

Synthesis and Characterization of Alanes for Automotive Applications

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(~1.5 FTEs funded in FY06)

BROOKHAVEN
NATIONAL LABORATORY

Part of the DOE Metal Hydride Center of Excellence

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Project ID
#ST 15

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- 20 % complete

Budget

- Expected total project funding:
 - \$3.00M (DOE)
- Funding received in FY05
 - 200K (DOE)
- Funding for FY06:
 - \$400K (DOE)

Barriers

- MYPP Section 3.3.4.2.1 On-Board Storage Barriers
- A. Weight & Volume
 - B. Cost
 - C. Efficiency
 - D. Durability/Operability
 - E. Charge/Discharge Rates
 - R. Regeneration Processes

Partners

- Coordinator of sub-team on aluminum hydride
 - JPL, U. Hawaii, U. Nevada, Savannah River, Sandia



Objectives

Understand the strengths/weaknesses of using AlH_3 as a storage medium by quantifying the reaction kinetics, thermodynamics, and energy requirements for regeneration

Synthesis (FY05-06): Synthesize 3 polymorphs of AlH_3 (α , β and γ) with material capacities $\geq 8\%$ $\text{kg-H}_2/\text{kg}$ (grav.) and ≥ 0.10 $\text{kg-H}_2/\text{L}$ (vol.)

Thermodynamics (FY06): Identify AlH_3 polymorphs with suitable H_2 pressures at temperatures near the operating temperature of a PEM fuel cell ($\sim 85^\circ \text{C}$)

Determine if AlH_3 can be formed by direct high-pressure hydrogenation of Al powder at pressures $< 10^3$ bar (Go/NoGo decision in FY06)

Kinetics (FY06): Identify AlH_3 phases with decomposition kinetics that meet DOE hydrogen “full flow” target of $0.02(\text{g/s})/\text{kW}$ at 85°C

Crystal Structures (FY06-07): Determine the crystallographic structure and atomic positions of β and γ AlH_3 for future first-principles modeling

Approach

- All AlH_3 polymorphs have same stoichiometry, but different crystal structures and atomic positions. Therefore, they all have the same high capacity but different thermodynamic and kinetic properties

Approach: Synthesize and characterize AlH_3 polymorphs and identify phases that meet or exceed DOE 2010 goals

Task 1: Synthesis (FY06 \$200k - 50% complete for FY06)

- Prepare α , β and γ - AlH_3
- Control particle size
- Preliminary regeneration studies

Task 2: Properties (FY06 \$175k - 50% complete for FY06)

- Decomposition thermodynamics & phase transformations (DSC, XRD)
- Determine Isothermal decomposition rates of α , β & γ - AlH_3
- Structural characterization of β and γ polymorphs
- Measure particle size & morphology

Approach

Task 3: Scale (1 kg) AlH₃ Tank study (FY06 \$0k)

- Stability/shelf life: determine rate of H₂ evolution at <50 C
- Thermal management: packing density, thermal conductivity
- Safety/Energy/Cost Analysis

Task 4: theory & modeling (FY06 \$0k)

- First principle AlH₃ chemistry: supported by BES
- Refueling strategy
 - on-board (high pressure hydrogenation)
 - off-board (transfer of liquid/powder, tank swap, etc.)

Task 5: Collaborations & reporting

(FY06 \$25k -50% complete for FY06)

- Partnerships and reporting: supplying partners with samples (e.g. AlH₃)
- Materials characterization at unique BNL facilities (e.g. National Synchrotron Light Source and the Center for Functional Nanomaterials)

Background: Aluminum Hydride



$C_{\text{grav.}} = 10.1 \text{ wt\%}$ (2010 S-Target = 6.0)

$C_{\text{vol}} = 149 \text{ g/L}$ (2010 S-Target = 45)

- High gravimetric and volumetric H capacity (volumetric capacity is greater than twice that of liquid hydrogen!)

- AlH_3 forms 7 different crystalline polymorphs: α , α' , β , γ , δ , ϵ , ζ

- α - AlH_3 well characterized over past 30 yrs
forms a metastable polymeric structure \longrightarrow

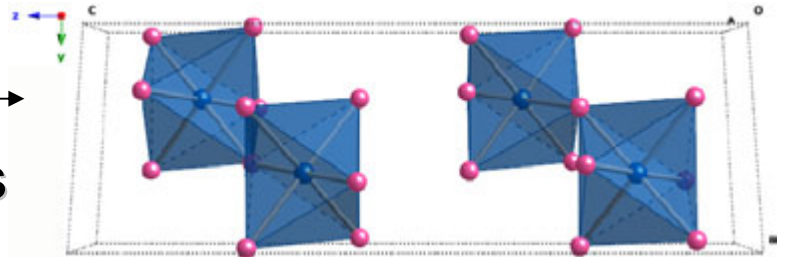
- α - AlH_3 decomposes to Al metal and H_2 gas at $T < 150^\circ \text{C}$

- Low ΔH ($\Delta H_{\alpha\text{AlH}_3} \approx 7.6 \text{ kJ/mol H}_2$ (20% of NaAlH_4)) - less heat required for decomposition

