Searching for New H-storage Material with High Capacity

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Search for a new material

Currently we have:

1. On-Board Rechargeable systems
   - $NaAlH_4$ (+$TiCl_3$) 4wt% 140-200C
   - $Mg(NH_2)_2$-2LiH 5wt% 180-200C
2. Off board re-generable systems
   - AlH_3 9-10wt% 100C
   - NH_3-BH_3 10wt% 100C

On-board vs. Off-board

- Great challenge: for heat dissipation in re-fueling (450 KW)*
- Energy supply needed for H_2 release

* G. Sandrock, et al, Appl. Phys. A 80, 687–690 (2005)

Wish list:

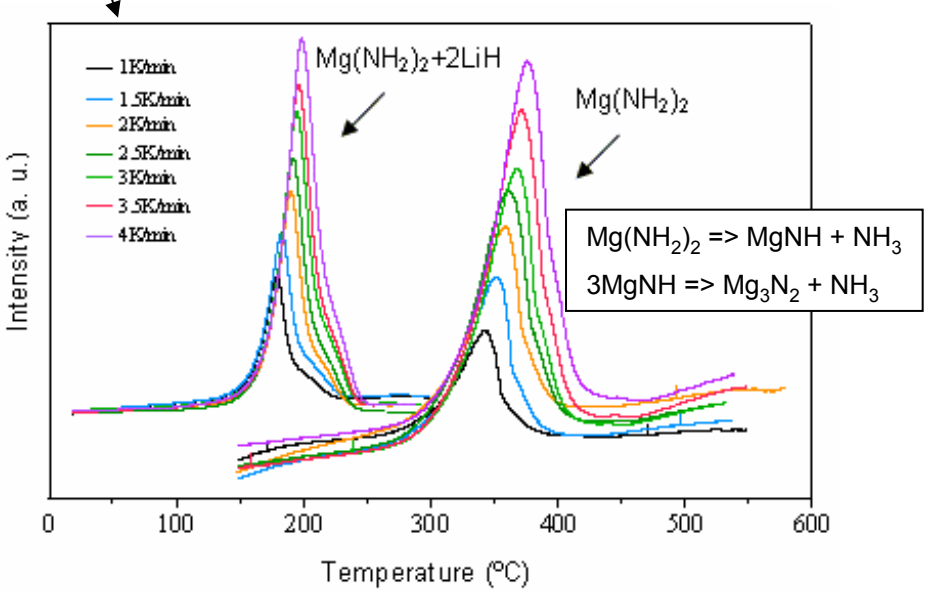
- Working temperature: 25C
- Easy cold-start
- No energy consumption for H_2 release
- Low cost material
- Low cost system
- Easy refill without heat removal
- Generate H_2 on demand
- Safe storage

Candidate Selection

Reference system:

$Mg(NH_2)_2 + 2LiH \Leftrightarrow Li_2Mg(NH)_2 + 2H_2$

$LiH = Li + ½\ H_2$ > 600°C



* P. Chen et al, J. Alloys and Comp, 398 (2005) 235.

Benefit from: $\delta+$ $\delta-$ $Mg(NH_2)_2 + LiH$

Approach:

Ammonia - metal hydride ⟶

NH_3-$LiAlH_4$

- H-capacity: 17% and 11%
- $\delta+$ and $\delta-$
- A possible reaction:

$4NH_3+3LiAlH_4 = Li_3N+3AlN+12H_2$

- Exothermic ΔH= -46kJ/H_2
- ~~Heat for H_2 release~~

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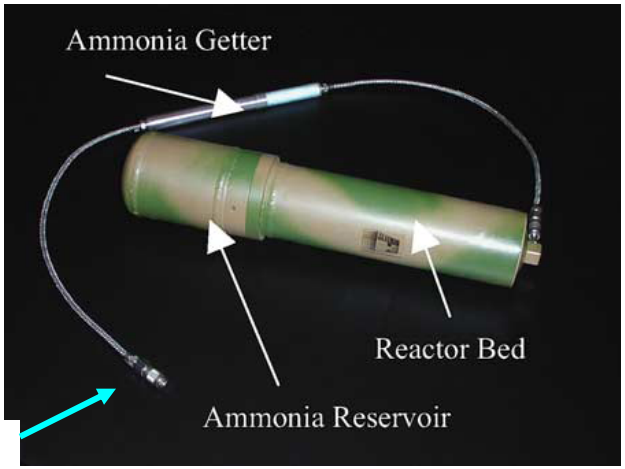
Material with High Capacity

Literature information



To fuel cell

N. Sifer and K. Gardner, J. Power Souces 132 (2004) 135-138.

Power profile	5W	5W	25–50W	25–50W
Temperature (◦C)	**2**	**23**	**23**	**47**
H2/NH3 (mol)	2.8	2.4	2.8	4.1
bed utilization (%)	**89**	**95**	60∗	70∗

∗ Ammonia getter failed/consumed. Not all ammonia consumed.

