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 ≥ 8% kg-H_2/kg (grav.) and ≥ 0.10 kg-H_2/L (vol.)

Thermodynamics (FY06): Identify AlH_3 polymorphs with suitable H_2 pressures at temperatures near the operating temperature of a PEM fuel cell (~85° 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(g/s)/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) AlH_3 Tank study (FY06 $0k)

- Stability/shelf life: determine rate of H_2 evolution at <50 C
- Thermal management: packing density, thermal conductivity
- Safety/Energy/Cost Analysis

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

- First principle AlH_3 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. AlH_3)
- Materials characterization at unique BNL facilities (e.g. National Synchrotron Light Source and the Center for Functional Nanomaterials)

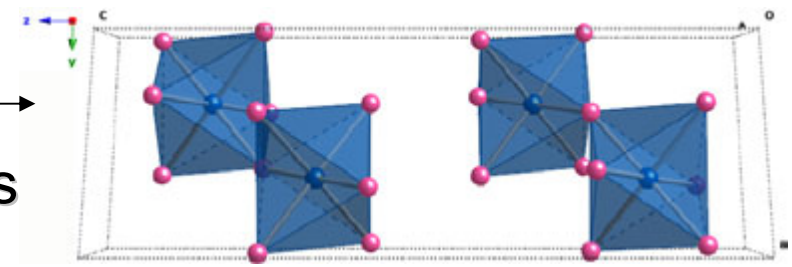
Background: Aluminum Hydride

$AlH_3 \rightarrow Al + 2/3\ H_2$

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

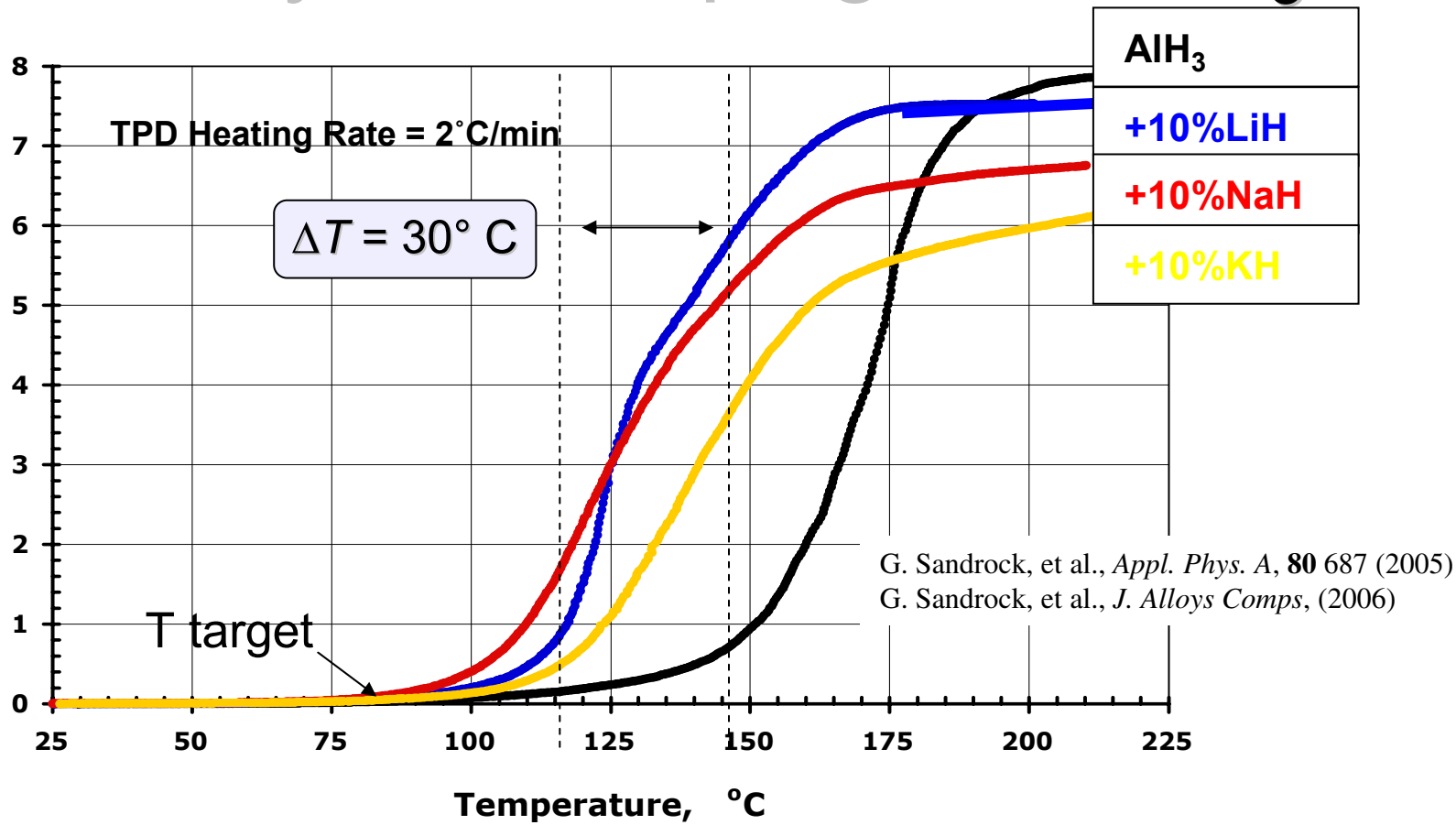
C_{vol} = 149 g/L (2010 S-Target = 45)