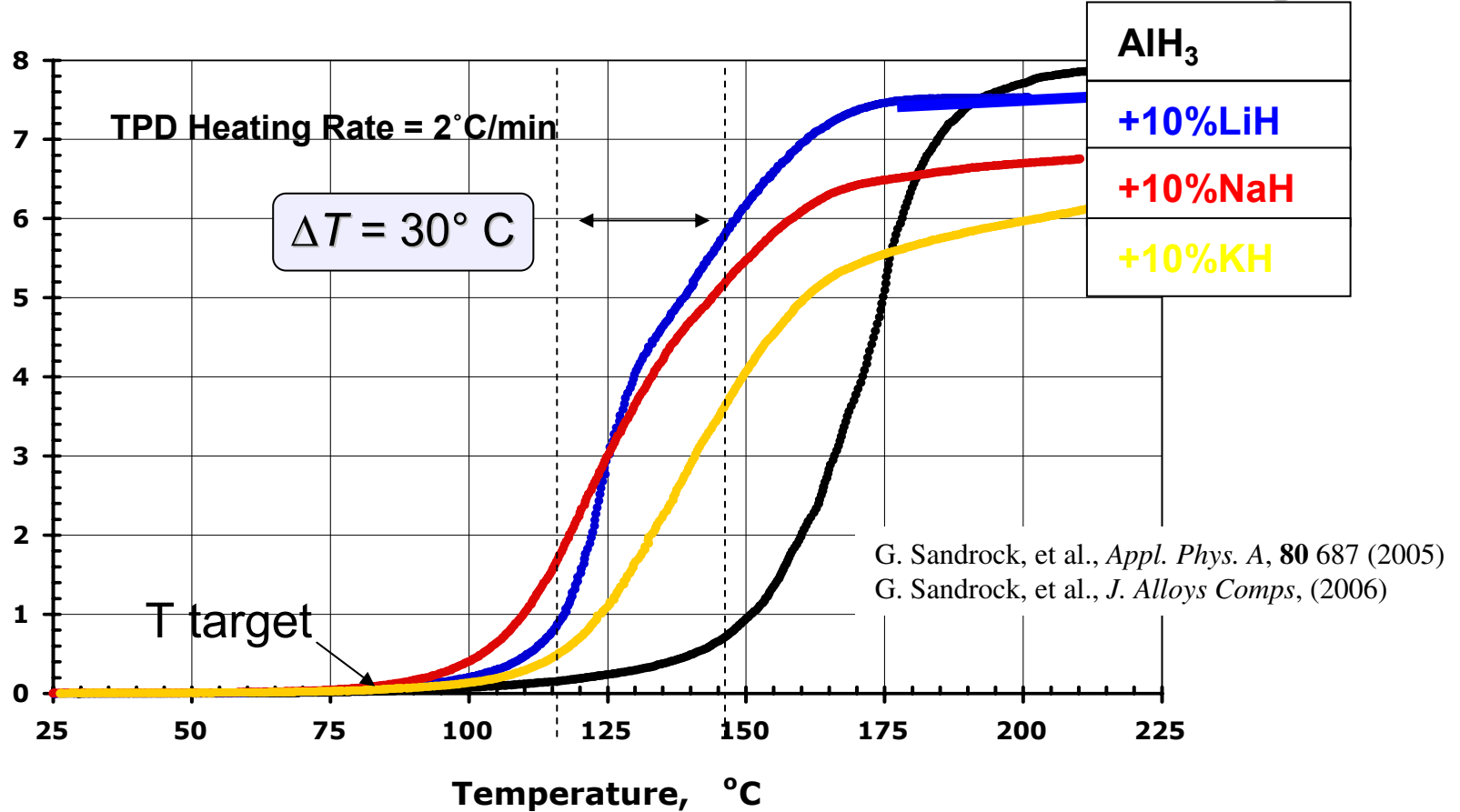
- Little is known about the other 6 AlH_3 polymorphs

- Refill likely performed off-board by chemical regeneration

- AlH_3 currently synthesized by ethereal reaction of $\text{AlCl}_3 + \text{LiAlH}_4$



Alkali Hydride Doping of α -AlH₃



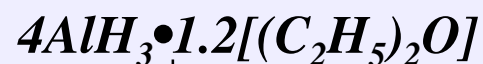
- FY05: Decomposition T of α -AlH₃ (DOW Chem. Co.) decreased by $\sim 30^\circ\text{C}$ with alkali hydride and alanate catalysts
- Work completed in FY05 demonstrated optimal low T kinetics with 10-20 mol% LiH
- This catalyst recipe will be applied to new AlH₃ materials in FY06-07

Synthesis of AlH₃ Polymorphs

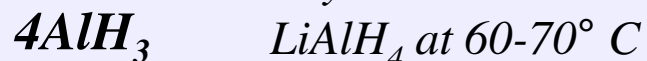
- Polymorphs prepared using organometallic synthesis



