THE POTENTIAL OF ALUMINUM HYDRIDE FOR VEHICULAR HYDROGEN STORAGE

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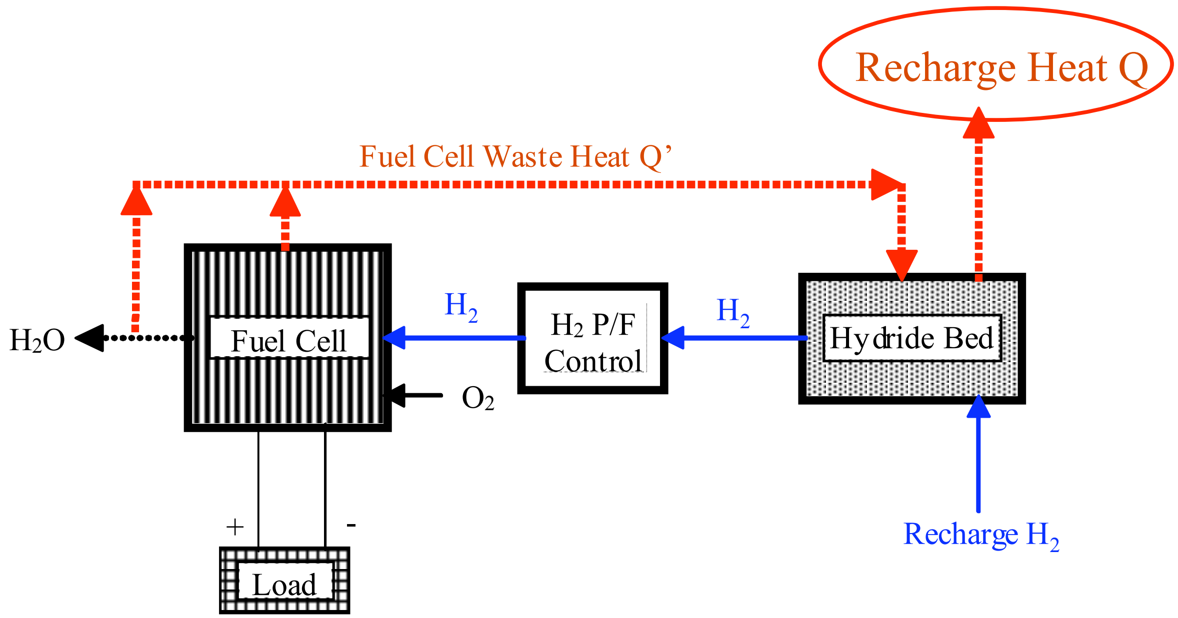
Onboard Recharging - The Heat Problem!



How much heat must be removed during recharging?

DOE 2010 Target = 3 min = 1.7 kg/min (5 kg H_2 tank)

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

Q total = 91.8MJ = 510 kw for 3 min $\Rightarrow$ Offboard recharging required??

Aluminum Hydride AlH_3

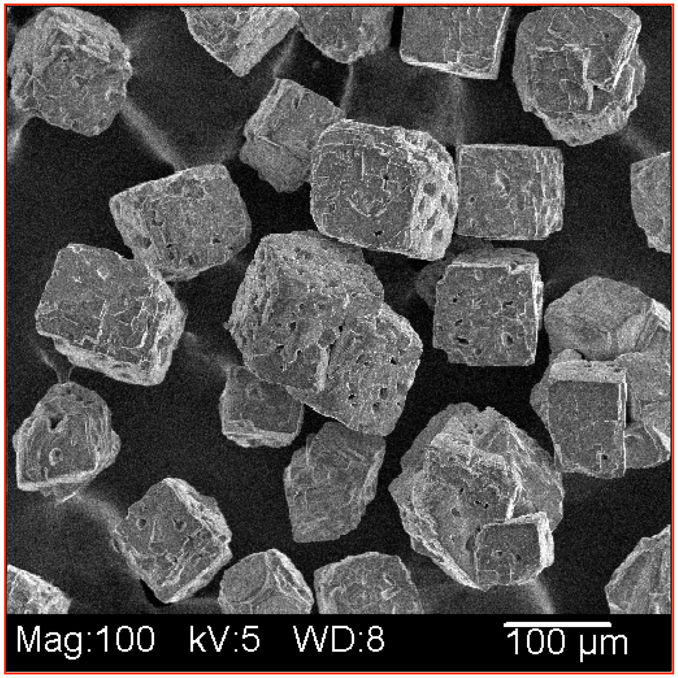
$$\alpha\text{-}AlH_3 \longrightarrow Al + 3/2\ H_2$$

H-capacity (g) = 10.1 wt% (DOE 2010 S-Target = 6.0)

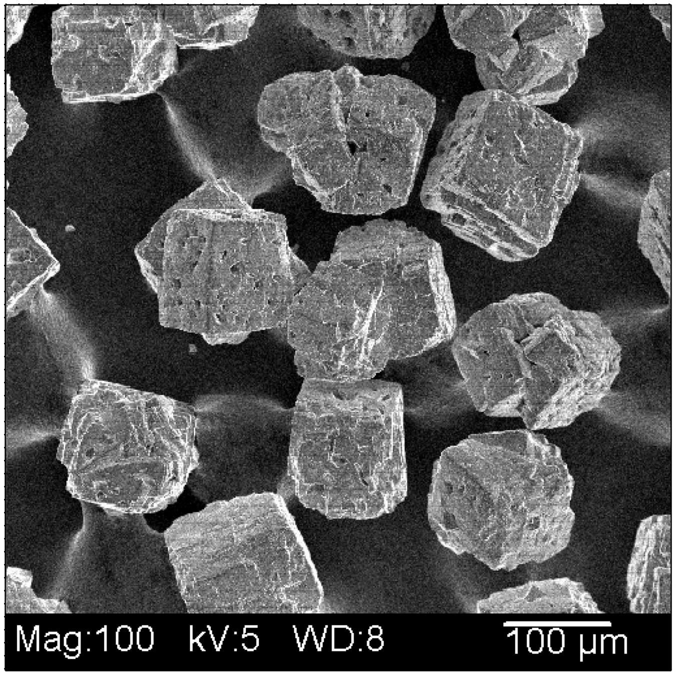
H-capacity (v) = 149 kg/m^3 (DOE 2010 S-Target = 45)