- 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 →



  - α-AlH_3 decomposes to Al metal and H_2 gas at T < 150° C
  - Low ΔH ($\Delta H_{\alpha AlH3} \approx 7.6$ 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 $AlCl_3$+$LiAlH_4$

Alkali Hydride Doping of α-AlH_3



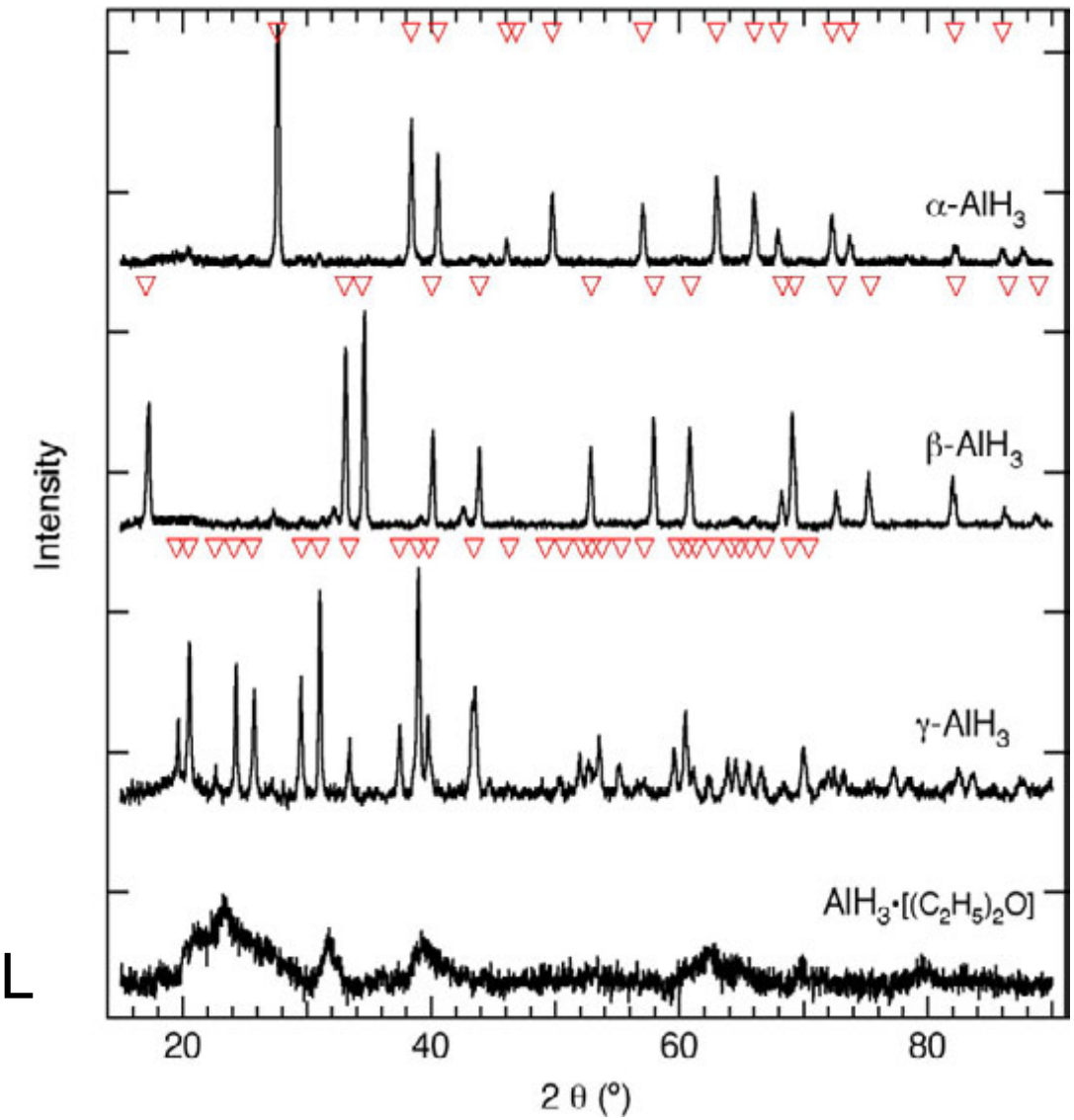
- FY05: Decomposition *T* of α-AlH_3 (DOW Chem. Co.) decreased by ~30° C with alkali hydride and alanate catalysts
- Work completed in FY05 demonstrated optimal low *T* kinetics with 10-20 mol% LiH
- This catalyst recipe will be applied to new AlH_3 materials in FY06-07

Synthesis of AlH_3 Polymorphs

- Polymorphs prepared using organometallic synthesis

$$3LiAlH_4 + AlCl_3 + ether$$
$$\downarrow$$
$$3LiCl + 4AlH_3 + ether$$
$$\downarrow \quad \textit{Filter and dry}$$
$$4AlH_3 \bullet 1.2[(C_2H_5)_2O]$$
$$\downarrow \quad \textit{Dry w/ excess } LiAlH_4 \textit{ at 60-70° C}$$
$$4AlH_3$$