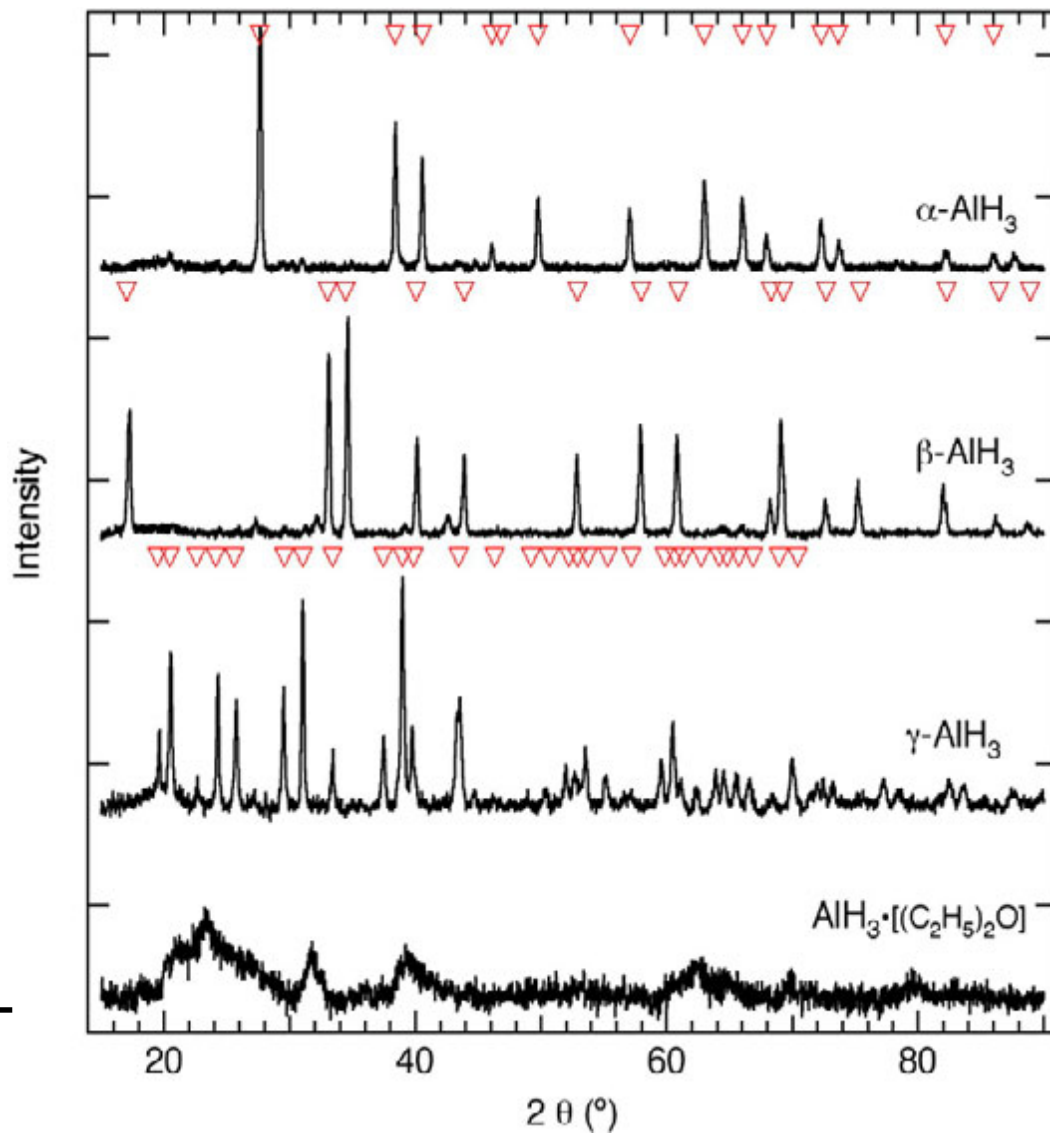
Filter and dry



Dry w/ excess



- Solvated AlH₃, α-AlH₃, β-AlH₃ and γ-AlH₃ synthesized at BNL

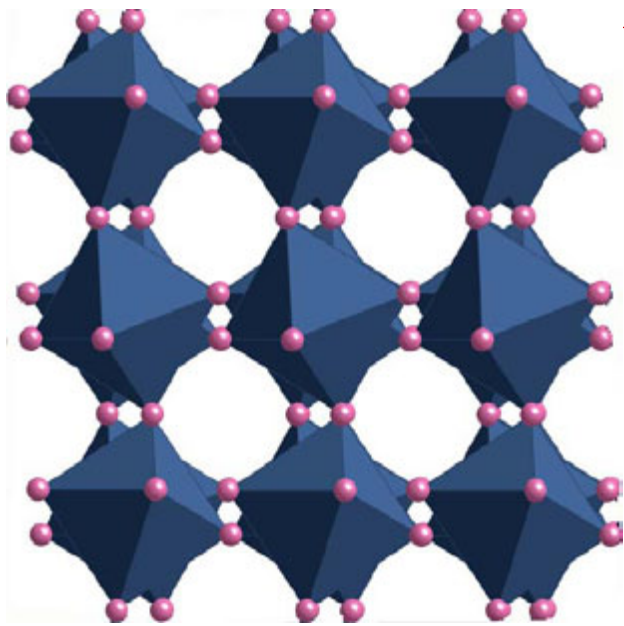


J. Graetz, et al., *J. Phys. Chem. B*, **109** 22181 (2005)

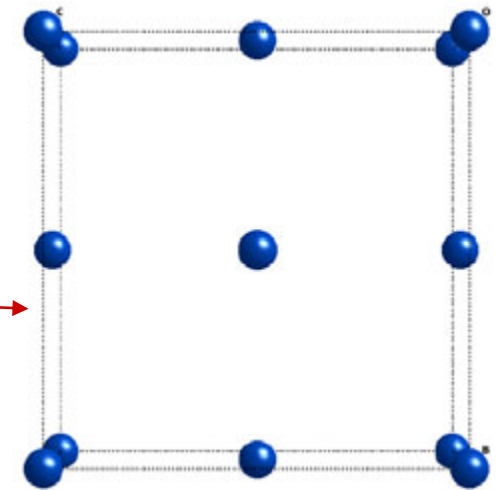
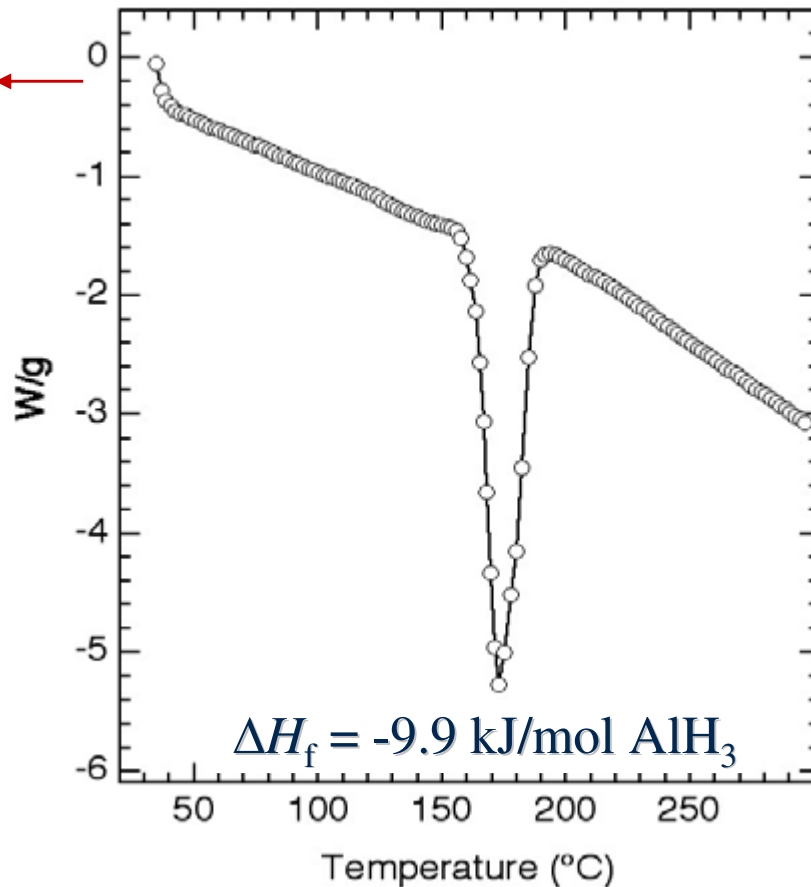
Reaction Pathway & Thermodynamics