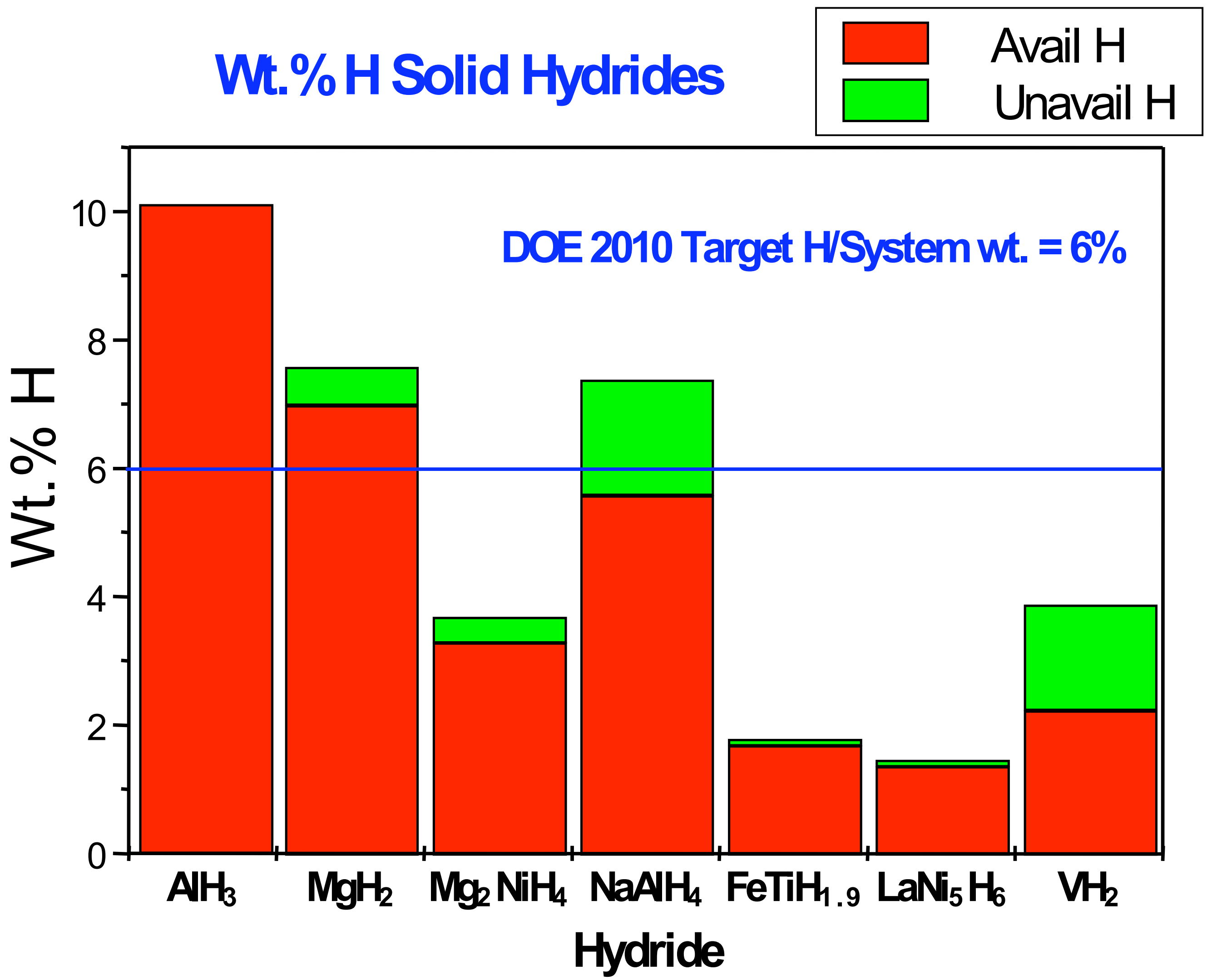
ΔH_{des} = 7.6 kJ/mol H_2 (only 20% of $NaAlH_4$)

