Destabilization of Metal Hydrides by Forming Nitrogen-containing Compounds

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High Hydrogen Capacity

Current status

Major players	Capacity	Operating conditions
Interstitial hydrides	Unsatisfactory	
Mg		Unsatisfactory
Sodium alanate	close to target	close to target

Grand Challenge !

$LiNH_2$-LiH Storage System[1]

Amide : $-NH_2$, $LiNH_2$ | **Imide : $>NH$, Li_2NH** | **Nitride : $\equiv N$, Li_3N**

1st Step:

$$LiNH_2 + LiH \xrightleftharpoons[1\ atm]{300^oC} Li_2NH + H_2$$ 6.5 wt%

2nd step:

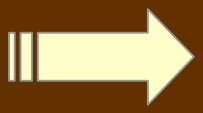
$$Li_2NH + LiH \xrightleftharpoons[0.05\ atm]{300^oC} Li_3N + H_2$$ **5 wt%**

Two steps in total:

11.5 wt%

Major limitations:

- Temperature too high
- Pressure too low

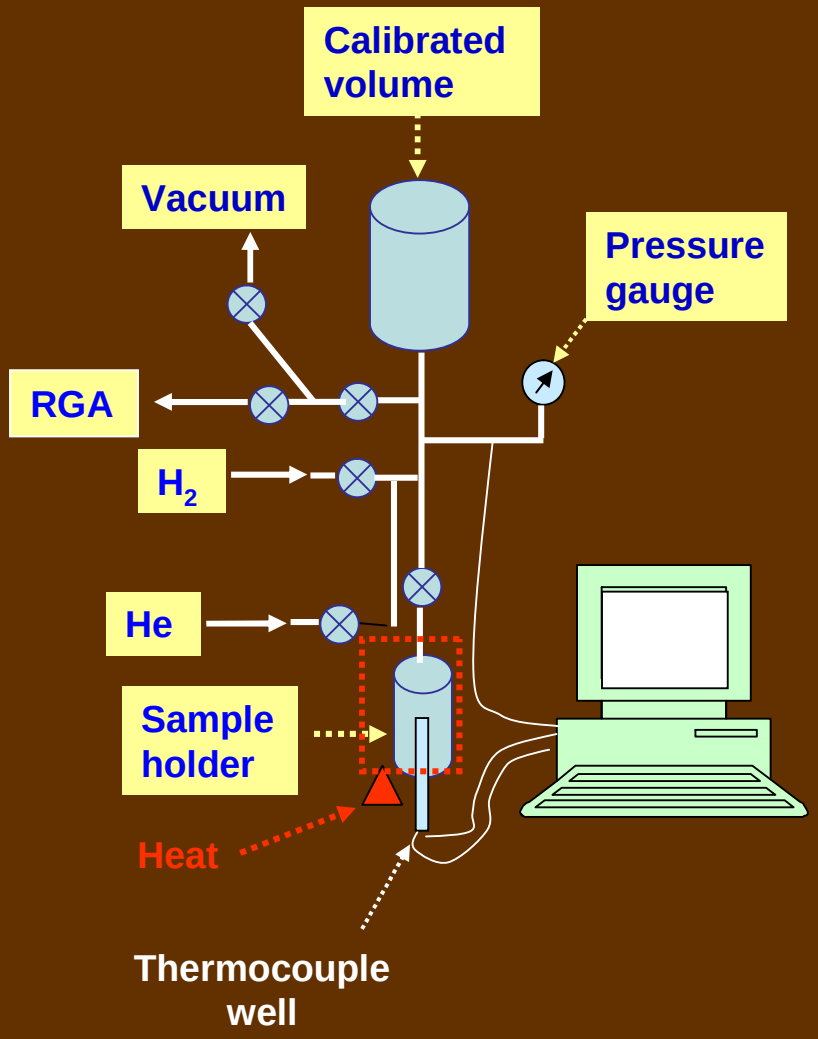


New system:[2-6]