- Heat flow measured during temperature ramp (10° C/min)
- Decomposition of $\alpha\text{-AlH}_3$ occurs in a single endothermic step
 - $\Delta H = -9.9 \text{ kJ/mol AlH}_3$
- Position of Al atoms do not change during decomposition

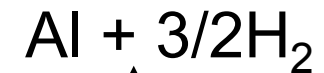
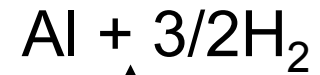
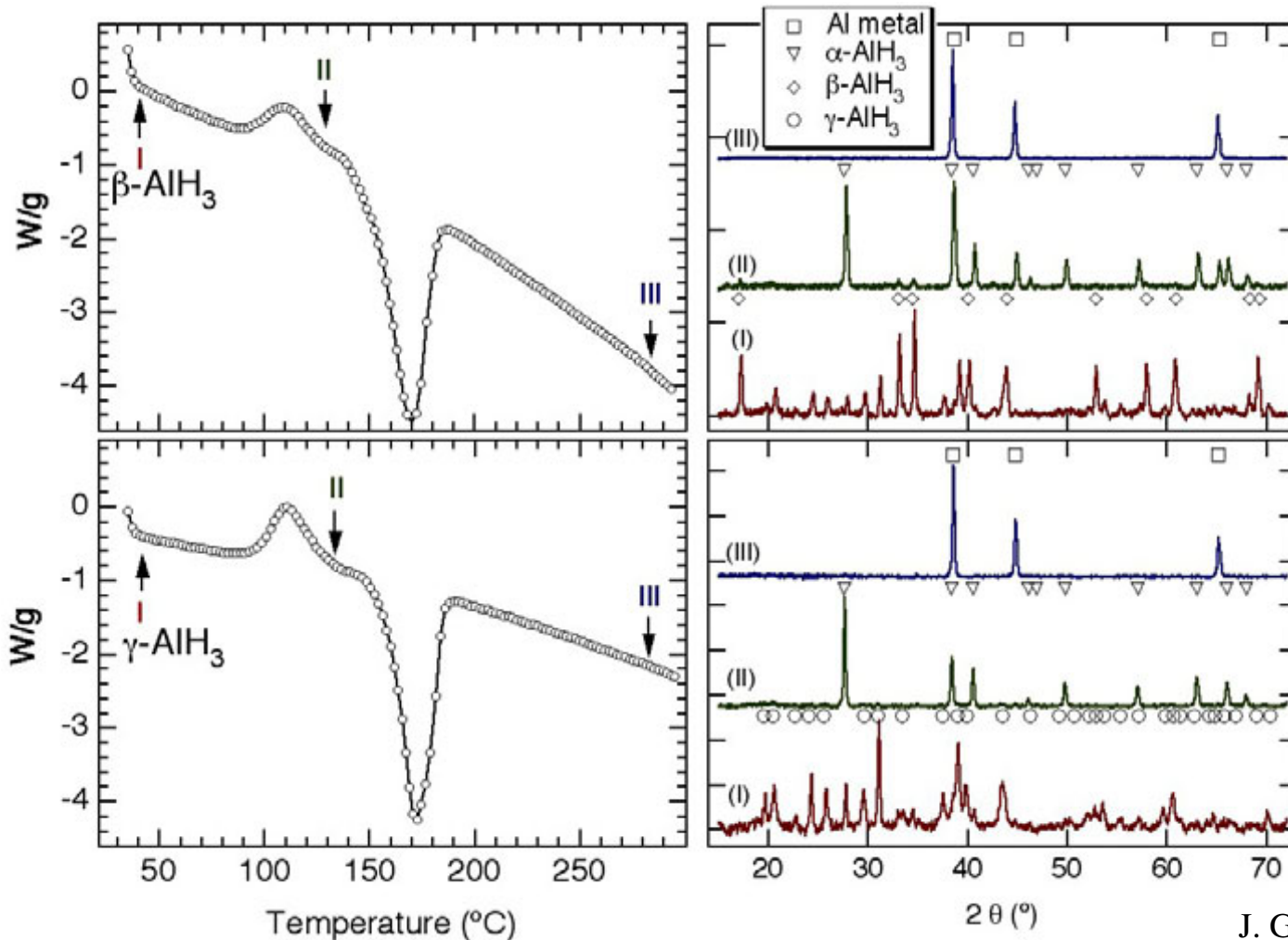


$\alpha\text{-AlH}_3$ (R-3c)



Al metal (fcc)