AlH_3



Depleted Al





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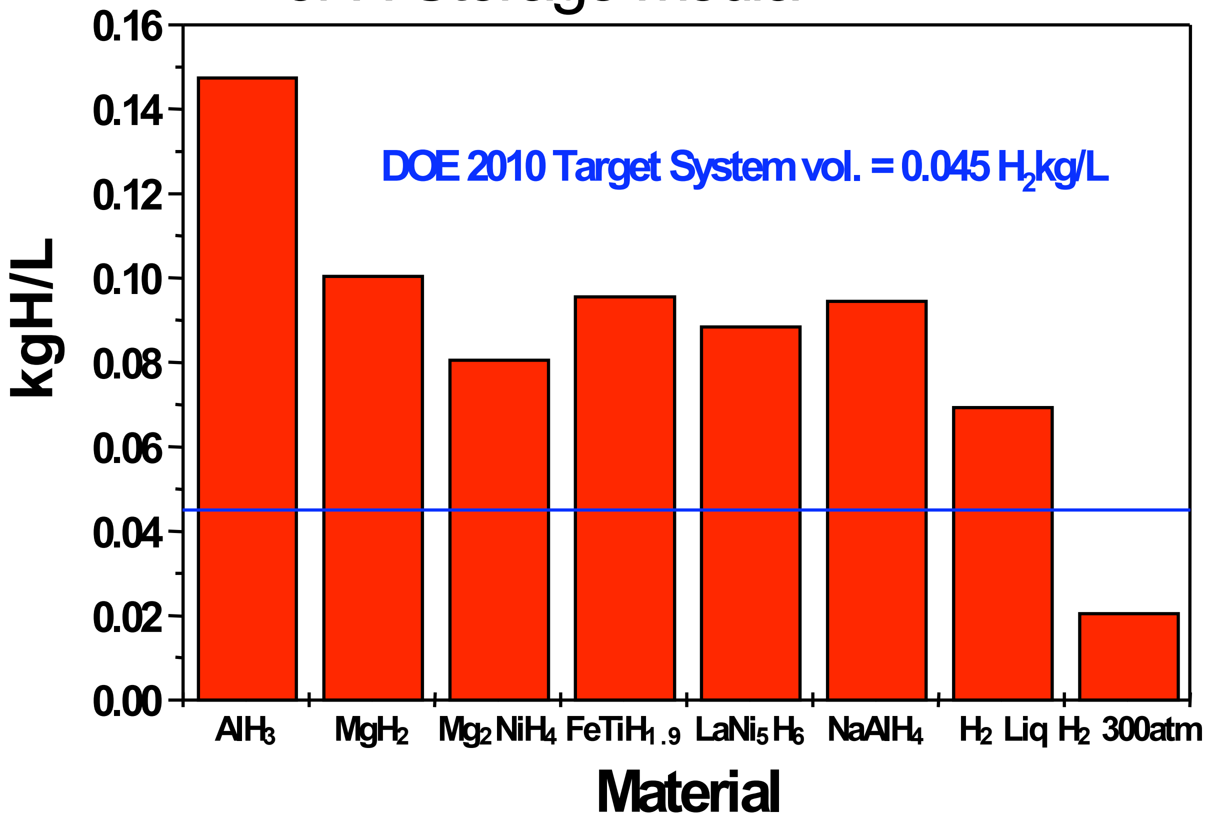
Volumetric Densities of H Storage Media



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Preparation of AlH_3

$$3LiAlH_4 + AlCl_3 \xrightarrow[\text{ether}]{} 4AlH_3 \downarrow + 3LiCl$$

Finholt , E.A. et al. J.Am. Chem. Soc. 69,1199(1947)

Note: There are 7 different non-solvated phases of AlH_3, α, α', β, γ, δ, ε, ζ.

F. M Brower, et al. J. Am. Chem. Soc., 98:9, April 28 1976.

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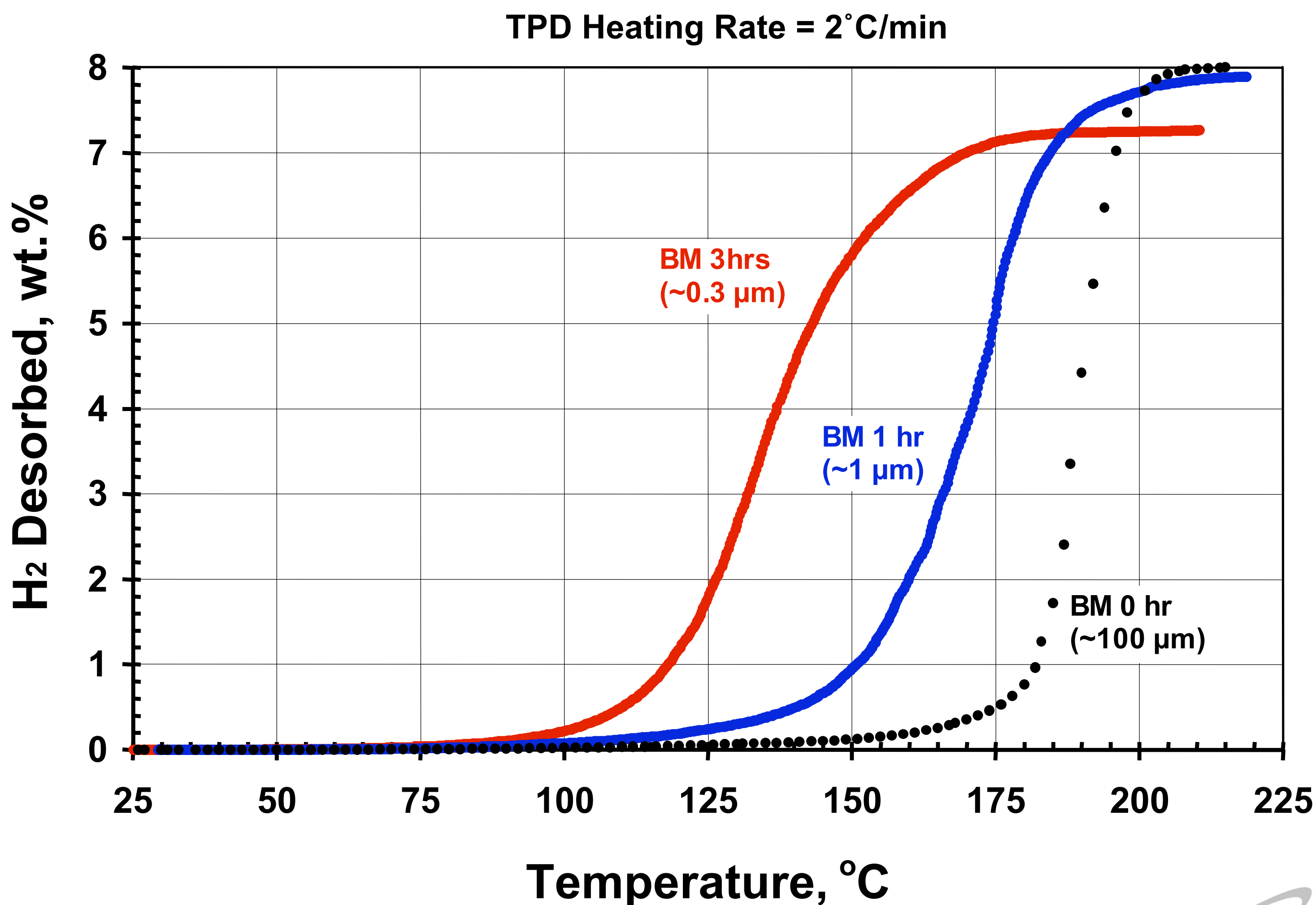
α-AlH_3 TPD Curves vs BM Time (Particle Size)



