Synthesis and Properties of Aluminum Hydride as a Hydrogen Storage Material

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– A Participant in the DOE Metal Hydride Center of Excellence –

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Washington, D.C., May 23, 2005

Project ID #
STP16

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- Percent complete: *New Project*

Budget

- Expected Total Project Funding:
  5 years: $3.00M
  - DOE Share: $2.60M
  - Contractor Share: $0.40M

  Funding for FY05:
  $200K (DOE),
  $150K (cost share BNL-LDRD)

Barriers

Hydrogen reversibility
Energy penalty of regeneration

Targets

Total system gravimetric : >8%
Total system volumetric : > 0.10 kg H_2/L
Tank operating temp: 85/95°C
Tank operating pressure: 2 bar (30 psig)

Partners

- Participant in DOE Metal-Hydride Center of Excellence; collaborations with MHCoE partners on modeling, regeneration and engineer tank design
- Coordinator of sub-team on aluminum hydride for onboard hydrogen storage systems (U. Hawaii, JPL, SRNL,U. Illinois Carnegie Mellon and SNL)

Background

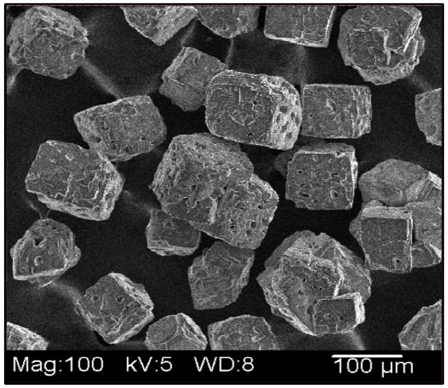
<u>Mission Statement:</u> ***To develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for on-board hydrogen storage.***

Decomposition of AlH_3

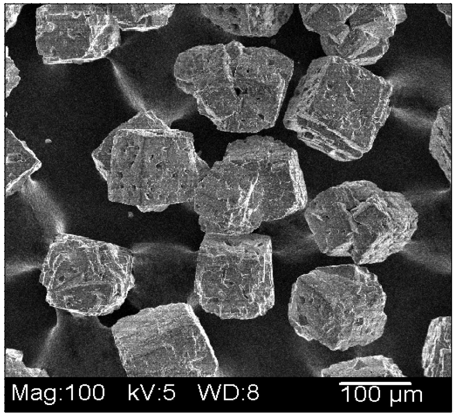
$AlH_3 \rightarrow 3/2H_2 + Al$ **(Temp. = 60° – 100° C)**

H-capacity (g) = 10.1 wt% (DOE 2010 Storage-Target = 6.0)
H-capacity (v) = 149 kg/m3 (DOE 2010 Storage-Target = 45)
ΔH_{des} = 7.6 kJ/mol H2 (only 20% of NaAlH4)

AlH_3



Depleted Al



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MHCoE Sub-Team on Aluminum Hydride