$4NH_3 + 3LiAlH_4 = Li_3N + 3AlN + 12H_2$

Possible reaction		**Hwt%**
$\mathbf{4}NH_3+3LiAlH_4 = Li_3N+3AlN+\mathbf{12}H_2$	(1)	**13.2wt%**
$\mathbf{4}NH_3+2LiAlH_4 = LiAl(NH)_2+\mathbf{8}H_2$	(2)	**11.6wt%**
$\mathbf{4}NH_3+LiAlH_4 = LiAl(NH_2)_4+\mathbf{4}H_2$	(3)	**7.6wt%**

What to measure?

- Pressure increase
- Gas composition analysis
- Weight increase in solid
- Crystalline structure change
- **To fuel cell (to be done)**

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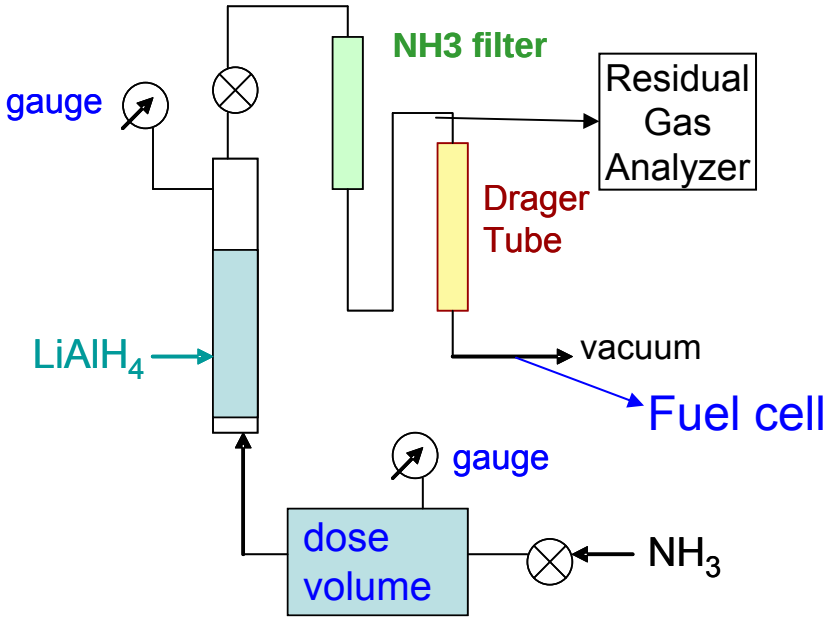
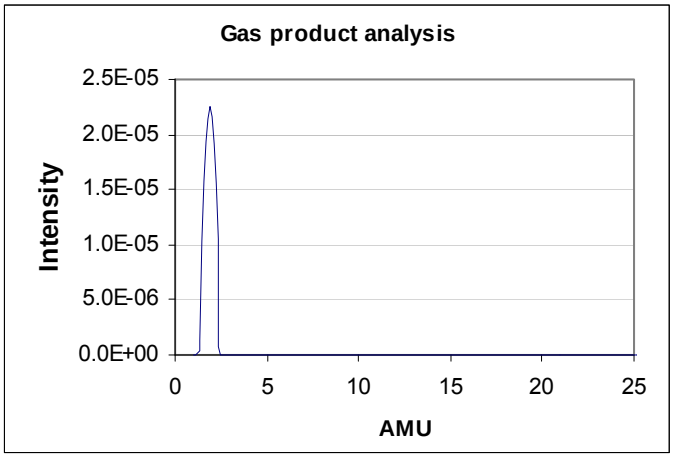
Case 1: Low Ratio of $NH_3/LiAlH_4$