- Solvated AlH_3, α-AlH_3, β-AlH_3 and γ-AlH_3 synthesized at BNL

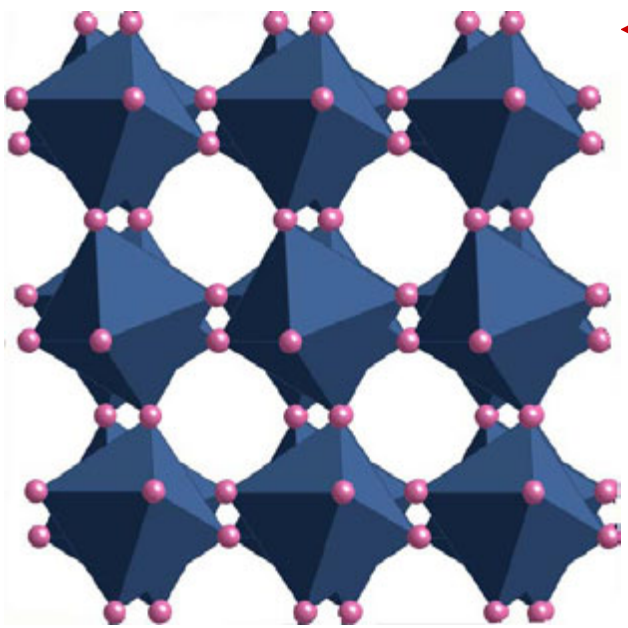


J. Graetz, et al., *J. Phys. Chem. B*, **109** 22181 (2005)

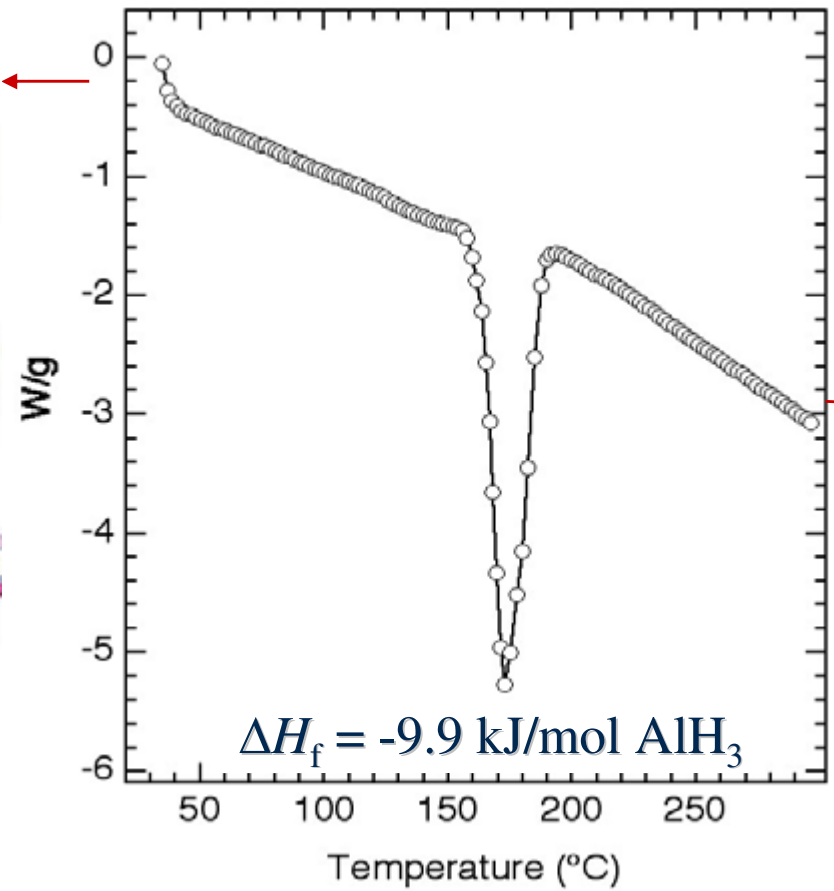
Reaction Pathway & Thermodynamics

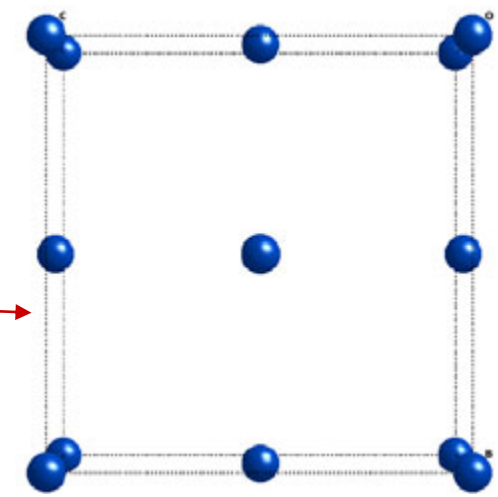
α-$AlH_3 \rightarrow Al + 3/2\ H_2$

- Heat flow measured during temperature ramp (10° C/min)
- Decomposition of α-AlH_3 occurs in a single endothermic step
  - ΔH = -9.9 kJ/mol AlH_3
- Position of Al atoms do not change during decomposition