METAL HYDRIDE CENTER OF EXCELLENCE

Brookhaven

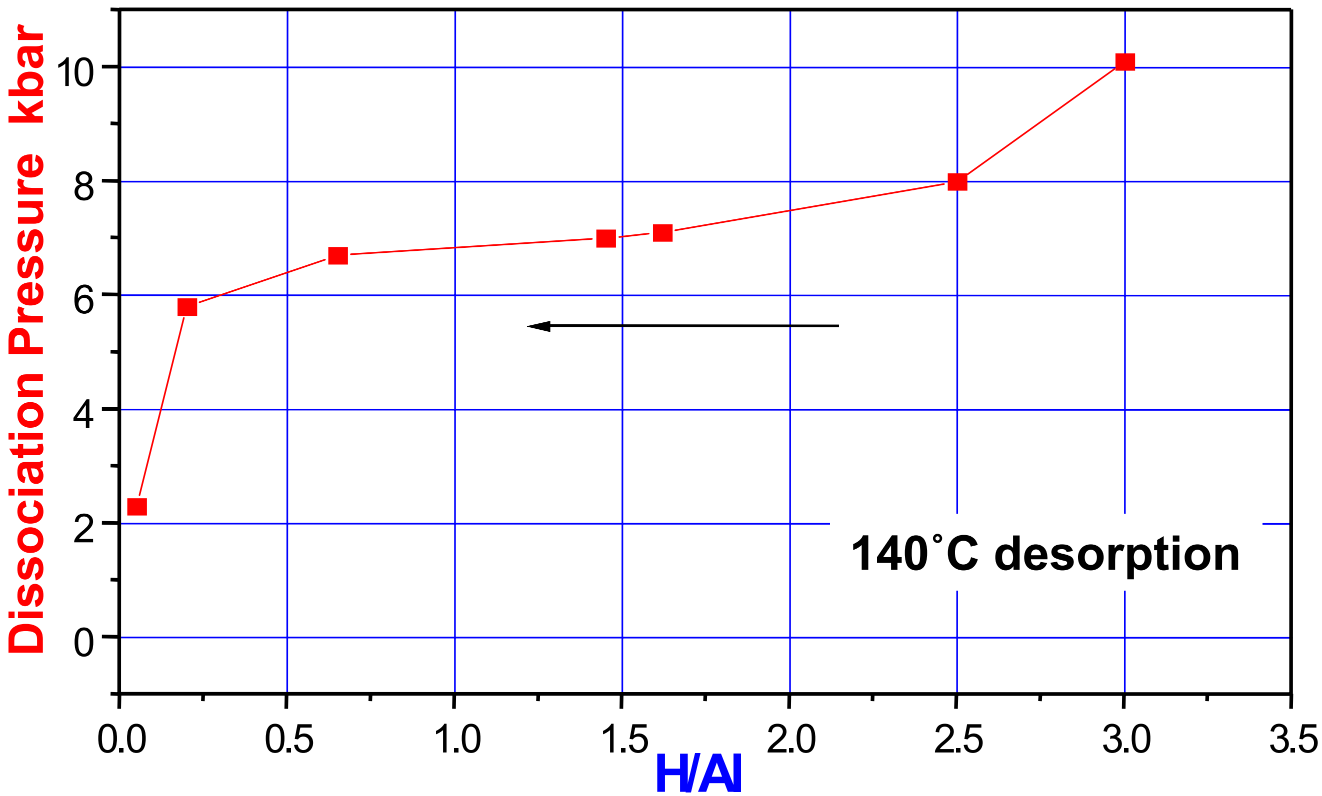
Team leader

Fundamental Understanding *Materials Development*
System Design & Engineering

- **U. Illinois & Carnegie Mellon** — ***1st principles modeling***
- **SRNL** — ***Aluminum hydride recharge development***
- **JPL** — ***Material performance, aging, kinetics &testing***
- **U. Hawaii** — ***Material synthesis & catalysis development***
- **SNL** — ***Material characterization; engineering properties***

Other partners in MHCoE will also contribute in areas of modeling, simulation and diagnostics

Thermodynamic Instability of Aluminum Hydride



Gas recharging: 28 kbar@300˚C !!

Baranowski & Tkacz, Z. Phys. Chem. NF, **135** (1983) 27

α-AlH_3 TPD Curves vs BM Time & Particle Size

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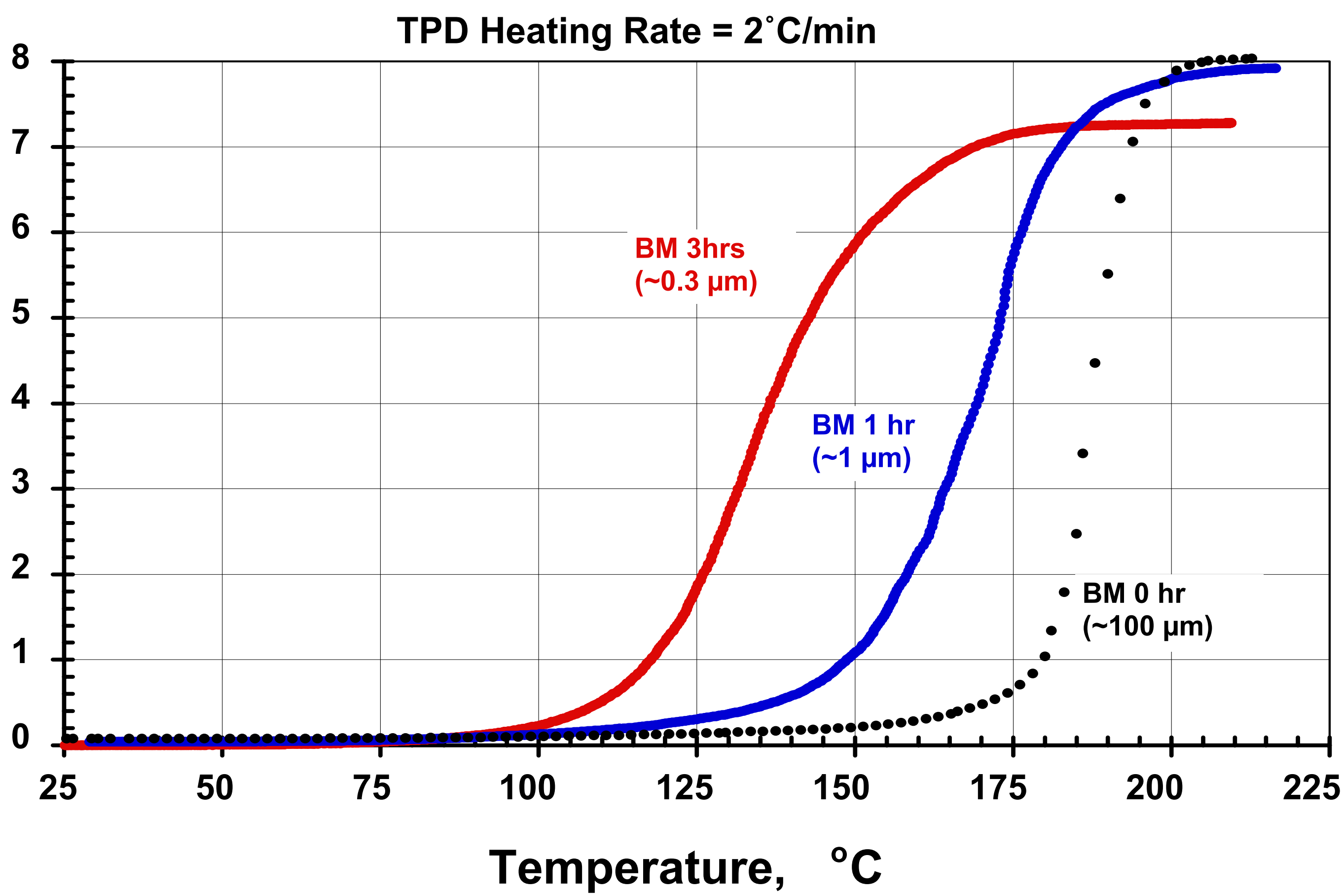
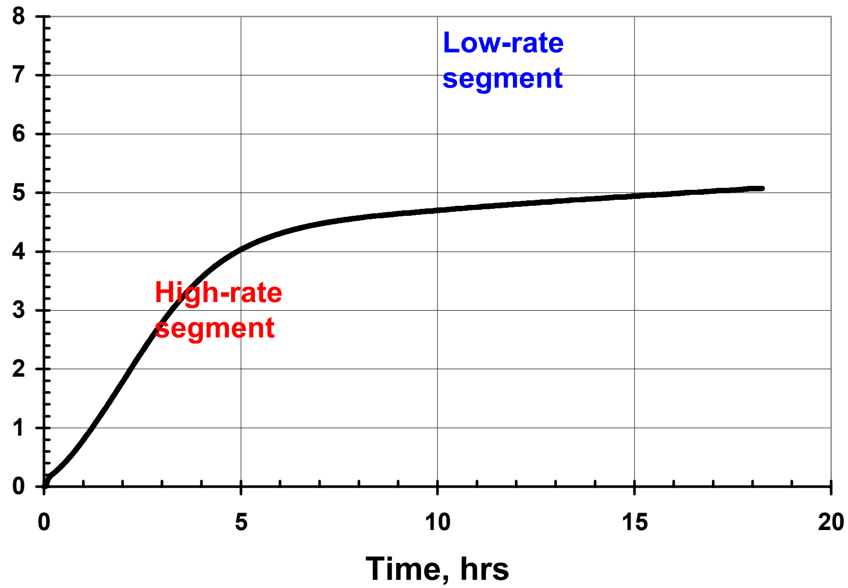