Partial Mg substitution

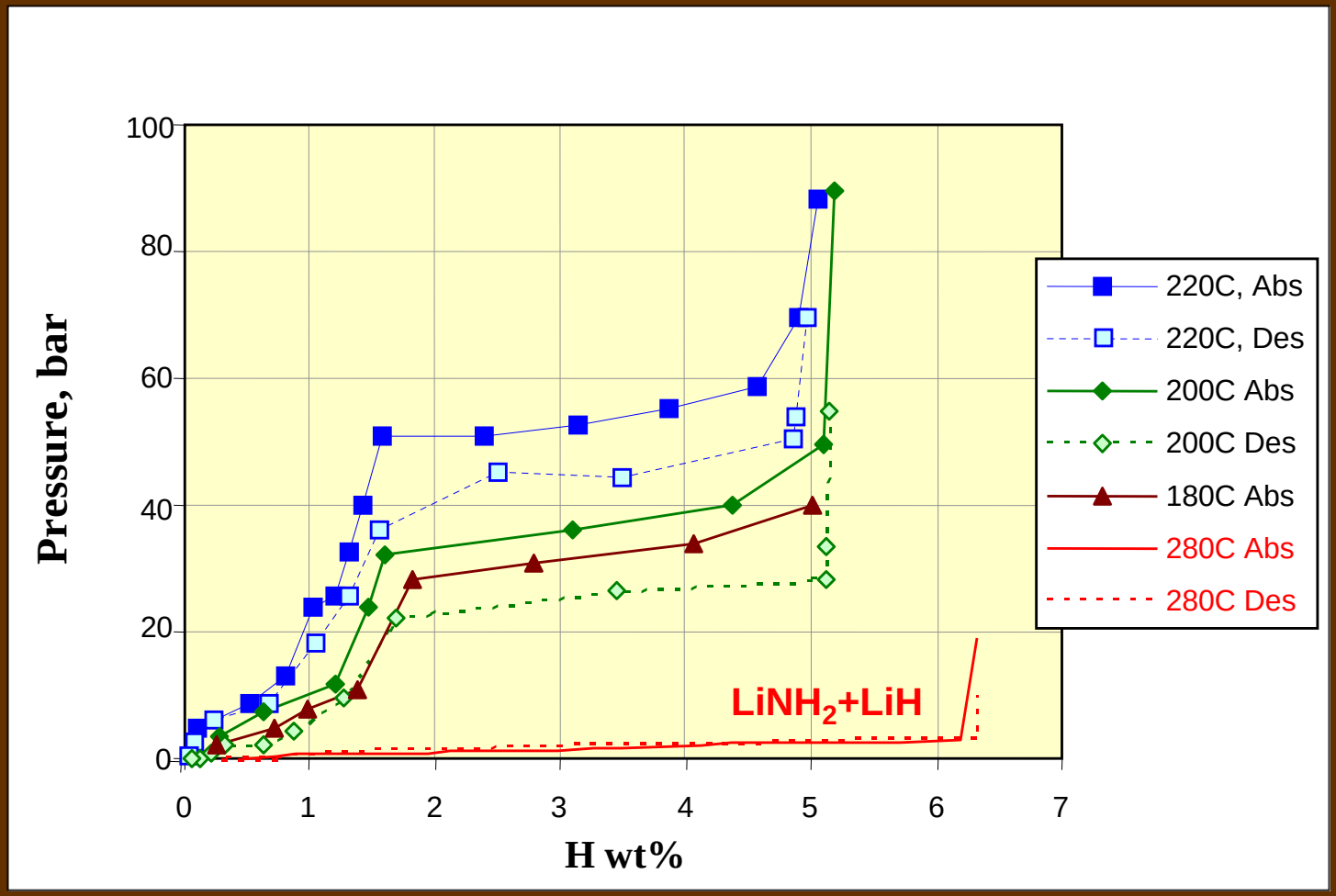
1. Chen, P. et al, *Nature* vol. **420**, (2002) 302.
2. Z. Xiong, G. Wu, J. Hu, P. Chen, Advanced Material, 16 No.17 (2004) 1522-1525
3. Y. Nakamori, S. Orimo, J. Alloys and Compounds, 370 (2004) 271-275.
4. H. Leng, T. Ichikawa, S. Hino, N. Hanada, J. Phys. Chem. B 108 (2004) 8763-8765.
5. Y. Nakamori, S. Orimo, J. Alloys and Compounds, 377 (2004) L1-L3.
6. W. Luo, J. Alloys and Comp., 381 (2004) 284-287.