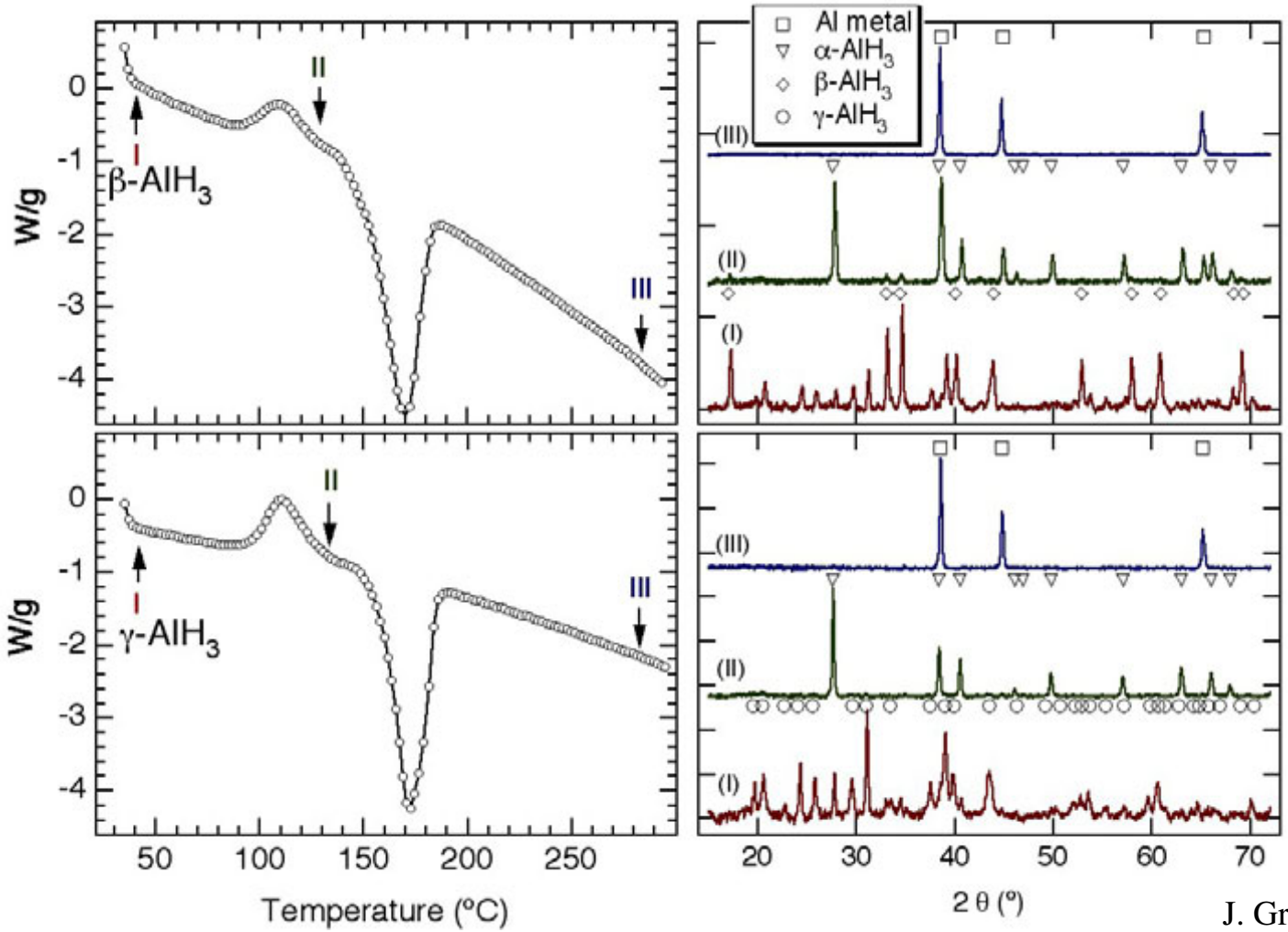
α-AlH_3 (R-3c)





Al metal (fcc)