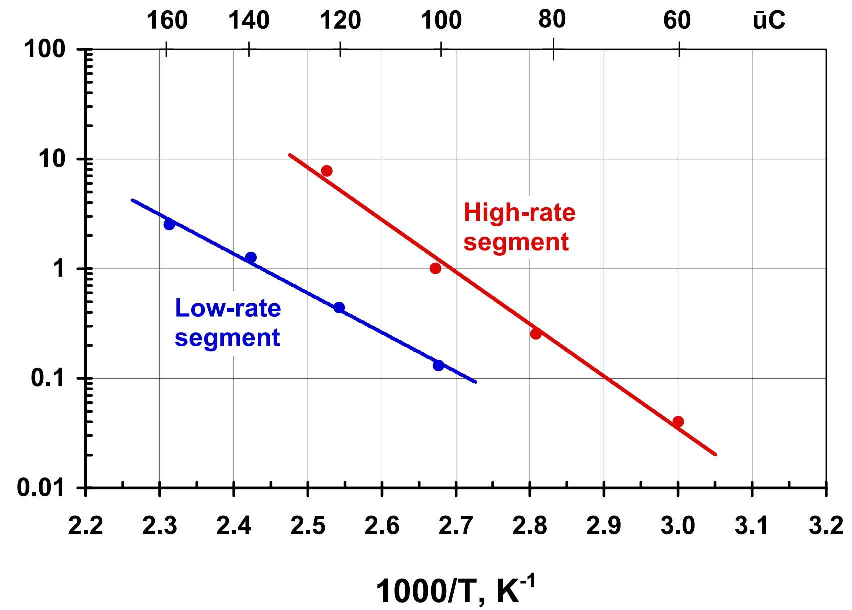
Sandrock et al, Appl. Phys. A, 80 (2005) 687-690

Isothermal Kinetics of α-AlH_3 (Dow) 20 mol% LiH

100˚C



Arrhenius PlotRate = k_0 exp (-Q/RT)



- high-rate segment: $k_0 = 6.5°*10^{12}$ and $Q = 91.3$ kJ/mol H_2
- lower-rate segment : $k_0 = 5.4°*10^{8}$ and $Q = 68.2$ kJ/mol H_2

Sandrock et al, Appl. Phys. A, 80 (2005) 687-690

AlH_3 Polymorphs

- A total of seven AlH_3 isomers are known to exist:
  - α, α', β, δ, ε, γ, ζ
- With exception of α-AlH_3, little is known about these polymorphs
- α, β, and γ phases can be grown using an organo-metallic synthesis method