Schematic Sieverts Apparatus



Sorption Isotherms for

($LiNH_2$+ LiH) and ($2LiNH_2$+ MgH_2)



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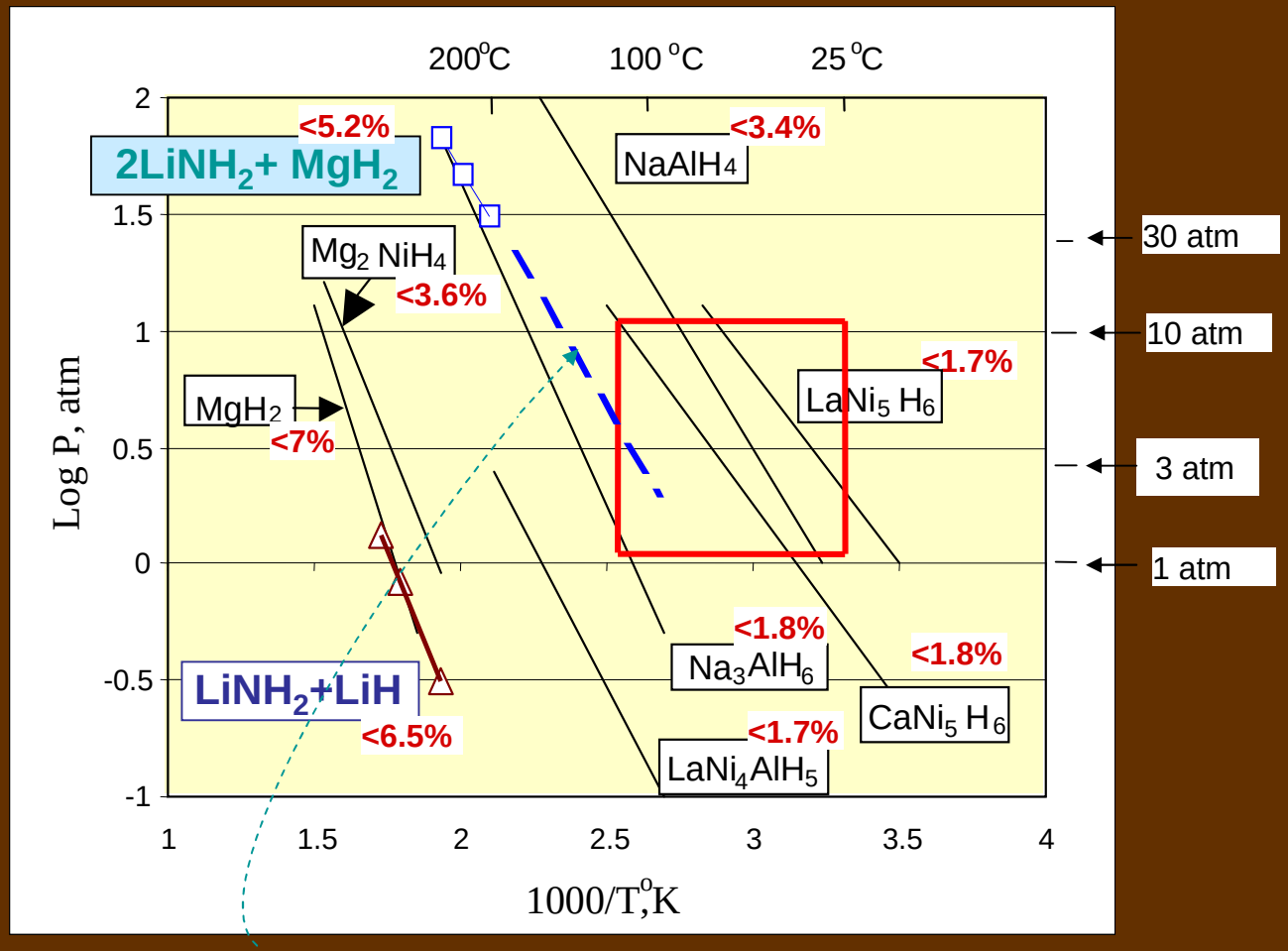
Van't Hoff Plots