Reaction Pathway & Thermodynamics



$Al + 3/2H_2$
↑
α-AlH_3
↑
β-AlH_3

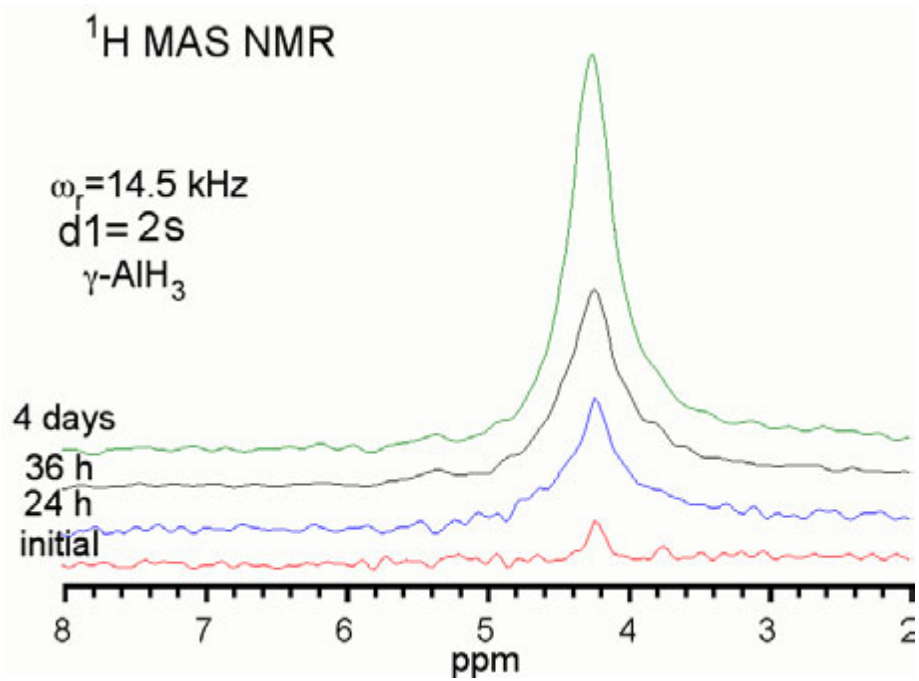
$Al + 3/2H_2$
↑
α-AlH_3
↑
γ-AlH_3

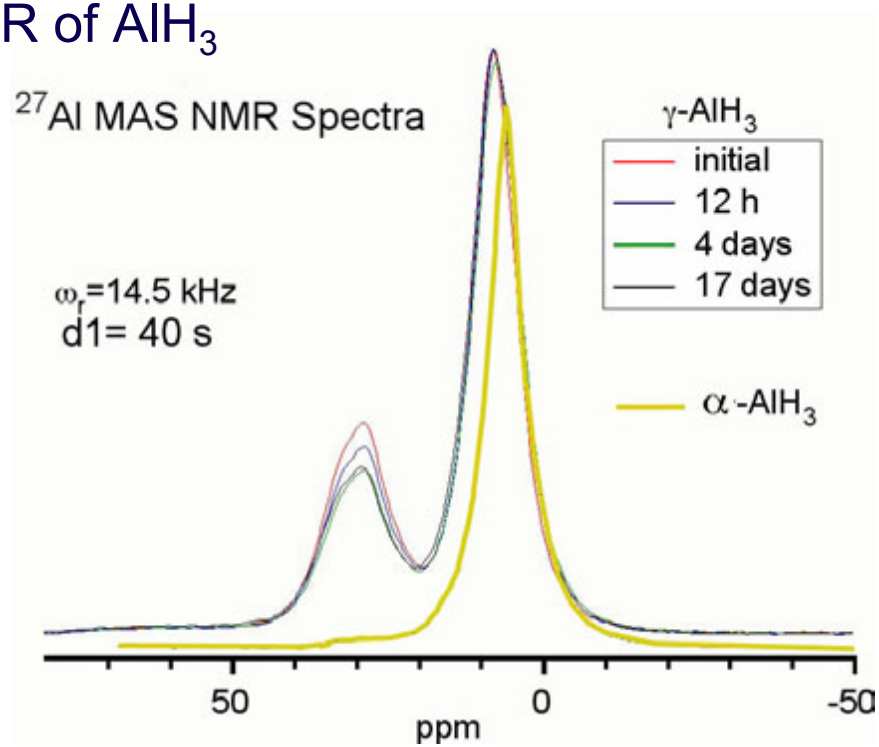
J. Graetz, et al., *J. Alloys. Comp.* (2006)

- T~100° C γ and β-AlH_3 undergo exothermic phase transition to α-AlH_3
- T~160° C endothermic decomposition of α-AlH_3 to $Al + 3/2H_2$
- $\Delta H_{\beta\text{-}\alpha} = 1.5 \pm 0.4$ kJ/mol AlH_3 and $\Delta H_{\gamma\text{-}\alpha} = 2.8 \pm 0.4$ 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: γ-AlH_3 → Al +3/2H_2

- Double peaks (40 & 10ppm) suggest 2 different Al positions in γ-AlH_3
- Decrease in 40ppm at 23°C peak due to γ→α transition

- At low *T* (<100° C) 2 decomposition pathways were observed:
  γ-AlH_3 → Al +3/2H_2 and **γ-AlH_3 → α-AlH_3 → Al +3/2H_2**

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Summary of Reaction Pathways and Thermodynamics

$T \geq 40°$ C: $\alpha\text{-}AlH_3 \rightarrow Al + 3/2H_2$

$T \geq 100°$ C: $\beta\text{-}AlH_3 \rightarrow \alpha\text{-}AlH_3 \rightarrow Al + 3/2H_2$ $\gamma\text{-}AlH_3 \rightarrow \alpha\text{-}AlH_3 \rightarrow Al + 3/2H_2$

$T < 100°$ C: $\beta\text{-}AlH_3 \rightarrow \alpha\text{-}AlH_3 \rightarrow Al + 3/2H_2$, $\rightarrow Al + 3/2H_2$ $\gamma\text{-}AlH_3 \rightarrow \alpha\text{-}AlH_3 \rightarrow Al + 3/2H_2$, $\rightarrow Al + 3/2H_2$

Polymorph	ΔH_0 (kJ/mol AlH_3)	ΔH_1(kJ/mol AlH_3)	ΔH (kJ/mol AlH_3)	ΔG (kJ/mol AlH_3)
α-AlH_3	-	-9.9 ±0.6	-9.9 ±0.6	48.5 ±0.6
β-AlH_3	1.5 ±0.4	-9.5 ±0.6	-8.0 ±1.0	50.5 ±1.0
γ-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 α-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 $\Delta S \approx 129$ 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 $\Delta S_{298K} \approx 129$ J/K mol