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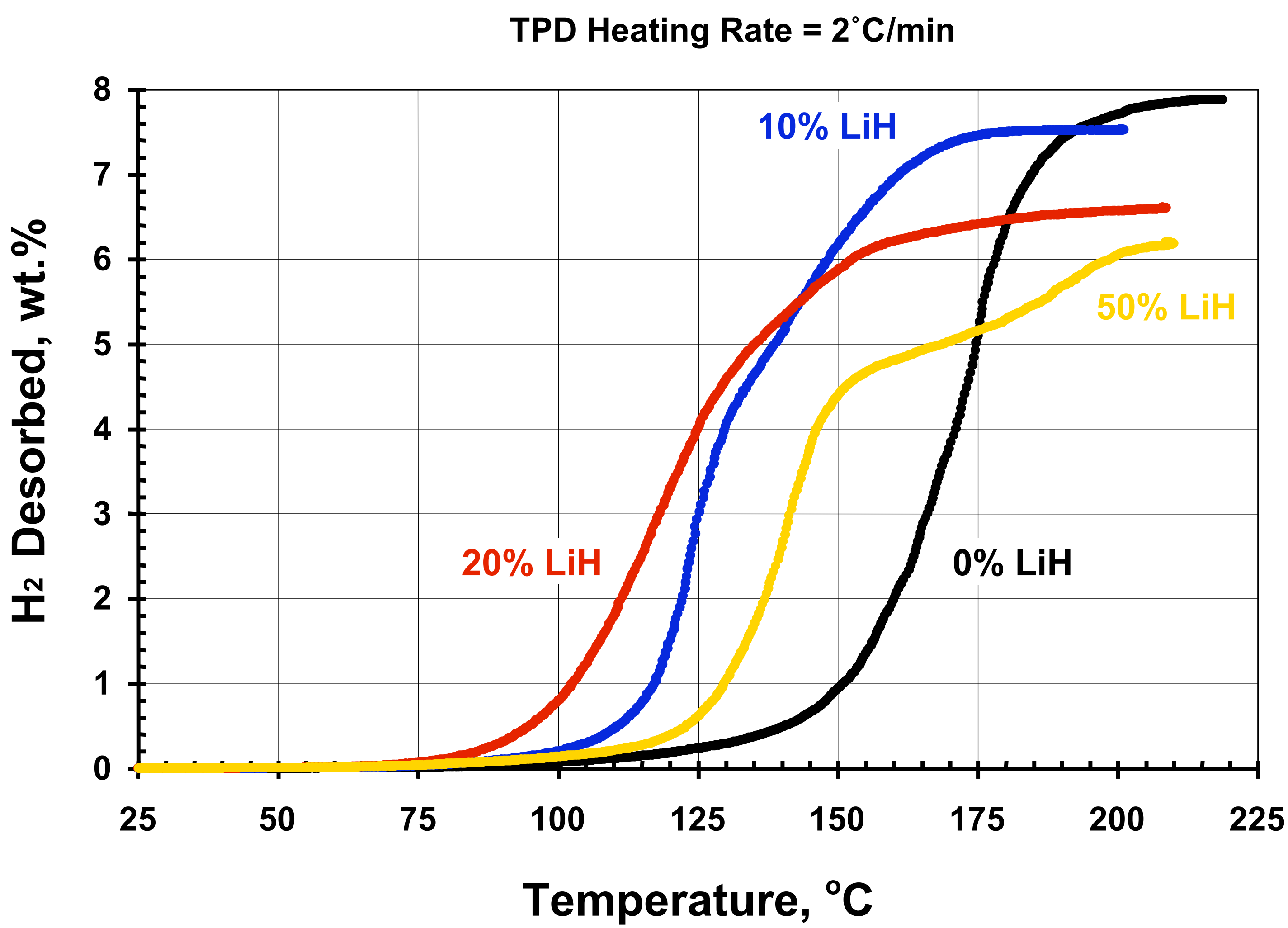
Effect of LiH Doping on AlH_3 TPD