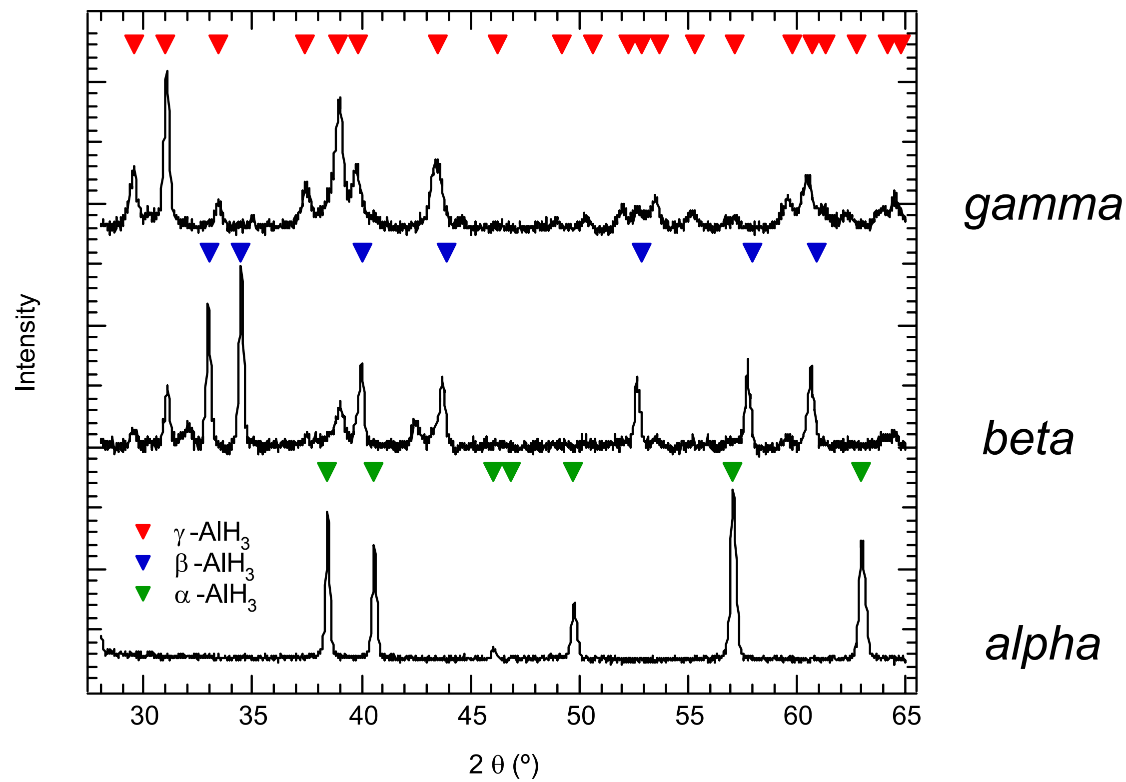
$3LiAlH_4 + AlCl_3$ + ether

↓ (filter)

$4AlH_3 + 3LiCl$ + ether

↓ (remove ether)

$4AlH_3$



AlH_3 Synthesis

- Ethereal reaction of $AlCl_3$ and $LiAlH_4$ yields solvated AlH_3
- Solvent removed by adding excess $LiAlH_4$ and heating at 60-70° C