Reaction Pathway & Thermodynamics

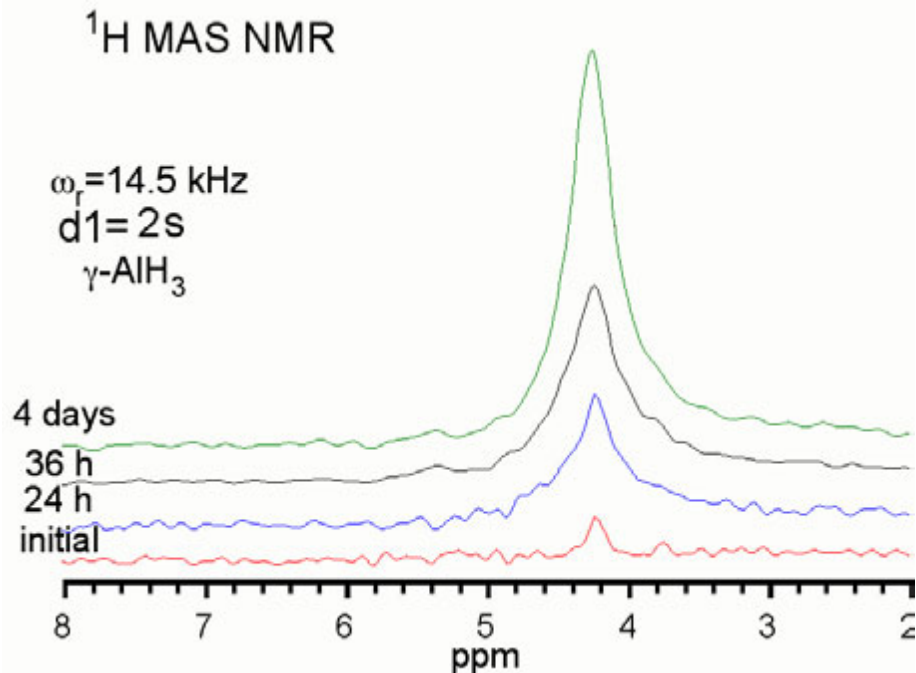


J. Graetz, et al., *J. Alloys. Comp.* (2006)

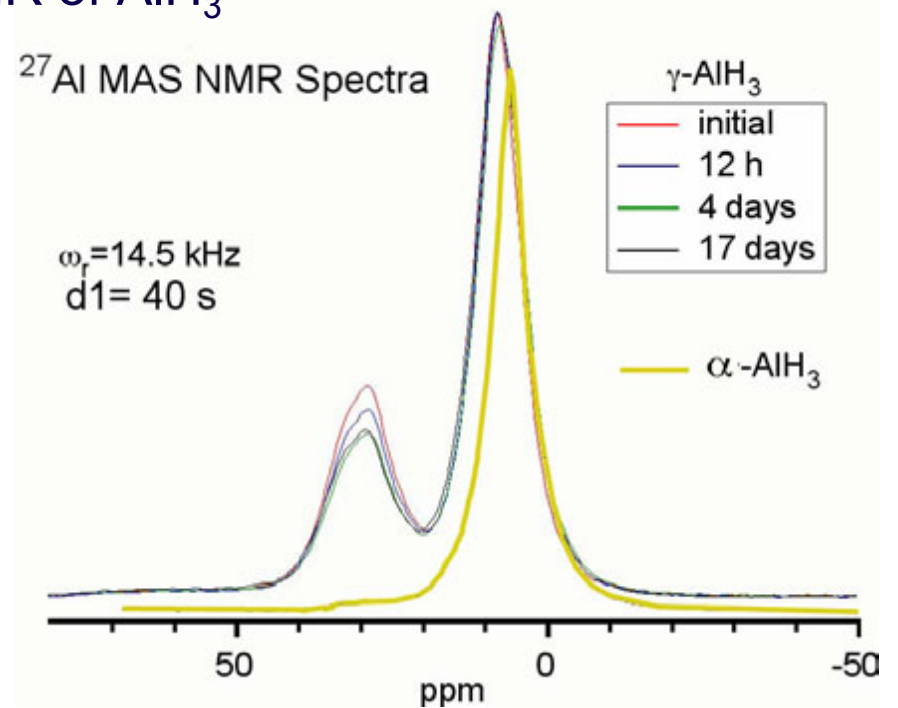
- $T \sim 100^\circ \text{C}$ γ and $\beta\text{-AlH}_3$ undergo exothermic phase transition to $\alpha\text{-AlH}_3$
- $T \sim 160^\circ \text{C}$ endothermic decomposition of $\alpha\text{-AlH}_3$ to $\text{Al} + 3/2\text{H}_2$
- $\Delta H_{\beta-\alpha} = 1.5 \pm 0.4 \text{ kJ/mol AlH}_3$ and $\Delta H_{\gamma-\alpha} = 2.8 \pm 0.4 \text{ kJ/mol AlH}_3$

Reaction Pathway (Low T)

Solid-state NMR of AlH_3



- Peak at 4ppm (H_2 gas) increases continuously at 23°C
- suggests some direct decomposition: $\gamma\text{-AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$



- Double peaks (40 & 10ppm) suggest 2 different Al positions in $\gamma\text{-AlH}_3$
- Decrease in 40ppm at 23°C peak due to $\gamma \rightarrow \alpha$ transition

- At low T ($<100^\circ\text{C}$) 2 decomposition pathways were observed:
 $\gamma\text{-AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$ and $\gamma\text{-AlH}_3 \rightarrow \alpha\text{-AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$

Summary of Reaction Pathways and Thermodynamics

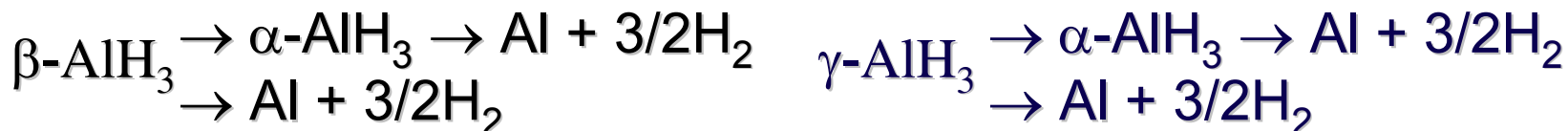
$T \geq 40^\circ \text{C}$



$T \geq 100^\circ \text{C}$



$T < 100^\circ \text{C}$



Polymorph	ΔH_0 (kJ/mol AlH ₃)	ΔH_1 (kJ/mol AlH ₃)	ΔH (kJ/mol AlH ₃)	ΔG (kJ/mol AlH ₃)
$\alpha\text{-AlH}_3$	-	-9.9 ± 0.6	-9.9 ± 0.6	48.5 ± 0.6
$\beta\text{-AlH}_3$	1.5 ± 0.4	-9.5 ± 0.6	-8.0 ± 1.0	50.5 ± 1.0
$\gamma\text{-AlH}_3$	2.8 ± 0.4	-9.9 ± 0.6	-7.1 ± 0.4	51.4 ± 1.0

ΔH_0 - enthalpy of exothermic peak (due to $\gamma \rightarrow \alpha$ or $\beta \rightarrow \alpha$ transition)

ΔH_1 - enthalpy of endothermic peak (due to decomposition of $\alpha\text{-AlH}_3$)

ΔH - total formation enthalpy ($\Delta H = \Delta H_0 + \Delta H_1$)

ΔG - total Gibbs free energy ($\Delta G = \Delta H - T\Delta S$ where $\Delta S \approx 129 \text{ J/K mol H}_2$)

Can we form AlH_3 directly from H_2 gas?