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

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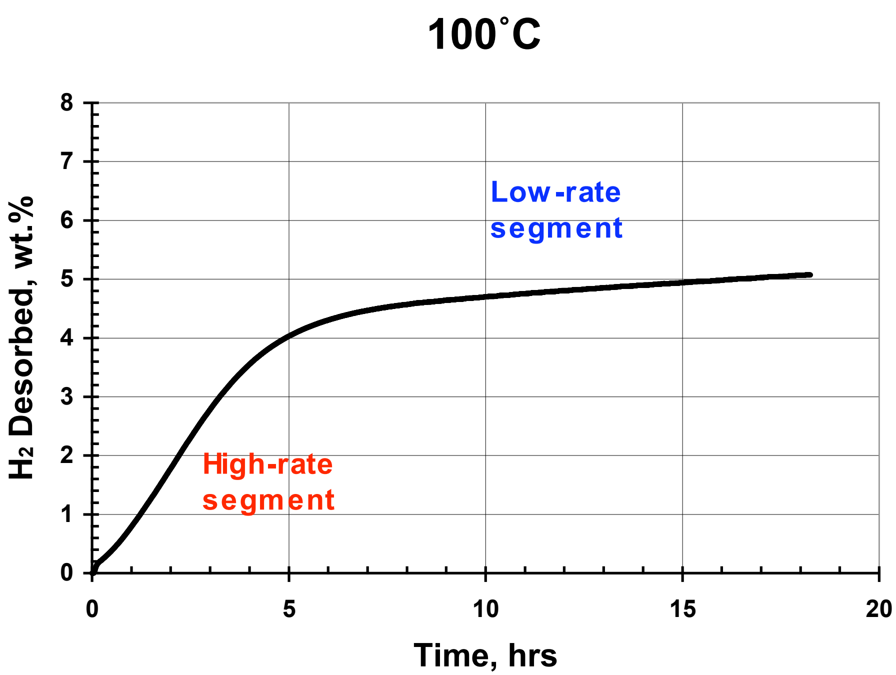
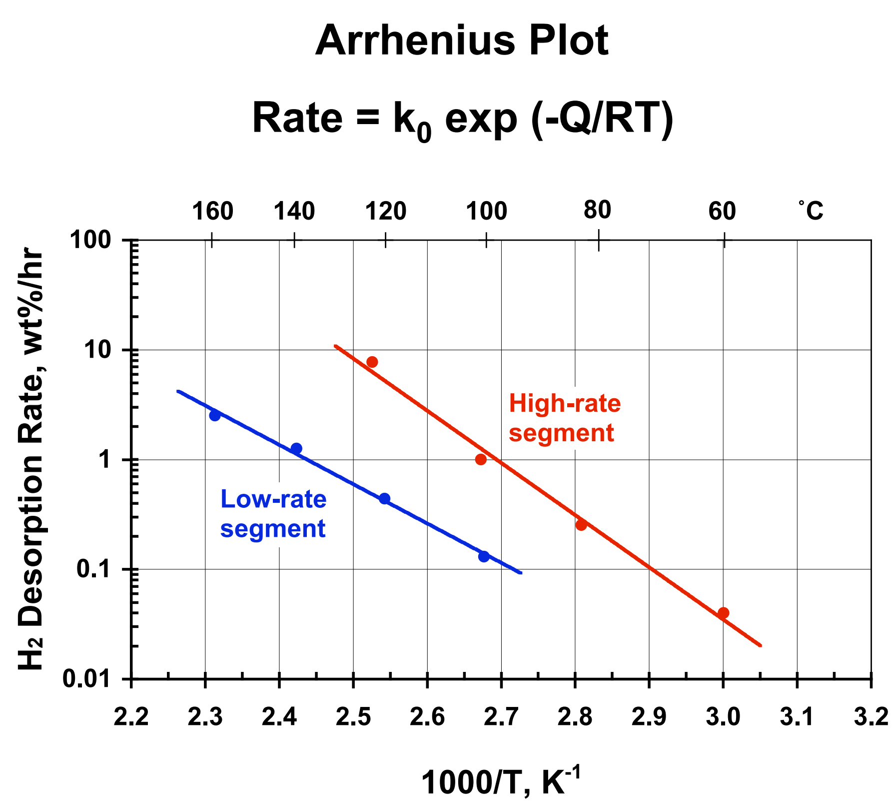
Isothermal Kinetics of AlH_3 - 20 mol% LiH





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

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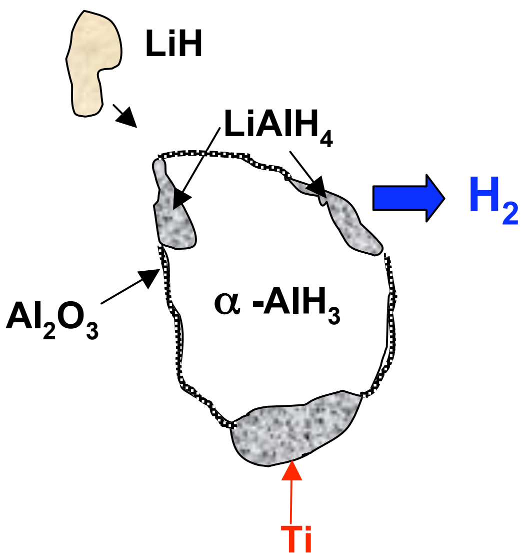
Likely Mechanisms of Doping