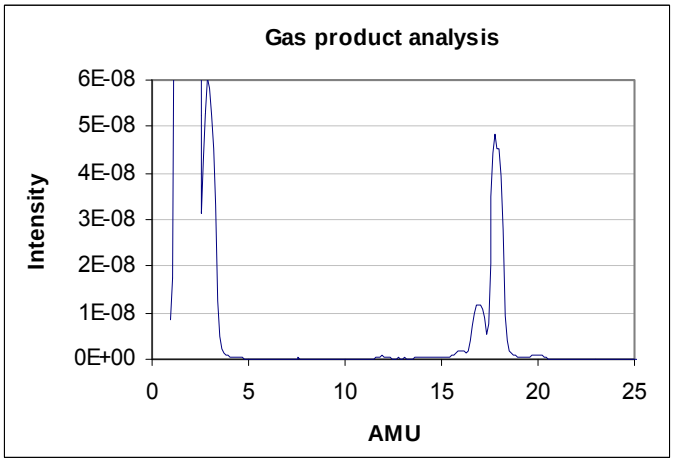
Volumetric measurement



Draeger Tube*

Gas composition analysis





Product gas: H_2 and trace H_2O

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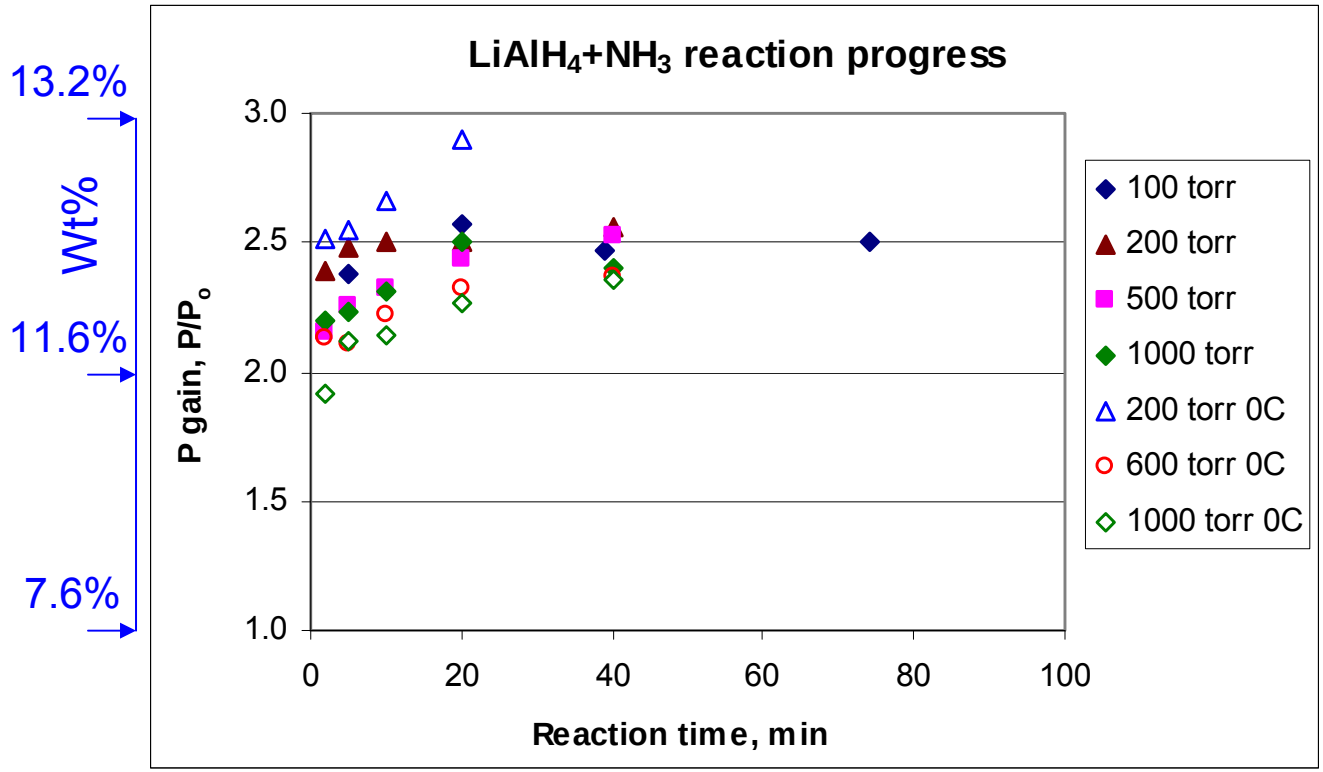
Case 1: Low Ratio of $NH_3/LiAlH_4$ (Continue-1)