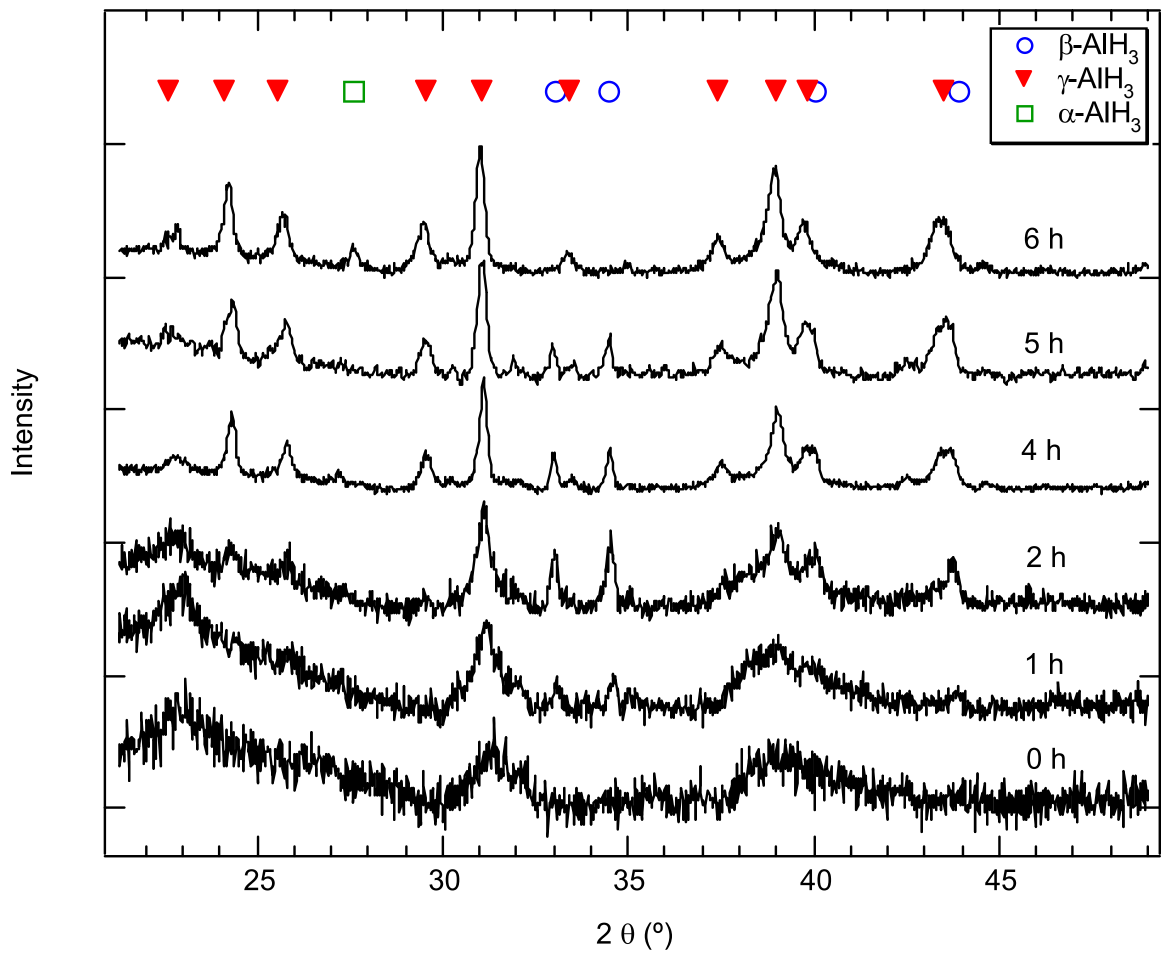
α-AlH_3

↑

β-AlH_3 + γ-AlH_3

↑

Solvated AlH_3 etherate



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Isothermal Decomposition of AlH_3

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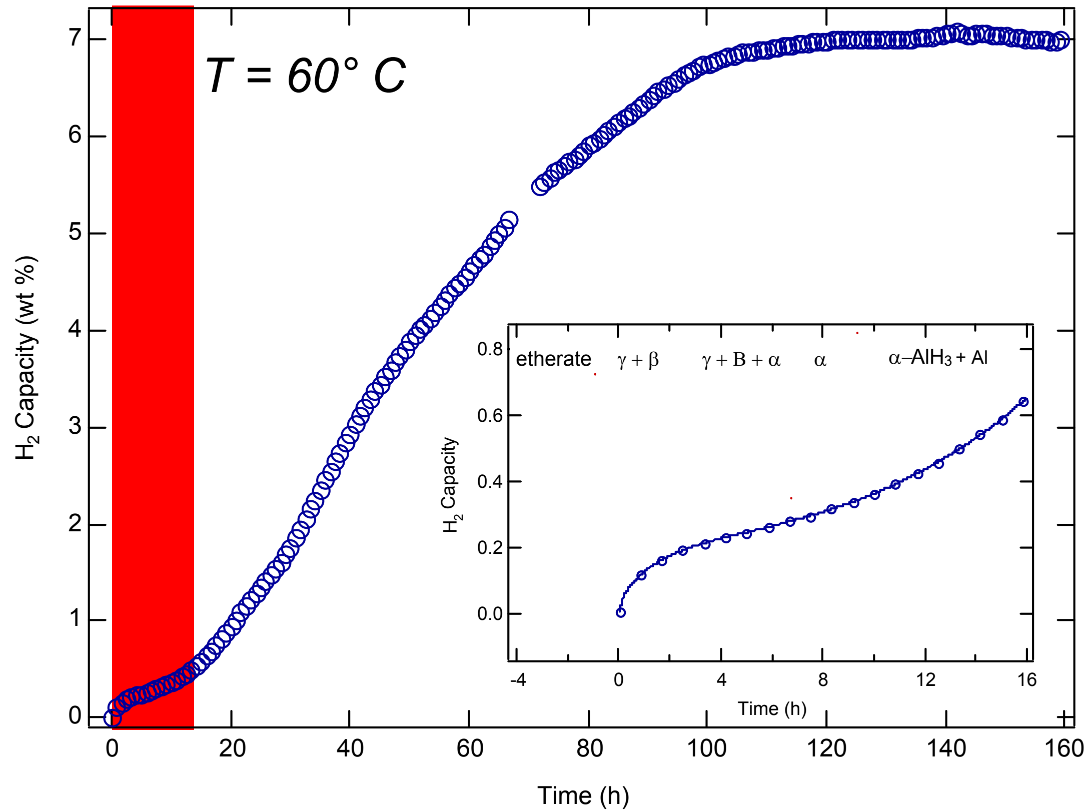
- Desolvated AlH_3 undergoes a number of phase transitions at 60° C

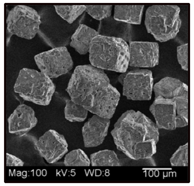
AlH_3 etherate → β + γ → α → Al

- Transformations occur with little/no H_2 evolution
- AlH_3 decomposition note induction period ~10 h at 60° C



γ–AlH3 and β-AlH3 <u>do not</u> appear to decompose directly to Al and H_2 at 60° C, rather, a transformation to a more stable polymorph (α-AlH_3) occurs first. α-AlH_3 then undergoes complete decomposition to the elements at 60° C (t~100 h).