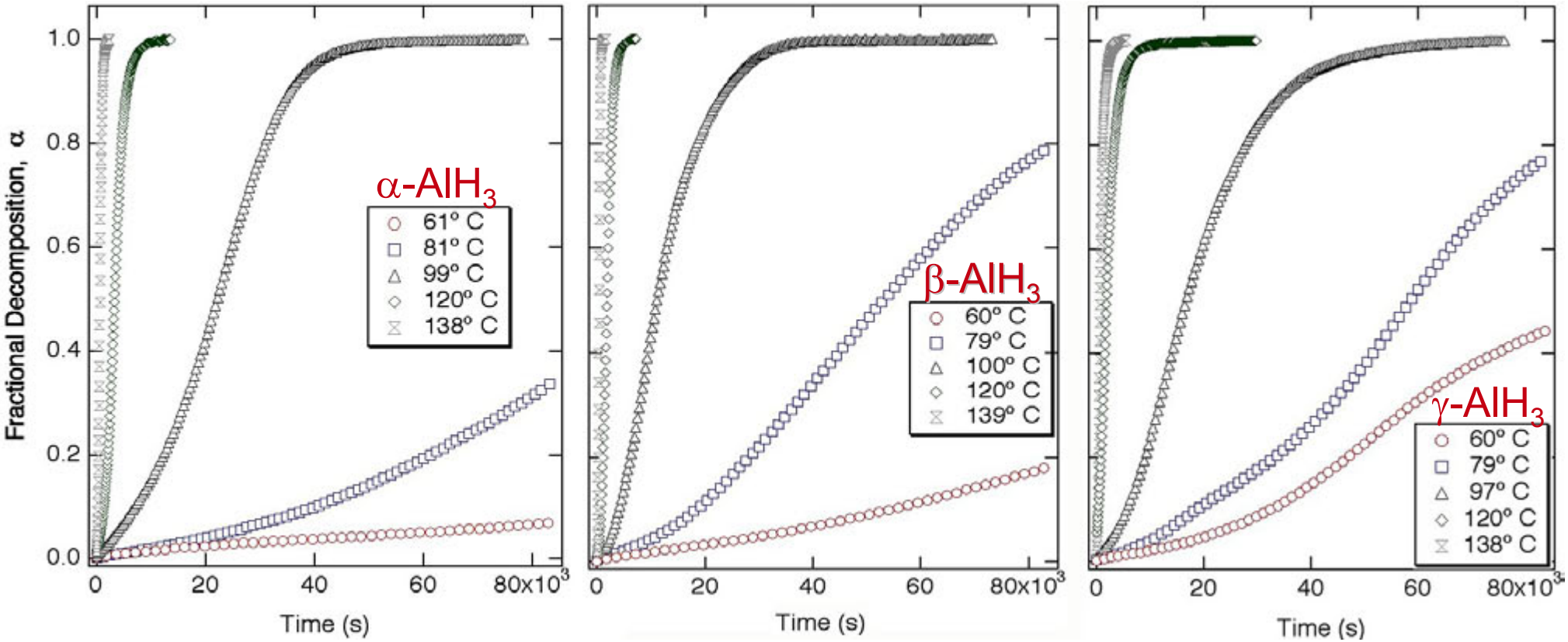
- H_2 equilibrium pressure calculated using: $P_{298K} = \exp\left[\frac{\Delta G_{f\,298K}}{RT}\right]$
- Giving an equilibrium pressure of:

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

- Hydrogenation of spent Al requires H_2 pressures > 10^5 bar
  - For comparison, decomposition of Na_3AlH_6 has a ΔH=47 kJ/mol and $P_{150^\circ C} \approx 5$ bar
- Claudy et al. predicted $P_{23^\circ C} \approx 10^5$ bar, but Baranowski et al. and Konovalov et al. measured $P_{300^\circ C} \approx 2.8\times10^4$ 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° C: Rates are similar for all 3 polymorphs
  - γ and β phases transform to α phase prior to decomposition
- T<100° C: γ and β phases exhibit faster kinetics than α phase
  - At least partial direct decomposition (e.g. no α transition, γ →Al+H and β →Al+H)