The molar ratio of $LiAlH_4/NH_3$ was **60:1** (NH_3 is the sum in 30 doses)



- Reaction is fast
- Similar rates at 22 and 0C

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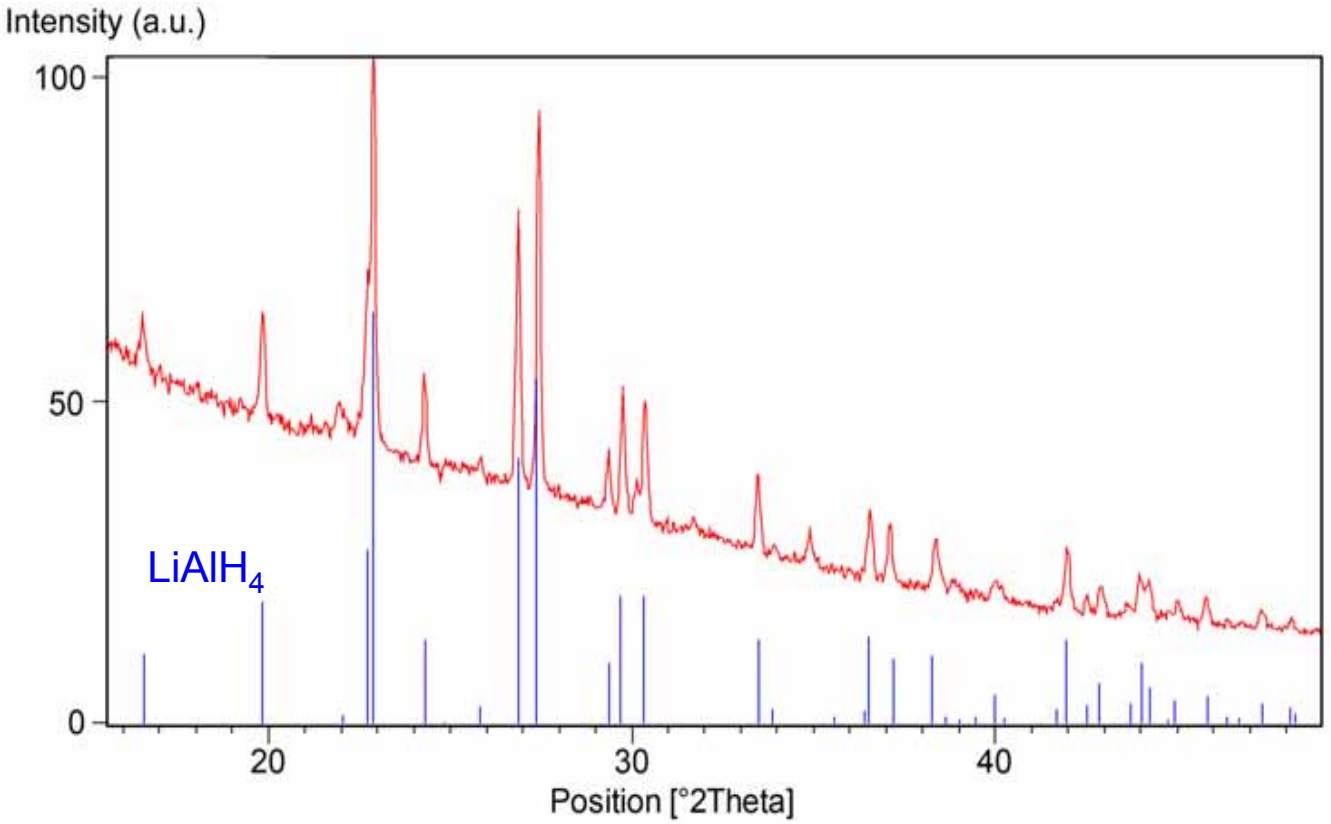
Case 1: Low Ratio of $NH_3/LiAlH_4$ (Continue-2)