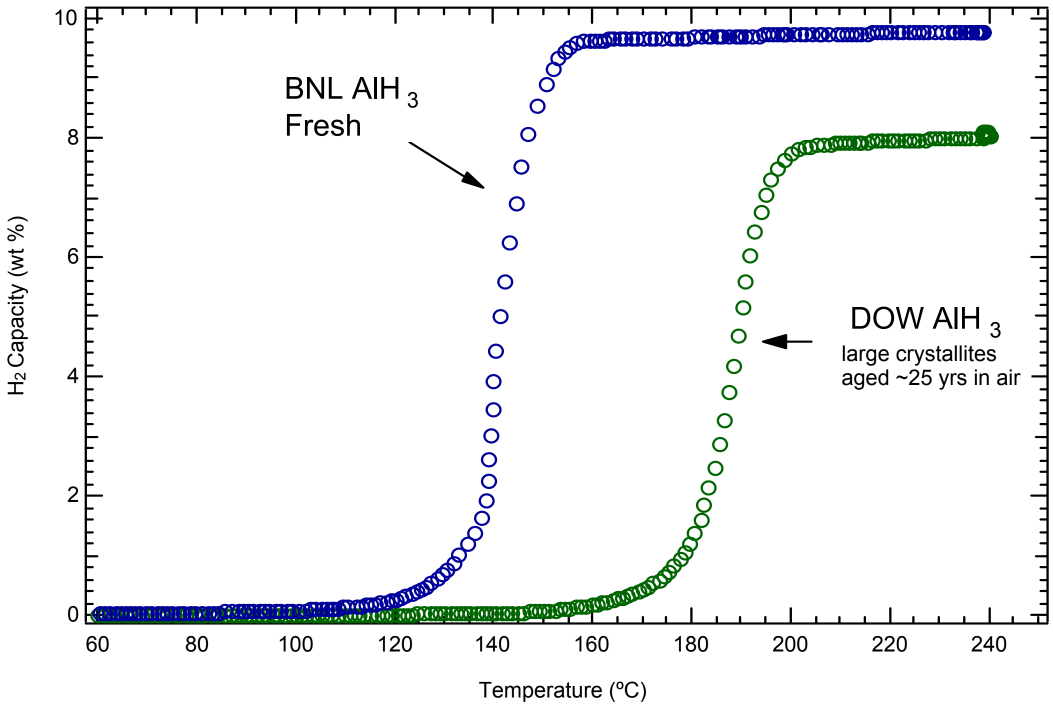
Temperature Programmed Decomposition



- αAlH_3 synthesized by DOW Chem. Co. composed of large crystallites (50 - 100 µm) aged 25 yrs in air:
  - measure hydrogen capacity 8 wt%
  - onset of rapid H2 evolution occurs at 160° C

?

- BNL synthesized AlH_3
  - measured hydrogen capacity ~10 wt%
  - onset of rapid H_2 evolution occurs at 120° C

