature* 420 (2002) 302
2. T. Ichikawa, S. Isobe, N. Hanada, H. Fujii, *J Alloy Compd.*, 365 (2004) 271
3. Y. Hu, E. Ruckenstein, *Ind Eng Chem Res* 42 (2003) 5135
4. Z. Xiong, J. Hu, G. Wu, P. Chen *Adv. Mater.* 16 (2004) 1522.
5. W. Luo, *J. Alloy. Compd.* 381 (2004) 284.
6. H. Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe and H. Fujii, *J. Phys. Chem. B* 108 (2004) 8763.
7. Y. Nakamori and S. Orimo, *J. Alloy. Compd.* 370 (2004) 271-275.
8. Z. Xiong, J. Hu, G. Wu, P. Chen, *J. Alloy. Compd*, published on line.
9. Y. Nakamori, G. Kitahara, S. Orimo *J. Power Source* 138 (2004) 309.
10. P. Chen, J. Z. Luo, Z. T. Xiong, J. Y. Lin and K. L. Tan, *J. Phys. Chem.* 107 (2003) 10967.
11. T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, *J. Phys Chem. B* 108 (2004) 7887.
12. F. Pinkerton, G. Meisner, M. Meyer, M. Balogh and M. Kundrat, *J. Phys Chem B* 109 (2005) 6.