Desorption enthalpy: -39 kJ / mol-H_2**

* B. Bogdanovic *et al*, J. Alloys and Compounds, 302, 36 (2000).

** W. Luo, J. Alloys and Compounds, 381 (2004) 284-287

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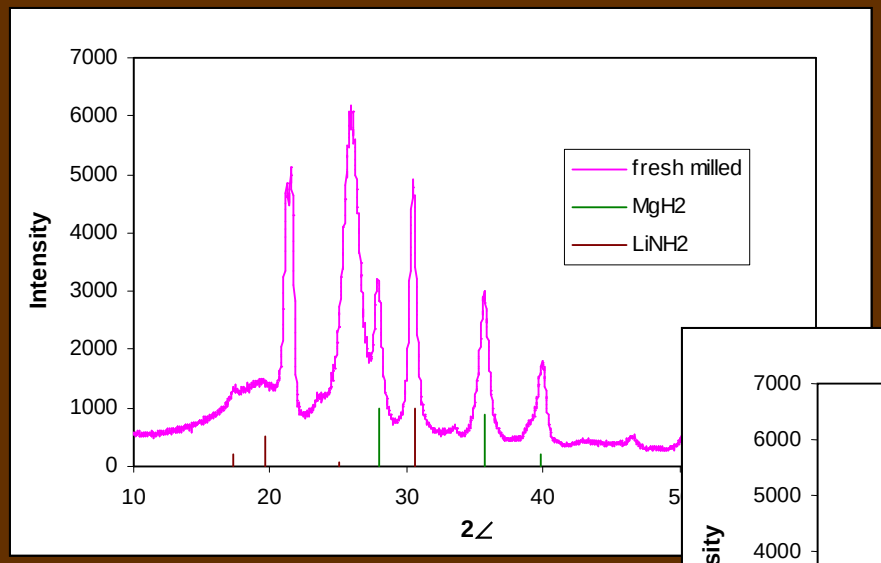
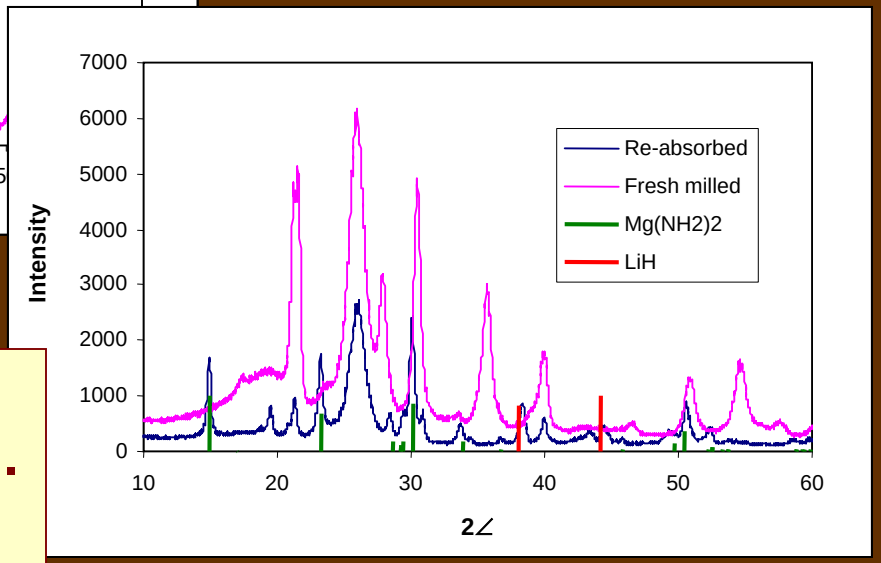
$(2LiNH_2 + MgH_2)$: Fresh milled & Re-Absorbed