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

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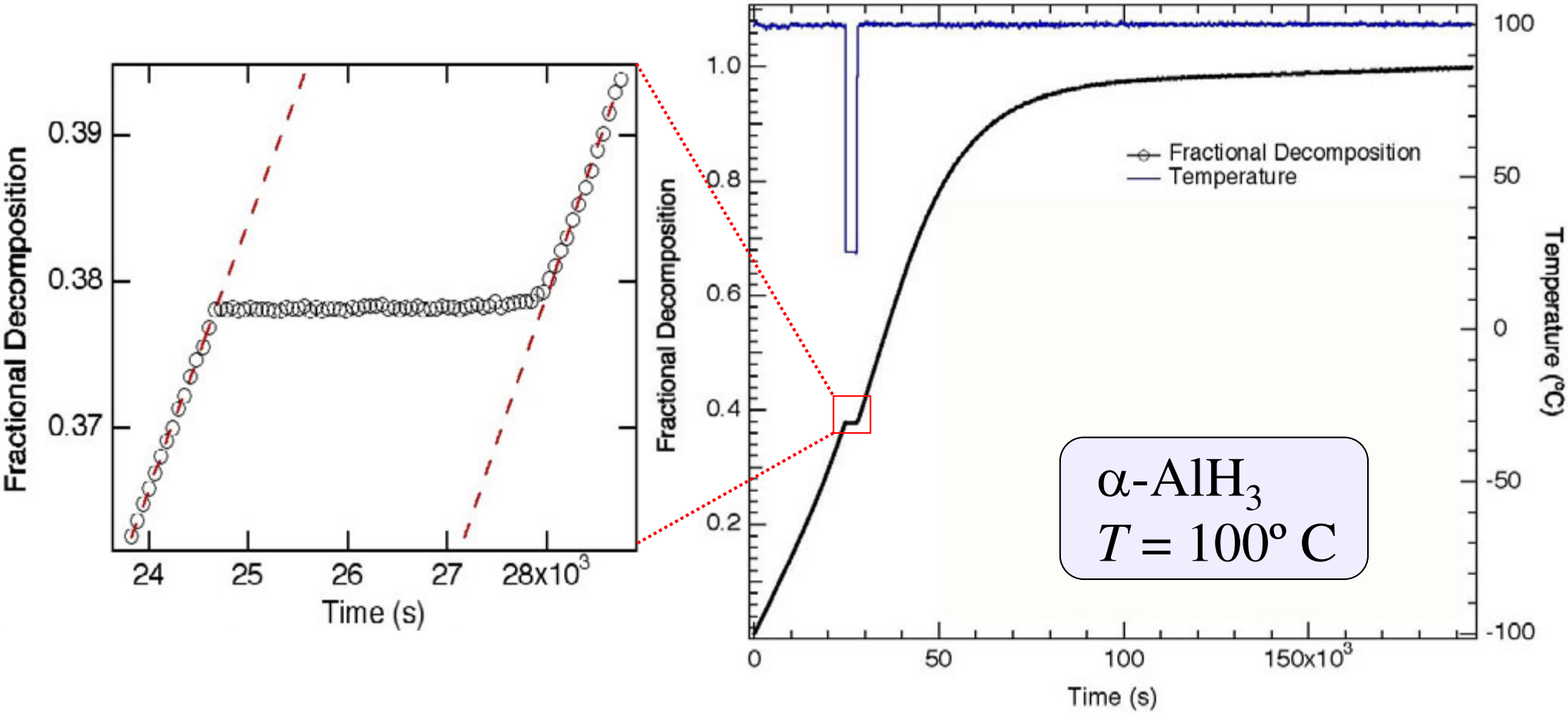
Temperature Controlled Decomposition



- 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 $23 \leq T \leq 110$°C

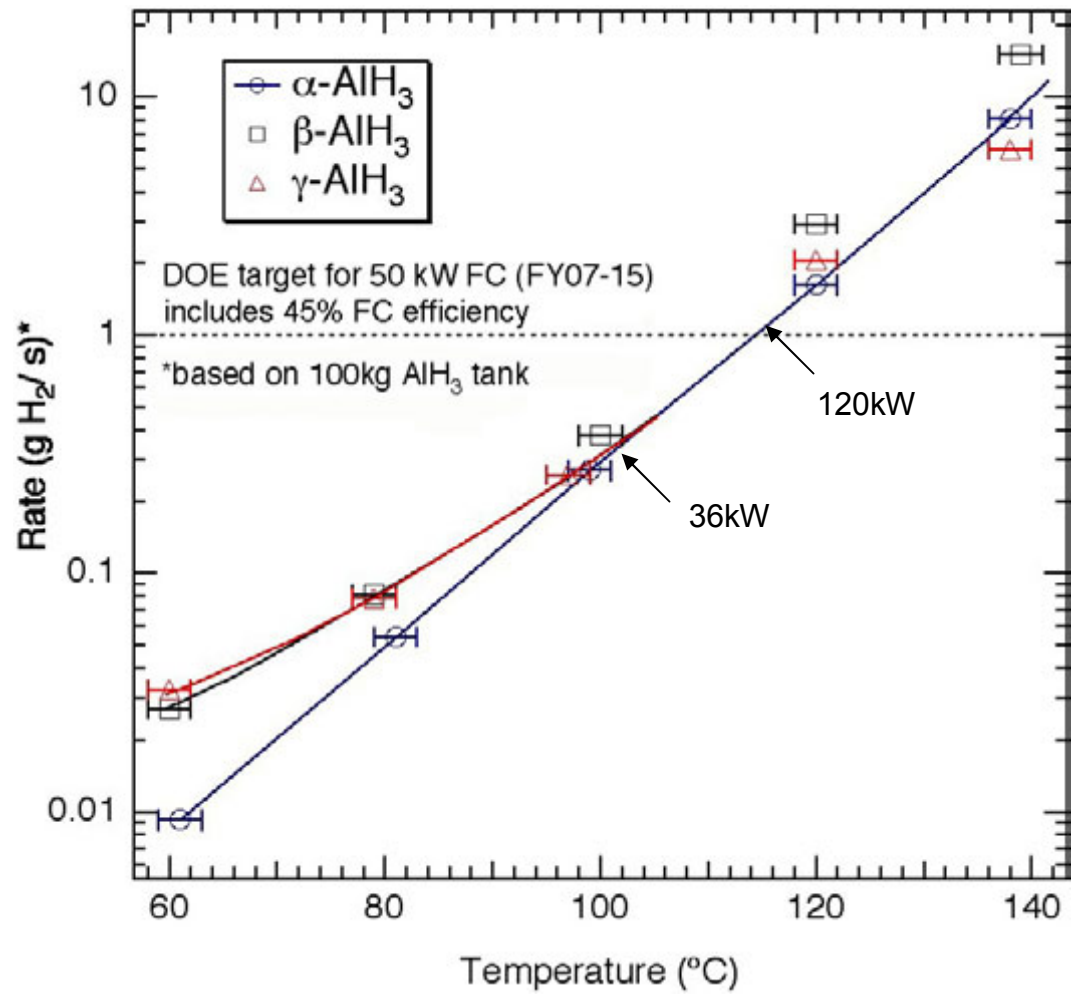
J. Graetz, et al., *J. Phys. Chem. B*, **109** 22181 (2005)