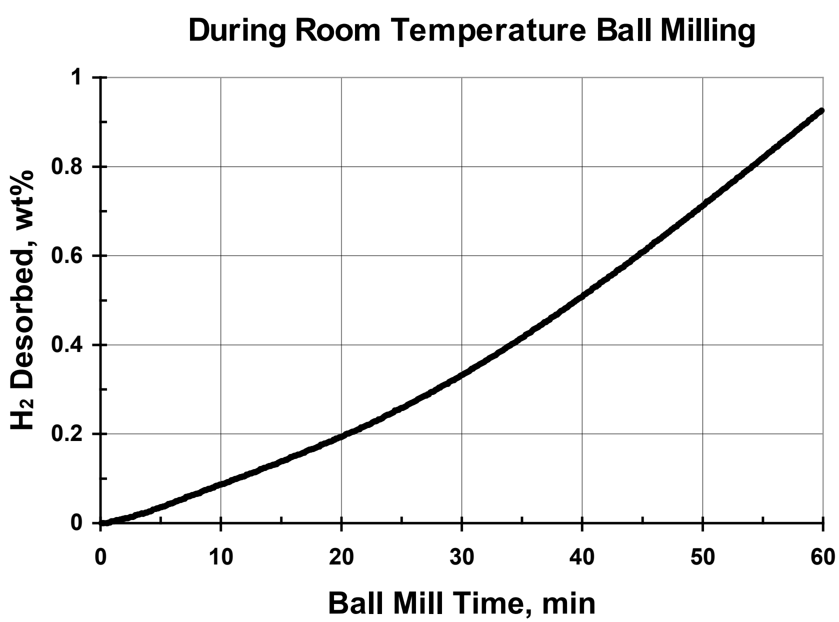


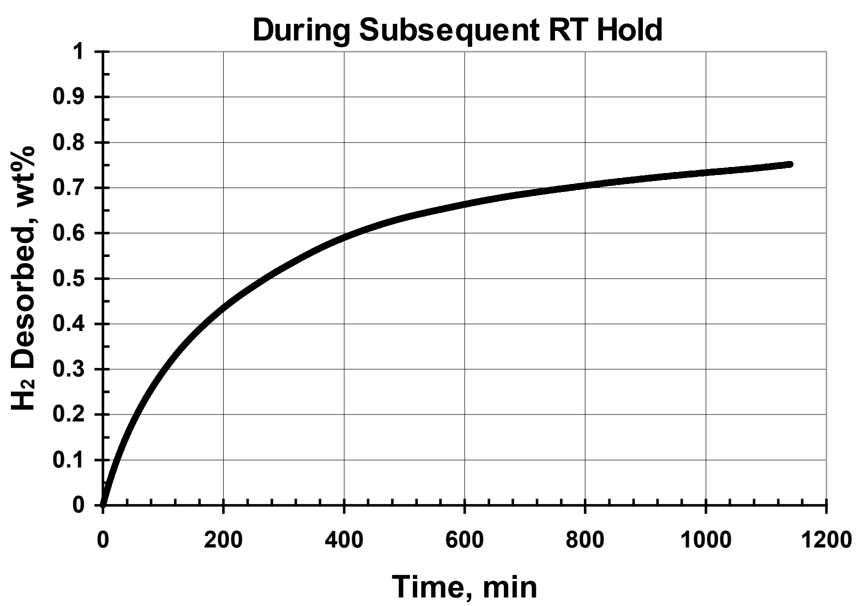
Likely Mechanisms:

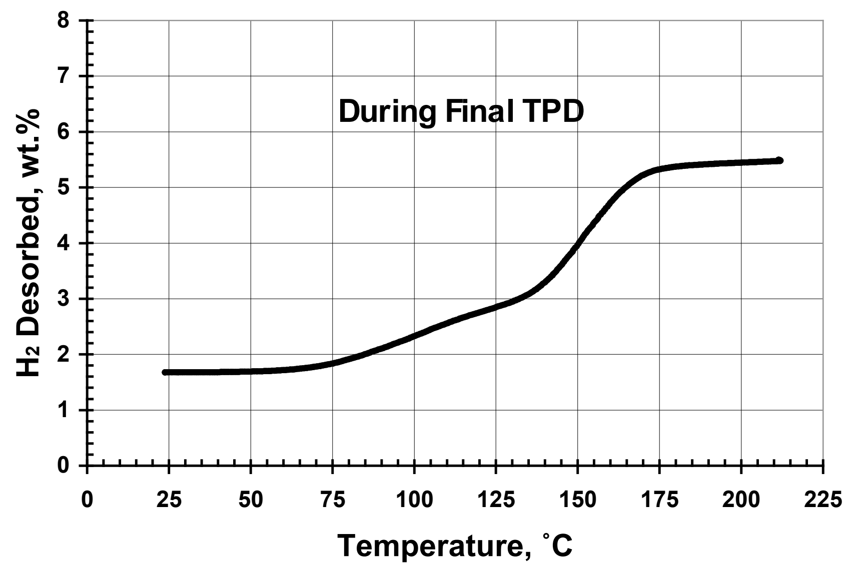
1. $LiH+AlH_3 \Rightarrow LiAlH_4$ during BM at RT (shown by contrast XRD with NaH doping)
2. $LiAlH_4$ serves as windows for H_2 egress from AlH_3
3. Also works with NaH & KH doping to form $NaAlH_4$ & $KAlH_4$ islands on surface
4. Can further dope $LiAlH_4$ with Ti by standard $TiCl_3$ alanate process, further enhancing H_2 transparancy

Room Temperature H_2-Desorption of Ti-doped Sample

$75\%AlH_3$-$20\%LiH$-$5\%TiCl_3$ (mol%)