Only un-reacted LiAlH4 was detected due to low conversion <2%

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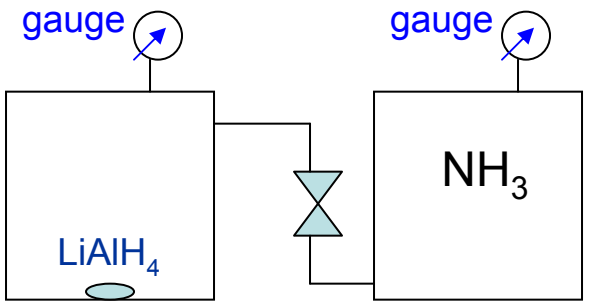
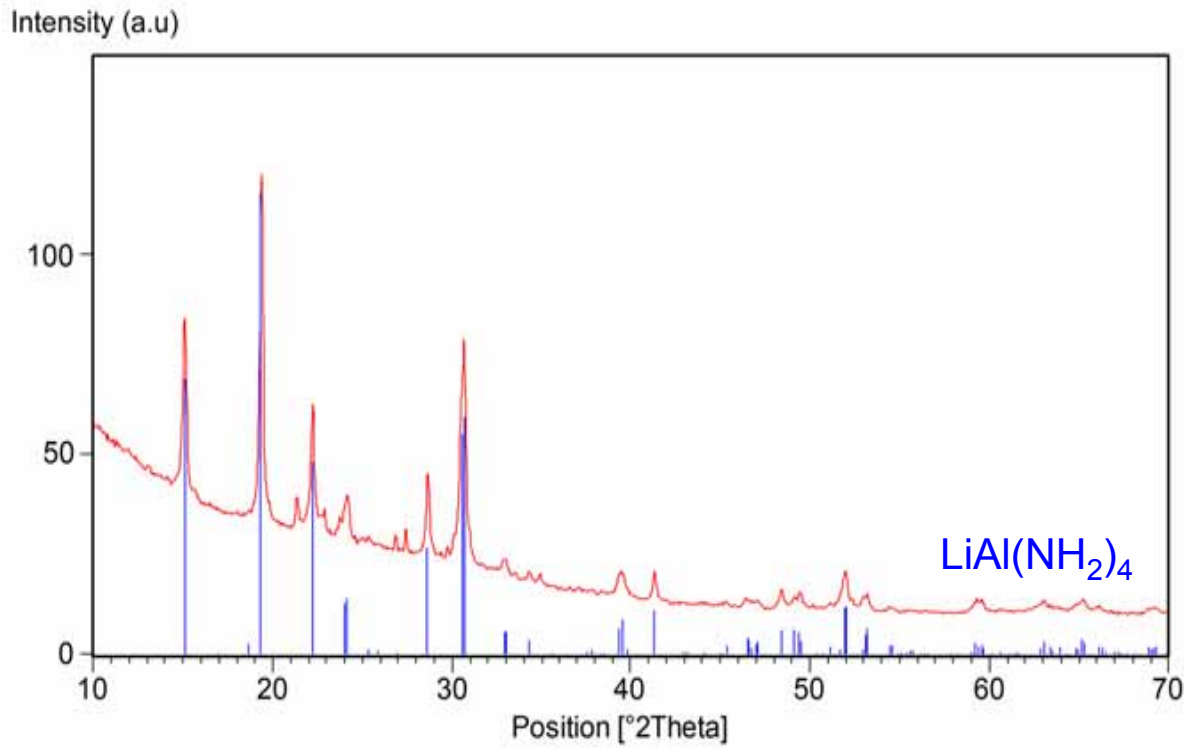
Case 2: High ratio of $NH_3/LiAlH_4$

Molar ratio of $NH_3/LiAlH_4$: **6.8:4.7**

Dose N_o	Time duration	Amount of NH_3, moles	P increase P/P_o
1	6 min	$3.41x10^{-3}$	1.62
2	4 days	$3.41x10^{-3}$	1.30





- Pressure gain: 1.3-1.62
- Structure: $LiAl(NH_2)_4$
- Solid weight gain:
  - Ininial: 0.17g
  - Final: 0.22g
  - Gain: 29%

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Conclusions

$4NH_3+3LiAlH_4 = Li_3N+3AlN+12H_2$	(1)	**13.2wt%**
$4NH_3+2LiAlH_4 = LiAl(NH)_2+8H_2$	(2)	**11.6wt%**
$4NH_3+LiAlH_4 = LiAl(NH_2)_4+4H_2$	(3)	**7.6wt%**

Generate H_2 at

- **Ambient temperature**
- **High rate**

Wish list:

- Working temperature: 25C
- Easy cold-start
- No energy consumption for H_2 release
- Low cost material
- Low cost system ✓ ?
- Easy refill ✓ ?
- Generate H_2 on demand
- Safe storage

More needs to be done:

- Reaction mechanism study
- Test with NH_3 flow-through $LiAlH_4$ bed
- Define utilization limit

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Thank you for your attention