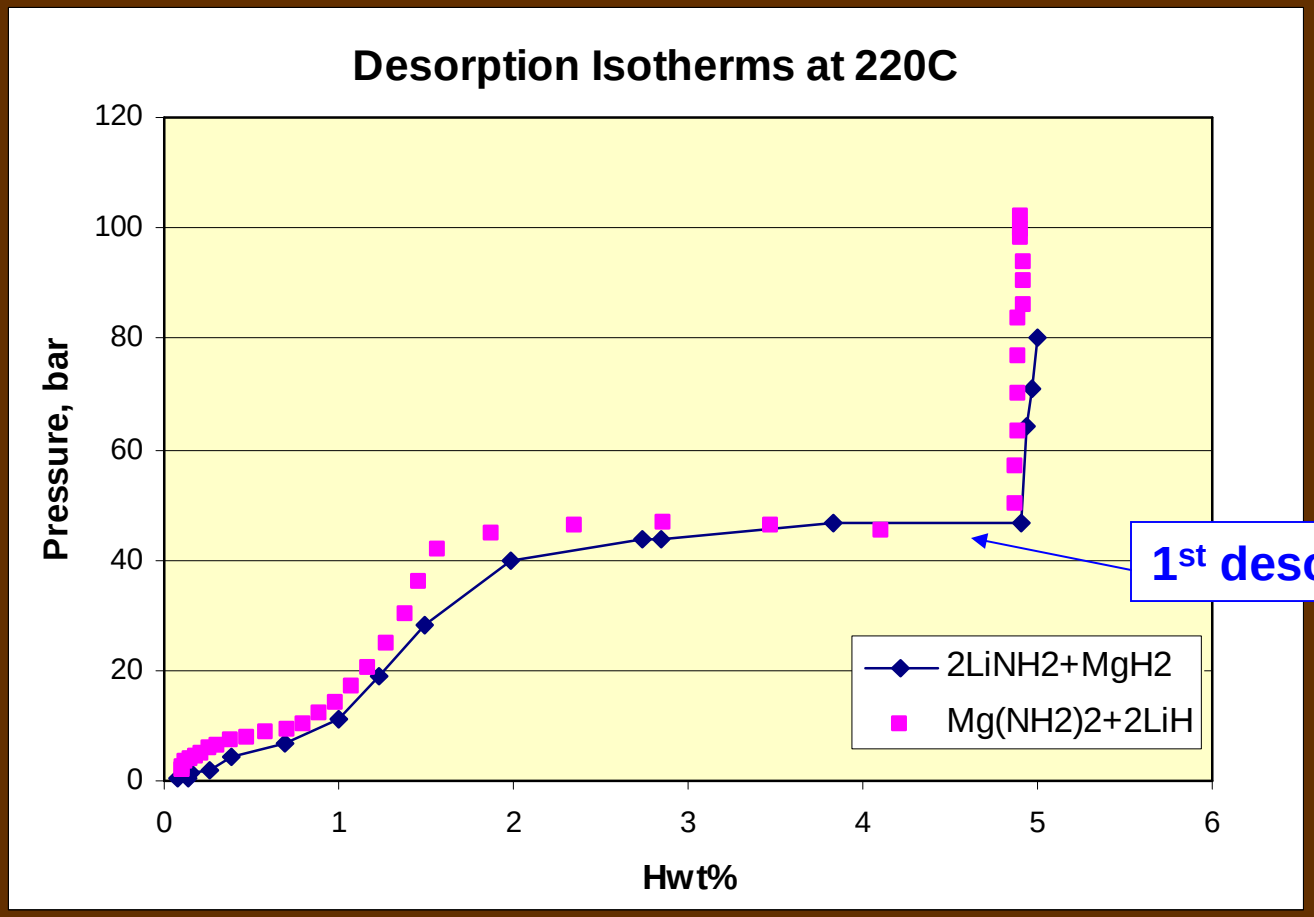




Crystalline structure changed upon sorption.