Decomposition Rates for AlH_3 Polymorphs

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

-H_2 evolution rates determined from "acceleratory" region of decomp. curve (90% of total)

- T≥100ºC rates similar for α, β and γ-AlH_3, but γ and β phases decompose more rapidly <100ºC



The 3 AlH_3 polymorphs exhibit similar H_2 evolution rates (0.1-0.3g/s) in the temperature range of interest (85º-100ºC). However, the γ and β polymorphs are much less stable at low T (≤ 60C).

α-AlH_3 exhibits low T stability with rapid H_2 evolution at moderate T

Future Work

Remainder FY06

- Kinetics - Preliminary studies on pure α, β and γ-AlH_3 complete
  - Low temperature (<60ºC) kinetic studies of α, β and γ-AlH_3
  - Identify and optimize additives (e.g. $LiAlH_4$) 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-AlH_3 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<100º C

– **Thermodynamics**: H_2 equilibrium pressure $\geq 10^5$ bar at 300 K; Decomposition pathways of α, β and γ delineated

– **Kinetics**: 1.0 gH_2/s (120 kW) at 112º C for α, β and γ-AlH_3; Best low temperature (60º C) stability with α-AlH_3; Demonstrated that the full spectrum of H_2 evolution rates can be obtained at T = 23-112ºC

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 wt. % H_2	2.0 6.0	2.5 7.5	3.17(3) 9.5(1)
Volumetric Capacity	kWh/L Kg H_2/L	1.5 0.045	3.97[x] 0.119	4.75(4)[x] 0.143(2)
Desorption Temperature	ºC	85	105	<100
Desorption Rate** 85 ºC / 112 ºC Power 85 ºC / 112 ºC	g/s/kW kW	1.0** 120**	0.08 / 0.83 10 / 100	0.14(1) / 1.0(1) 17(2) / 120(12)

* Data is based on material only, not system value
** Based on 50kW FC with 45% efficiency for 100kg AlH_3
[x] Does not account for packing density (a conservative estimate for packing density is 50%)

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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.

Alanes (AlH3)		Go/No-Go on continuation of alane R&D for meeting 2015 storage targets
	1	aluminum hydride synthesis: Synthesis of alanes that meet 2010 storage targets
BNL	1.1	Complete synthesis of pure and mixed phases of aluminum hydride
UN	1.2	Complete study of aluminum hydride with catalysts
BNL	1.3	Complete measurements on surface coatings and particle size
TBD	1.4	Synthesis of 100kg alane material for prototype tank
	2	Aluminum hydride properties: Downselect alane materials that meet 2010 storage targets
UH	2.1	Complete thermodynamic properties of alanes and ball milled alanes phases by DSC
BNL	2.1	Complete thermodynamic study of the alpha, beta and gamma polymorphs of AlH3
BNL	2.1	Complete thermodynamic study of other phases of AlH3
BNL	2.2	Complete kinetic study of the alpha, beta and gamma polymorphs of AlH3
BNL	2.2	Complete kinetic study of other phases of AlH3
UH	2.3	Complete molecular structure determination of selected alanes via neutron diffraction
BNL	2.3	Complete crystallographic structure determination of gamma and beta AlH3 using x-ray diffraction
BNL	2.3	Complete crystallographic structure determination of other phases of AlH3 using x-ray diffraction
JPL	2.4	Complete nuclear magnetic resonance (NMR) characterization on selected alanes
	3	Alane Regeneration: Demonstrate alane regeneration laboratory process
BNL	3.1	Go/No-Go on gas-phase direct rehydriding
SRNL	3.2	Complete electrochemical regeneration cell fabrication and initial tests
SRNL	3.2	Go/No-Go on electrochemical rehydriding of aluminum hydride
BNL	3.3	Complete initial tests on liquid-phase on-board rehydriding
BNL	3.3	Go/No-Go on liquid-phase on-board rehydriding
TBD	3.4	Complete study of off-board regeneration (e.g. NaCl splitting)
BNL	3.5	Downselect alane regeneration approaches for 2010 targets
TBD	3.6	Alane regeneration for 5kg H2 prototype tank
	4	AlH3 tank study: Complete prototype alane tank system meeting 2010 targets
BNL	4.1	Complete study on stability and shelf life of aluminum hydride
BNL	4.2	Output fuel tank design parameters to SRNL
TBD	4.3	Complete alane life cycle analysis
SNL	4.4	Output engineering properties measurements to SRNL