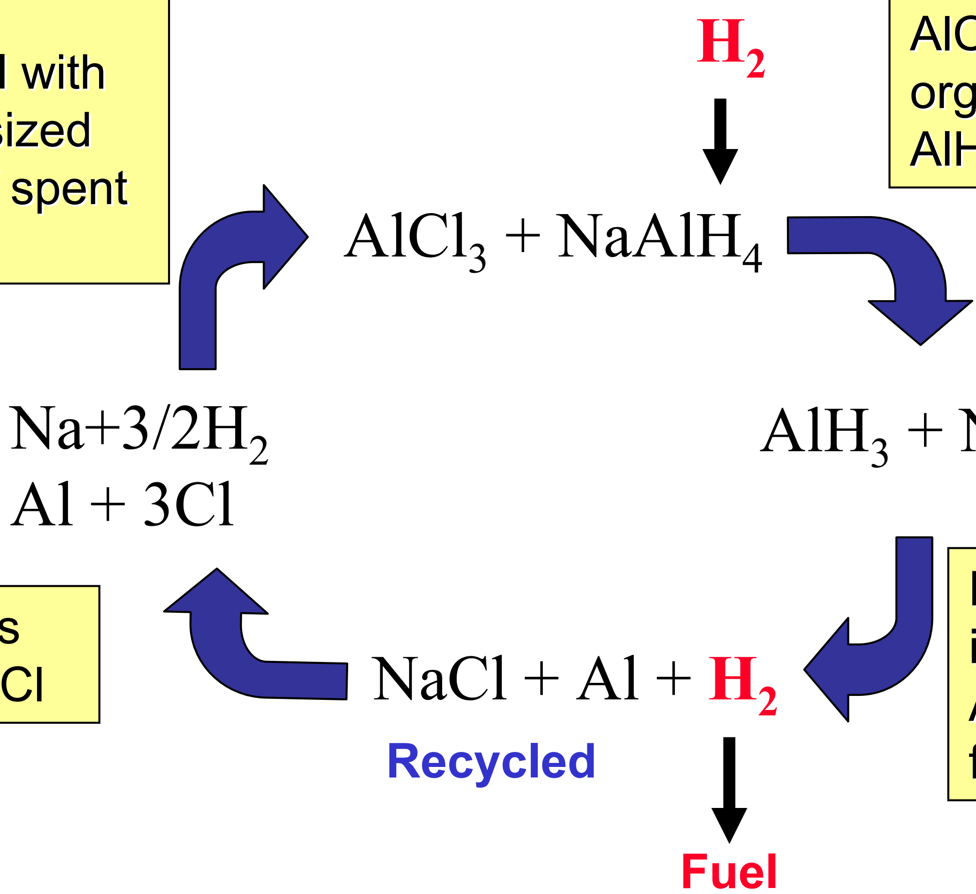


Reversible AlH_3

- AlH_3 may be regenerated from recovered products after hydrogen fuel is spent

$AlCl_3$ prepared by reaction of spent Al with Cl. $NaAlH_4$ synthesized through reaction of spent Al with NaH + H_2

$AlCl_3$ and $NaAlH_4$ in organic solvent yields AlH_3 and NaCl

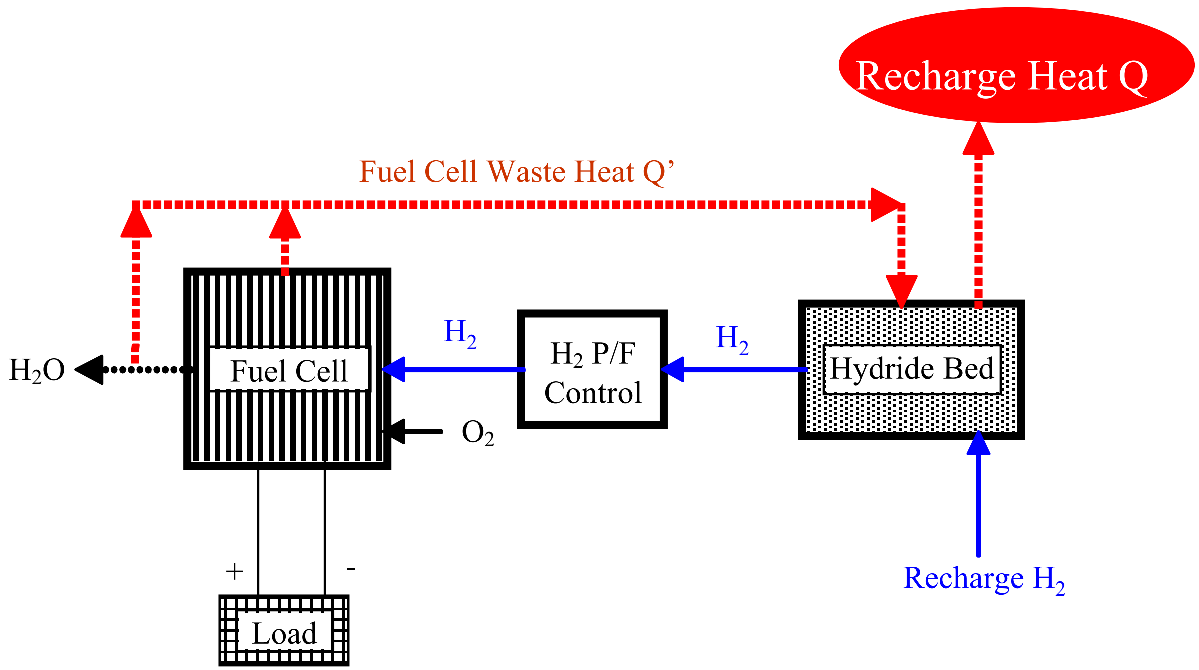


NaCl electrolysis to give Na and Cl

NaCl recovered from initial reaction
Al recovered after H_2 fuel is exhausted

Note: system is "reversible" since all products are recovered and re-used (except hydrogen).

Onboard Recharging
Problem with Conventional Hydrides



How much heat must be removed during recharging?