When does it start?

Comparison of Desorption Isotherms: $(2LiNH_2 + MgH_2)$ and $(Mg(NH_2)_2 + 2\ LiH)$



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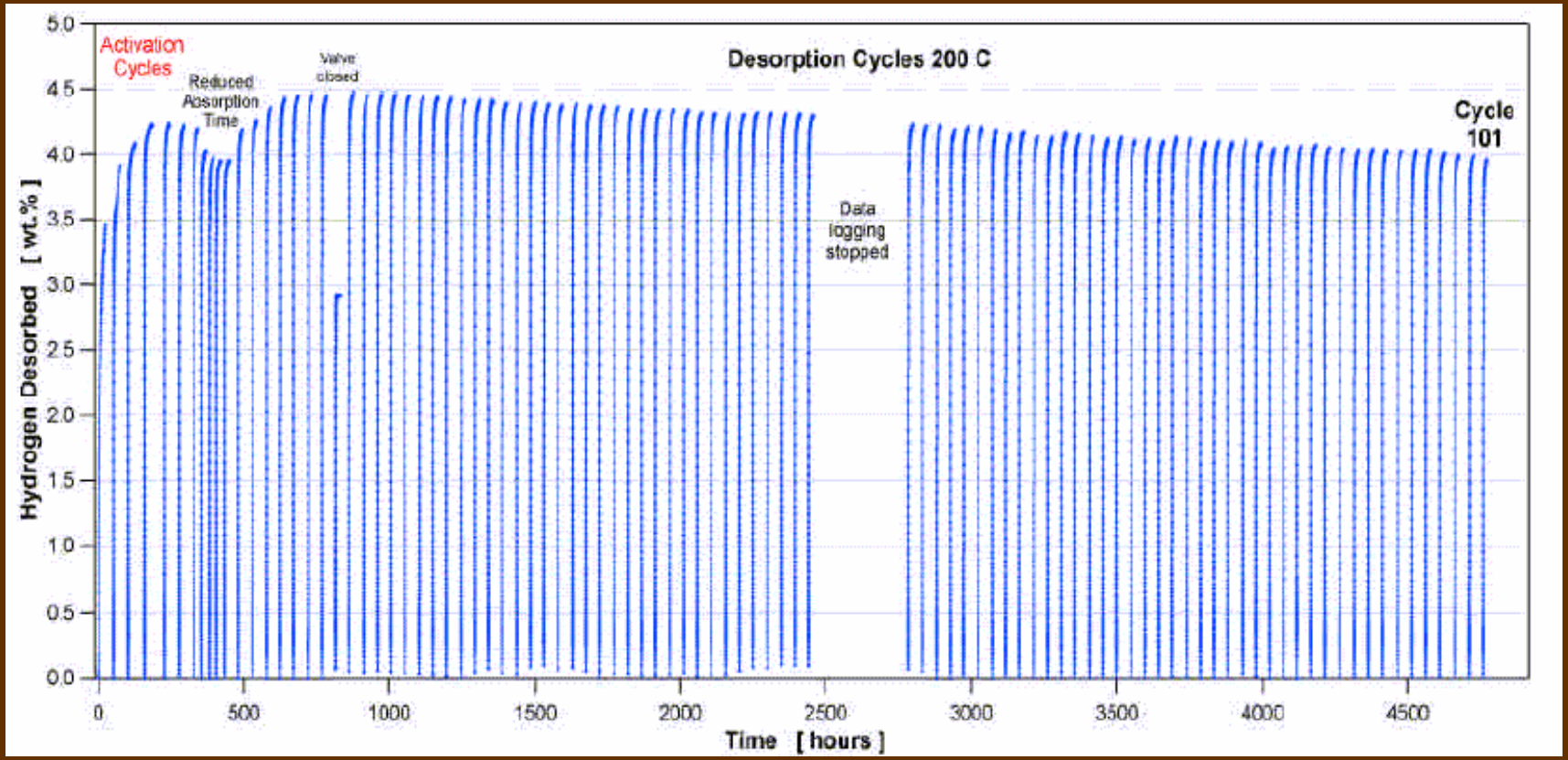
Capacity in 101 cycles



Average capacity loss: 0.005wt% per cycle.