- Formation enthalpy from DSC measurements:

$$\Delta H_f = -9.9 \pm 0.6 \text{ kJ/mol AlH}_3$$

- Gibbs free energy of formation at 298 K:

$$\Delta G_{f298K} = 48.5 \pm 0.6 \text{ kJ/mol AlH}_3$$

using $\Delta S_{298K} \approx 129 \text{ J/K mol}$

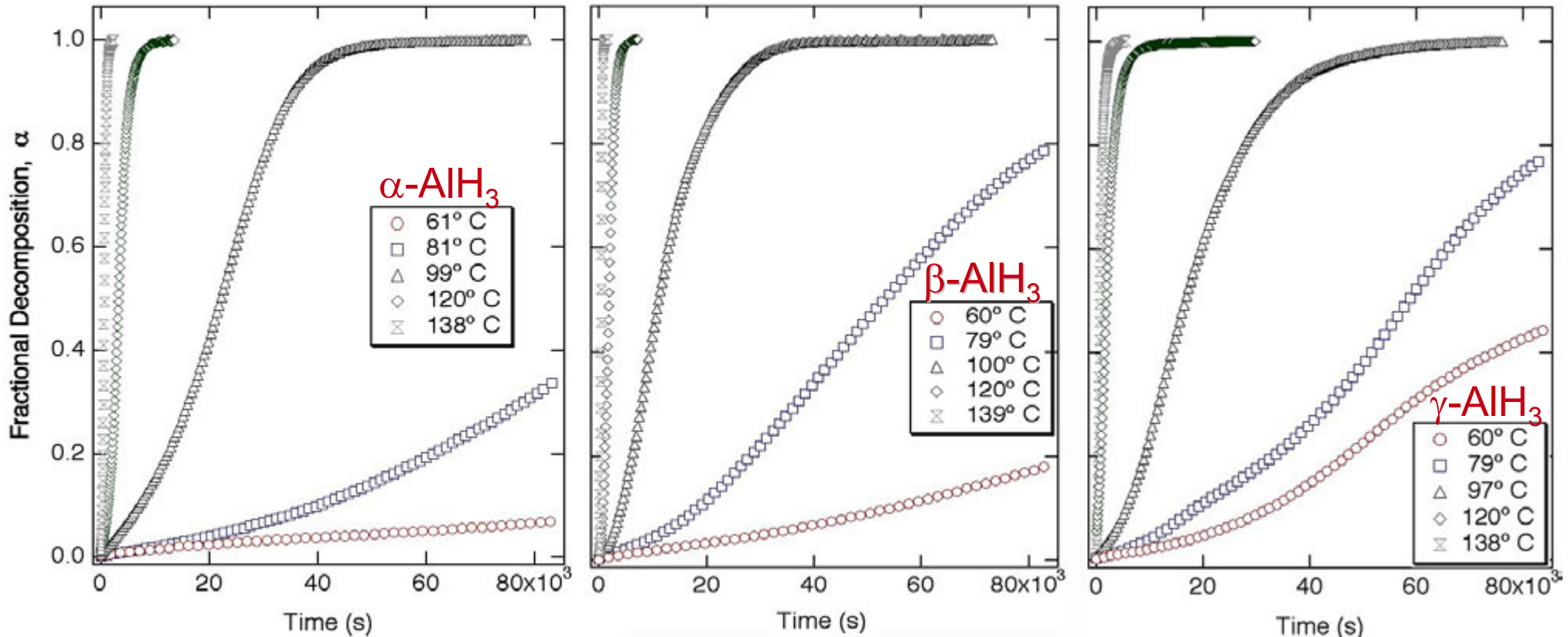
- H_2 equilibrium pressure calculated using: $P_{298K} = \exp\left[\frac{\Delta G_{f298K}}{RT}\right]$
- Giving an equilibrium pressure of:

$$P_{298K} \approx 10^5 \text{ bar}$$

- Hydrogenation of spent Al requires H_2 pressures $> 10^5$ bar
 - For comparison, decomposition of Na_3AlH_6 has a $\Delta H=47 \text{ kJ/mol}$ and $P_{150^\circ\text{C}} \approx 5 \text{ bar}$
- Claudy et al. predicted $P_{23^\circ\text{C}} \approx 10^5 \text{ bar}$, but Baranowski et al. and Konovalov et al. measured $P_{300^\circ\text{C}} \approx 2.8 \times 10^4 \text{ bar}$

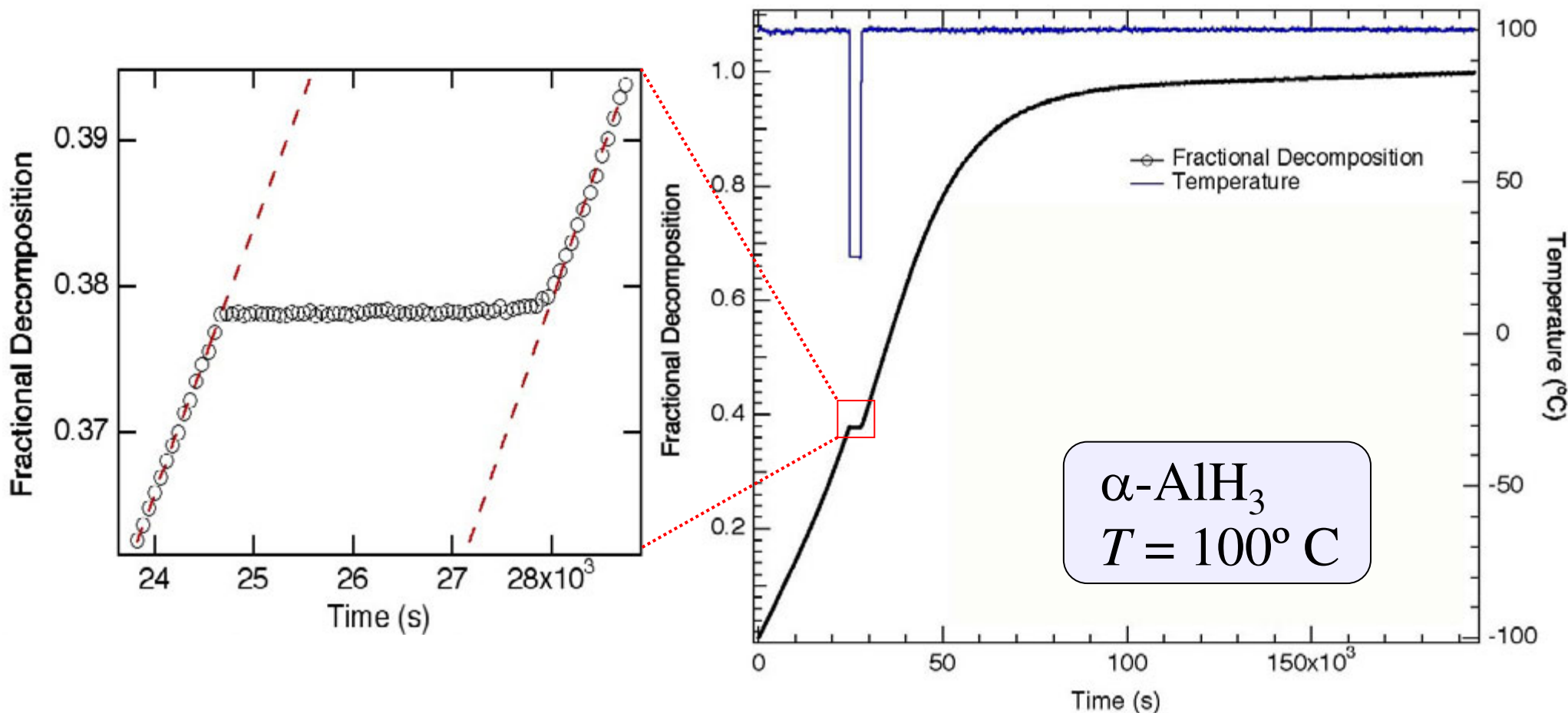
No-Go on direct hydrogenation of Al powder