DOE 2010 Target = 3 min = 1.67 kg/min (5 kg H_2 tank)

Take as example $NaAlH_4$ (ΔH = -37 kJ/mol H_2)

dQ/dt = 510 kw or Q total = 91.8MJ !! ⇒ Offboard recharge required

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Milestones/Decision Points

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Deliverables:

- 10 gm. AlH_3 samples to SwRI; 8% or better by wt. @ 150°C; FY 06
- 10 gm. AlH_3 samples to SwRI; 9% or better by wt. @ 85/95°C; FY07
- 1000 gm AlH_3 samples to SNL for fuel tank development and testing; FY 08

Decision Points:

- selection of either direct or chemical method of regeneration; FY 06
- selection of additives and optimum particle size for AlH_3; FY 07
- selection of tank refueling method; FY 08

Go/No-Go:

- on the direct onboard re-hydriding of spent aluminum powder; FY 06

Milestones

- complete stability and shelve life studies on AlH_3; FY 07
- complete thermal management studies on the control release of H_2; FY 08
- selection of method for regenerating AlH_3; FY 09

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Summary of Program Plans

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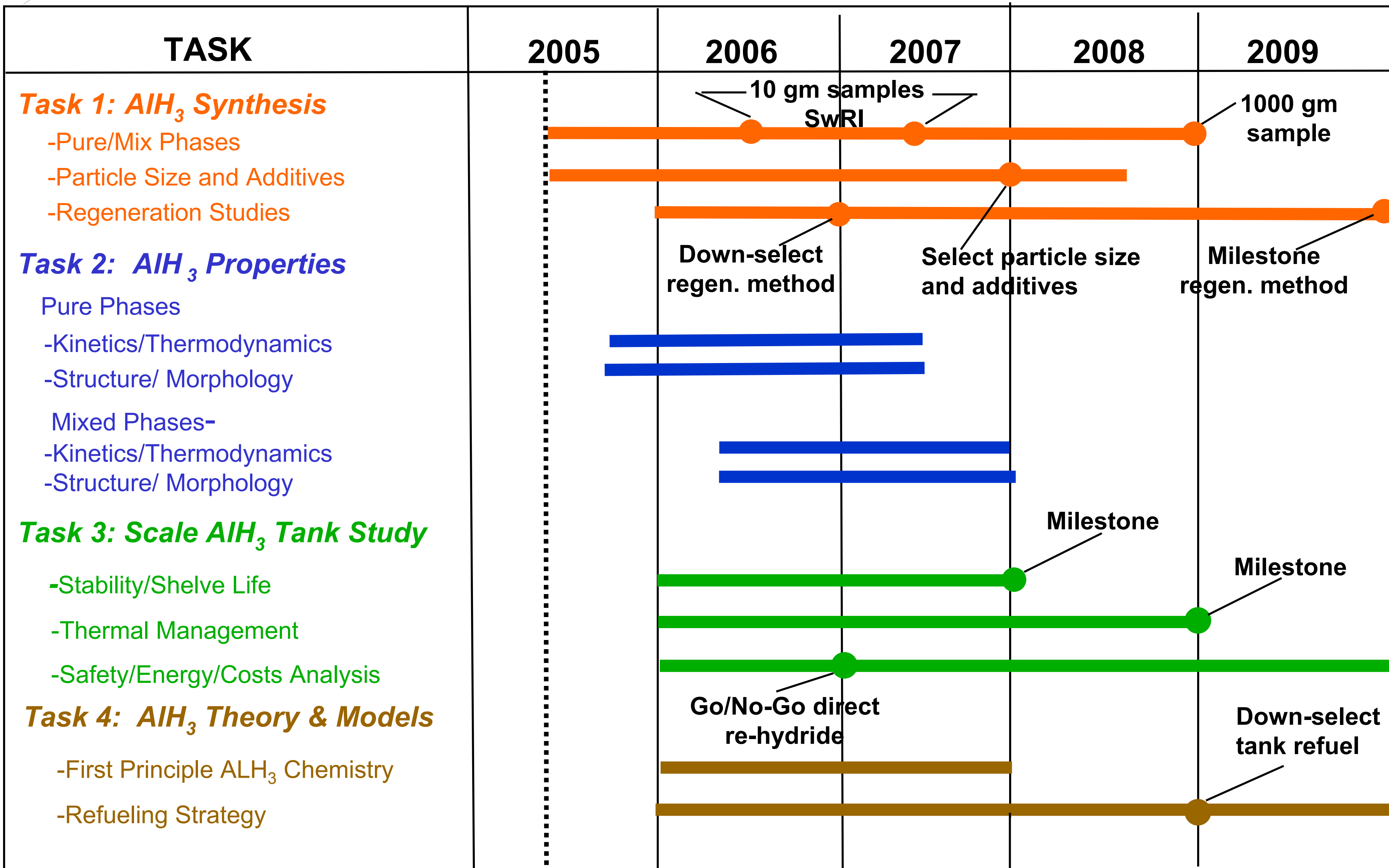

α-AlH_3 Conclusions

1. AlH_3 is a promising H_2 fuel source for a PEM fuel cell due to the high gravimetric/volumetric hydrogen capacity and the low heat required to extract H_2 (7.6 kJ/mol H_2).
2. Doping aged AlH_3 (DOW) with LiH, NaH or KH increases low-temperature decomposition kinetics.
3. α, β and γ AlH_3 have been synthesized at BNL using organo-metallic methods
4. Hydrogen capacities approaching 10 wt% at T < 100º C have been demonstrated with freshly prepared AlH_3
5. Recharging of spent Al back to AlH_3 likely to be done with an offboard process yet to be developed.