(Without formulation optimization)

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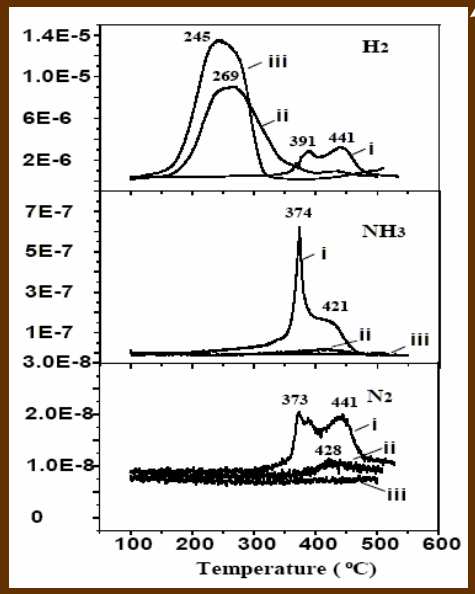
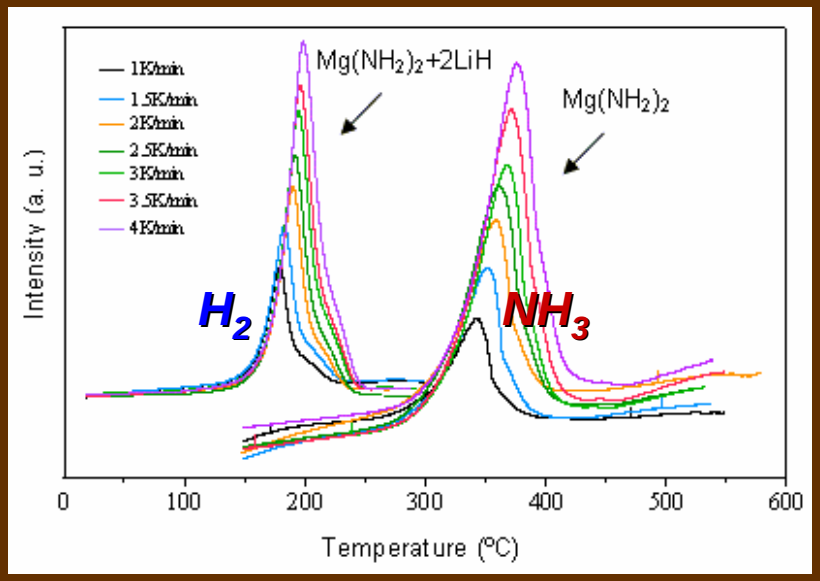
Reaction Mechanism: Path

TPD





i. Pure $LiNH_2$; ii. $LiNH_2$+LiH (1/1); iii. $LiNH_2$+2LiH (1/2)

P. Chen et al, Nature 420 (2002) 302

P. Chen et al, J. Alloys and Compounds, in press

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Summary

- The mix of ($2LiNH_2$+MgH_2) absorbs 5.2 wt% H_2 reversibly.
- The desorption pressure:
  - ✓ 30 bar at 200°C;
  - ✓ should be 3 bar at 100°C according to extrapolated van't Hoff plot.
- 101 sorption cycles for ($2LiNH_2$+MgH_2) reported. About 0.005wt% capacity loss per cycle.
- Reaction mechanism study could lead to more efficient search for storage materials.

Acknowledgement

- Thanks to E. Majzoub for carrying out XRD test and Ken Steward for set up equipment and prepare samples for tests.
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