Isothermal Kinetics



- AlH_3 polymorphs decomposed isothermally into vacuum (experiments performed with a back pressure (2 bar) showed similar results)
- $T > 100^\circ \text{C}$: Rates are similar for all 3 polymorphs
 - γ and β phases transform to α phase prior to decomposition
- $T < 100^\circ \text{C}$: γ and β phases exhibit faster kinetics than α phase
 - At least partial direct decomposition (e.g. no α transition, $\gamma \rightarrow \text{Al} + \text{H}$ and $\beta \rightarrow \text{Al} + \text{H}$)

Temperature Controlled Decomposition



- Reaction rate goes to zero as T is reduced to 23°C and returns to the same rate when T is increased back to 100°C (0.3 g/s for 100 kg AlH_3)
- The full spectrum of H_2 evolution rates (min-max) can likely be obtained with a variable temperature hydride where $23 \leq T \leq 110^\circ\text{C}$

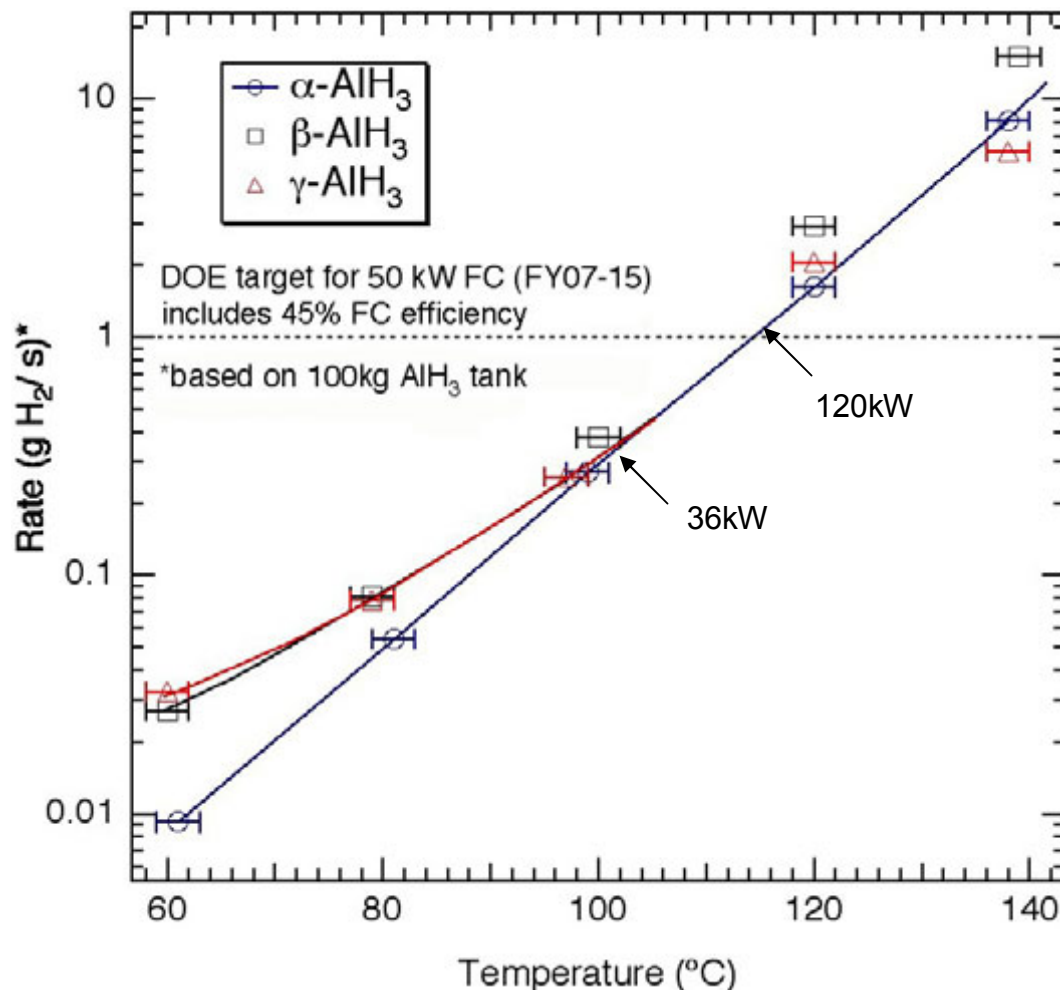
J. Graetz, et al., *J. Phys. Chem. B*, **109** 22181 (2005)

Decomposition Rates for AlH₃ Polymorphs

- Shape of fractional decomposition curves suggest kinetics are limited by nucleation & growth of Al phase

- H₂ evolution rates determined from “acceleratory” region of decomp. curve (90% of total)

- T ≥ 100°C rates similar for α, β and γ-AlH₃, but γ and β phases decompose more rapidly < 100°C



The 3 AlH₃ polymorphs exhibit similar H₂ evolution rates (0.1-0.3g/s) in the temperature range of interest (85°-100°C). However, the γ and β polymorphs are much less stable at low T (≤ 60C).