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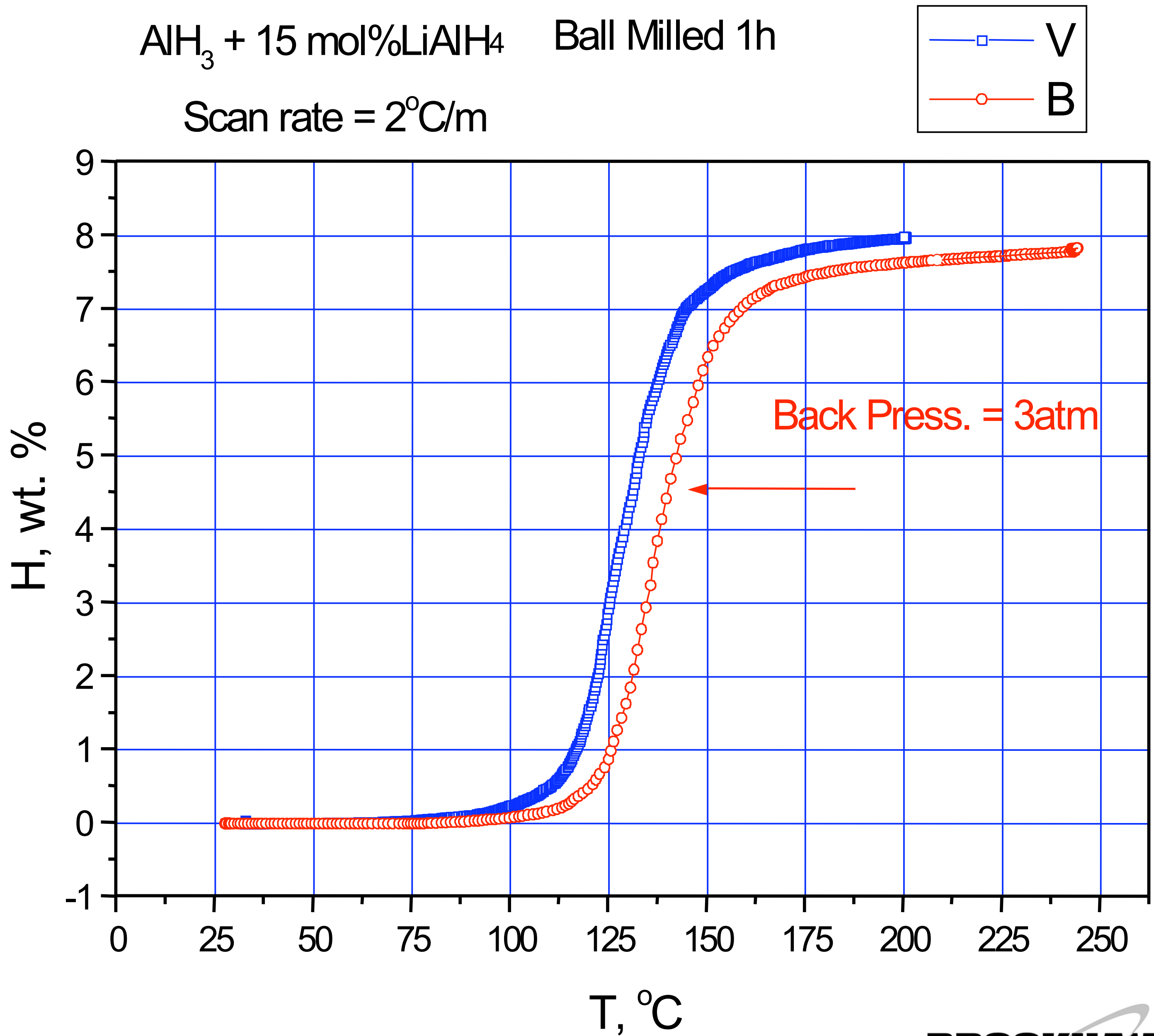

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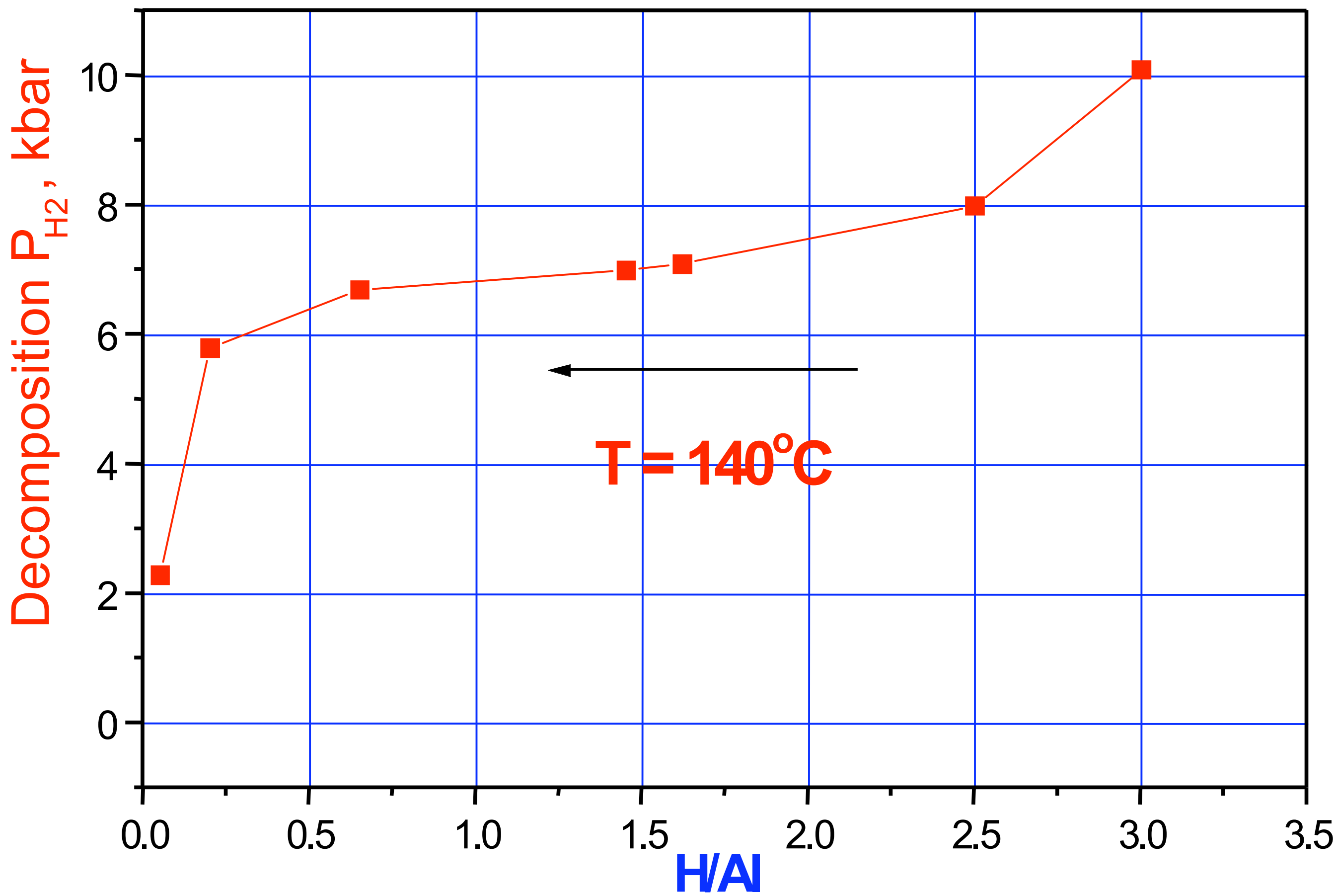
Equil. Disociation Pressure of α AlH_3