α-AlH₃ exhibits low T stability with rapid H₂ evolution at moderate T

Future Work

Remainder FY06

- **Kinetics** - Preliminary studies on pure α , β and γ -AlH₃ complete
 - Low temperature (<60°C) kinetic studies of α , β and γ -AlH₃
 - Identify and optimize additives (e.g. LiAlH₄) and particle morphology to meet DOE full flow target 0.02(g/s)/kW at 85° C
- **Thermodynamics** - TD studies on pure α , β and γ -AlH₃ complete
- **Crystal structures** - synchrotron XRD acquired on α , β and γ phases ongoing effort with U. Hawaii and IFE (Norway)
- **Regeneration** - Complete literature search and environmental safety review for alane regeneration experiments proposed for FY07
- **Collaboration with MHCoe Partners**
 - Lead the alane subgroup
 - Provide samples SRNL, JPL, U.Nevada

Proposed Future Work

- Regeneration (FY07-09)
 - Direct high-pressure hydrogenation in “liquid” state: Reduce ΔG by lowering ΔS and ΔH during hydrogenation ($P_{eq} \sim \exp[\Delta G]$)
 - Electrochemical charging - Savannah River National Lab
 - Conventional organometallic synthesis (recycling) - starting with activated aluminum
- Scale (<1kg) AlH_3 Tank Study - preliminary study of kinetics and thermal properties leading to a tank design study
 - Stability and shelf life, thermal management, safety/energy/cost
- Theory and Refueling Models - First principle AlH_3 chemistry (funded by BES) and Refueling strategy
 - on-board (high pressure hydrogenation)
 - off-board (transfer of liquid/powder, tank swap, etc.)
- Collaboration with MHCoe Partners
 - Lead the alane subgroup
 - Provide samples SRNL, JPL, U.Nevada

Project Summary

Objective: Understand the strengths/weaknesses of using AlH_3 as a storage medium by quantifying the reaction kinetics, thermodynamics, and energy requirements for regeneration

Approach: Synthesis, characterization & regeneration studies of AlH_3

Accomplishments

- **Synthesis:** α , β and γ AlH_3 synthesized at BNL with capacities approaching 10 wt% and 0.149 kg/L at $T < 100^\circ \text{C}$
- **Thermodynamics:** H_2 equilibrium pressure $\geq 10^5$ bar at 300 K; Decomposition pathways of α , β and γ delineated
- **Kinetics:** 1.0 g H_2 /s (120 kW) at 112°C for α , β and γ - AlH_3 ; Best low temperature (60°C) stability with α - AlH_3 ; Demonstrated that the full spectrum of H_2 evolution rates can be obtained at $T = 23$ - 112°C

Collaborations: Active partnerships with JPL, U. Hawaii, U. Nevada, SRNL and Sandia; IPHE collaboration with IFE, Norway

Future Research: Regeneration of spent Al back to AlH_3 ; Identify and optimize additives and particle morphology; scale tank studies

Project Summary

Storage Parameter	Units	2010 System Target	FY05 materials*	FY06 materials*
Gravimetric Capacity	kWh/kg	2.0	2.5	3.17(3)
	wt. % H ₂	6.0	7.5	9.5(1)
Volumetric Capacity	kWh/L	1.5	3.97 ^x	4.75(4) ^x
	Kg H ₂ /L	0.045	0.119	0.143(2)
Desorption Temperature	°C	85	105	<100
Desorption Rate** 85 °C / 112 °C	g/s/kW	1.0**	0.08 / 0.83	0.14(1) / 1.0(1)
		Power 85 °C / 112 °C	120**	10 / 100

* Data is based on material only, not system value

** Based on 50kW FC with 45% efficiency for 100kg AlH₃

^x Does not account for packing density (a conservative estimate for packing density is 50%)

End of presentation

Publications and Presentations

Publications

1. J. Graetz and J. J. Reilly, “Thermodynamics of the α , β and γ polymorphs of AlH_3 ” *J. Alloys Comp.*, (2006).
2. J. Graetz , J. Reilly, G. Sandrock, J. Johnson, W.-M. Zhou, and J. Wegrzyn, “Aluminum hydride, AlH_3 , as a hydrogen storage compound” *TMS Proceedings* (2006).
3. J. Graetz and J. J. Reilly, “Decomposition kinetics of the AlH_3 polymorphs”, *J. Phys. Chem. B*, **109** 22181 (2005).
4. G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson and J. Wegrzyn, “Alkali metal hydride doping of α - AlH_3 for enhanced H_2 desorption kinetics” *J. Alloys Comp.*, (2005).
5. J. Graetz, Y. Lee, J. J. Reilly, S. Park and T. Vogt, “Structure and thermodynamics of the mixed alkali alanates”, *Phys. Rev. B*, **71** 184115 (2005).
6. J. Graetz and J. J. Reilly, “Nanoscale energy storage materials produced by hydrogen-driven metallurgical reactions”, *Adv. Eng. Mat.*, **7** 597 (2005).
7. G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson and J. Wegrzyn, “Accelerated thermal decomposition of AlH_3 for hydrogen-fueled vehicles”, *Appl. Phys. A*, **80** 687 (2005).

Patent Applications

1. G. Sandrock, J. Reilly, J. Graetz, W.M. Zhou, J. Wegrzyn, J. Johnson, K. Gross, “Activated aluminum hydride hydrogen storage compositions and uses thereof” U.S. Patent application 2005.

Publications and Presentations

Presentations

1. Solid state NMR studies of the aluminum hydride phases, *MRS Spring Meeting* 2006.
2. Decomposition kinetics and thermodynamics of the α , β and γ polymorphs of aluminum hydride, *MRS Spring Meeting* 2006.
3. Aluminum Hydride (AlH_3) as a Hydrogen Storage Compound”, *TMS Annual Meeting*, 2006.
4. Synthesis and Characterization of the AlH_3 Polymorphs”, Gordon Research Conference on Hydrogen-Metal Systems, 2005.
5. New Reversible Complex Metal Hydrides”, *March Meeting of American Physical Society*, 2005.
6. Doping of AlH_3 with alkali metal hydrides for enhanced decomposition kinetics”, *March Meeting of the American Physical Society*, 2005.