Direct H_2 gas recharging: 28 kbar@300˚C !!

Baranowski & Tkacz, Z. Phys.Phs. Chem. N.F., Bd. 135, 27(1983)

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Safety - Some Pyrophoricity

Composition	As Ball Milled	Ball Milled & Dehydrided
AlH_3	Not pyrophoric	Not pyrophoric
AlH_3+20%LiH	Not pyrophoric	Pyrophoric
AlH_3+20%LiH+ 5%$TiCl_3$	? (not tested)	? (not tested)

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– **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 synthesized using organo-metallic reactions**

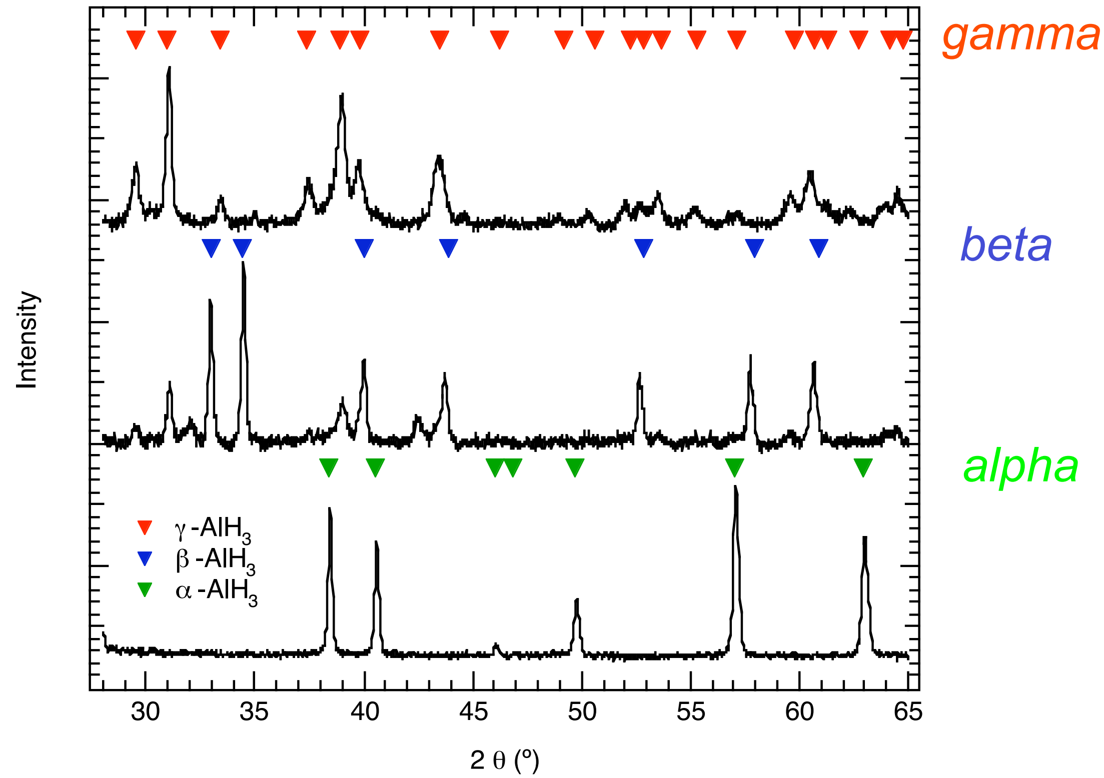
$3LiAlH_4$ + $AlCl_3$ + ether

↓

$4AlH_3$ + $3LiCl$ + ether

↓ Filter and dry

$4AlH_3$



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AlH_3 Conclusions

1. At this time no known reversible metal hydrides will likely meet the DOE 2010 systems criteria for automotive H storage at T < 100˚C.
2. Heat dissipation will be a major problem for onboard recharging. Need to rethink the possibility of offboard recharging.
3. 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.
4. Doping aged α-AlH_3 (DOW) with LiH, NaH or KH increases low-temperature decomposition kinetics. Finite room temperature kinetics can be accomplished with further Ti doping.
5. α, β and γ AlH_3 have been synthesized at BNL using organo-metallic methods.
6. Hydrogen capacities approaching 10 wt% at T < 100º C have been demonstrated with freshly prepared AlH_3.
7. Recharging of spent Al back to AlH_3 likely to be done with an offboard process.

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Collaborations

Brookhaven National Lab collaborates with the following US organizations within the US DOE Metal Hydride Center of Excellence:

Sandia National Laboratories

University of Hawaii

Savannah River National Laboratory

NASA Jet Propulsion Laboratory

HRL Laboratories

International collaborations to be determined.