

Aluminum Hydride

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Project ID #
ST 034

Overview

Timeline

- Project start date: FY05
- Project end date: Continuing

Budget

- Funding received in FY10
 - \$800K (DOE)
- Planned Funding for FY11
 - \$200K (DOE)

Barriers

MYPP Section 3.3.4.2.1 On-Board Storage Barriers

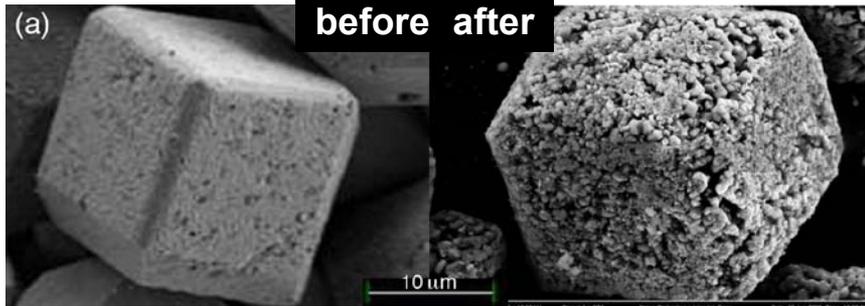
- A.** Weight & Volume
- B.** Cost
- C.** Efficiency
- D.** Durability/Operability
- E.** Charge/Discharge Rates
- R.** Regeneration Processes

Partners and Collaborators

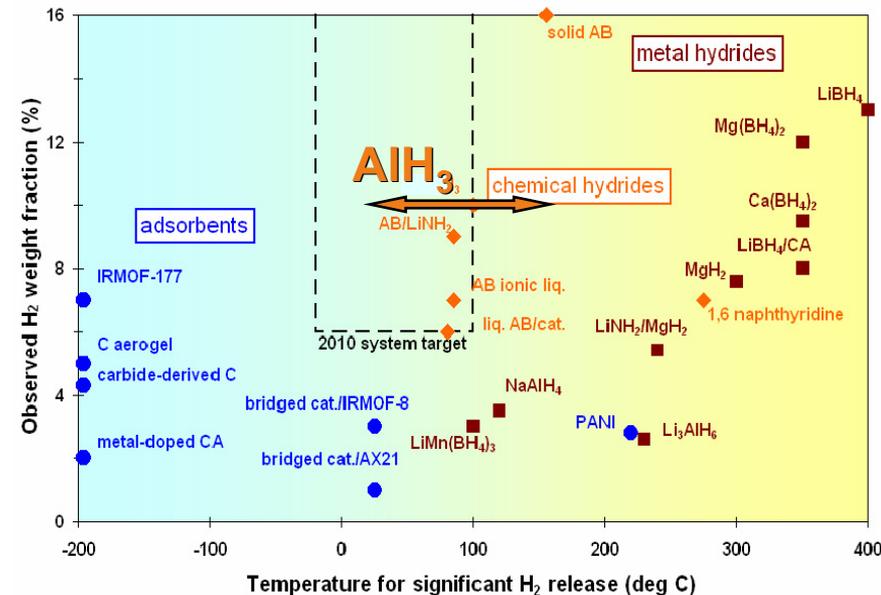
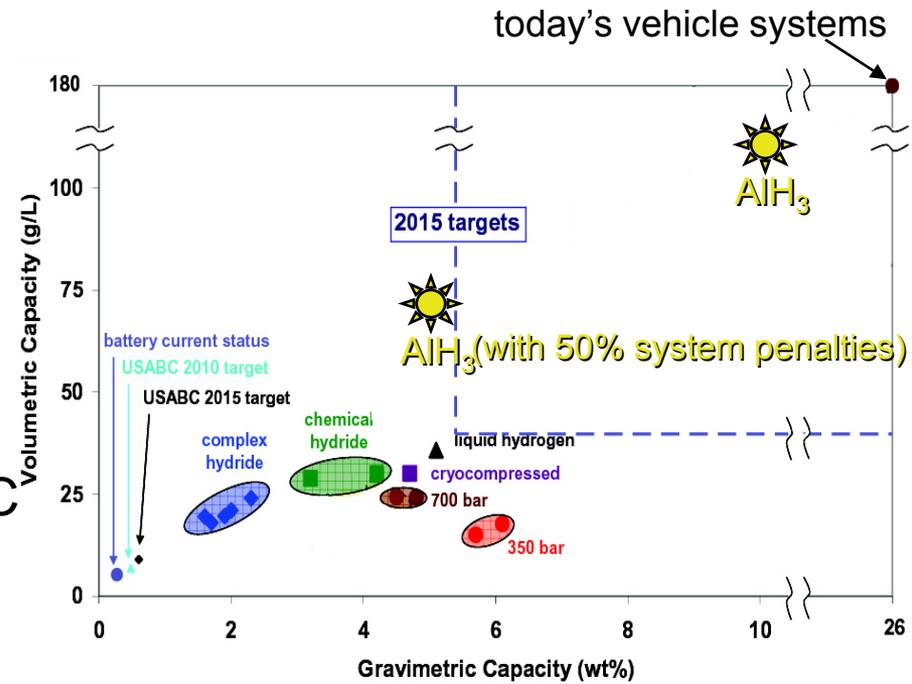
- UH-UNB, ORNL, SRNL, **SNL**
- Other collaborations: JPL, UIUC, ANL
- Chemical Hydride Groups: LANL, PNNL
- International Energy Agency (IEA)

Relevance: AlH_3

- High capacity: **10.1 wt%** and **149 g/L**
- Low decomposition enthalpy:
 $\Delta H \approx 7 \text{ kJ/mol H}_2 (\approx 1/5 \Delta H_{\text{NaAlH}_4})$
- Rapid H_2 evolution rates at low T
 Meets DOE target (0.02 gH_2/s) at $<100^\circ\text{C}$
- Decomposition rates can be tuned through particle coatings
- High purity H_2 - AlH_3 decomposes to Al and H_2 (no side reactions)



Challenge: AlH_3 not “on-board” reversible and decomposition cannot be controlled by H_2 overpressure



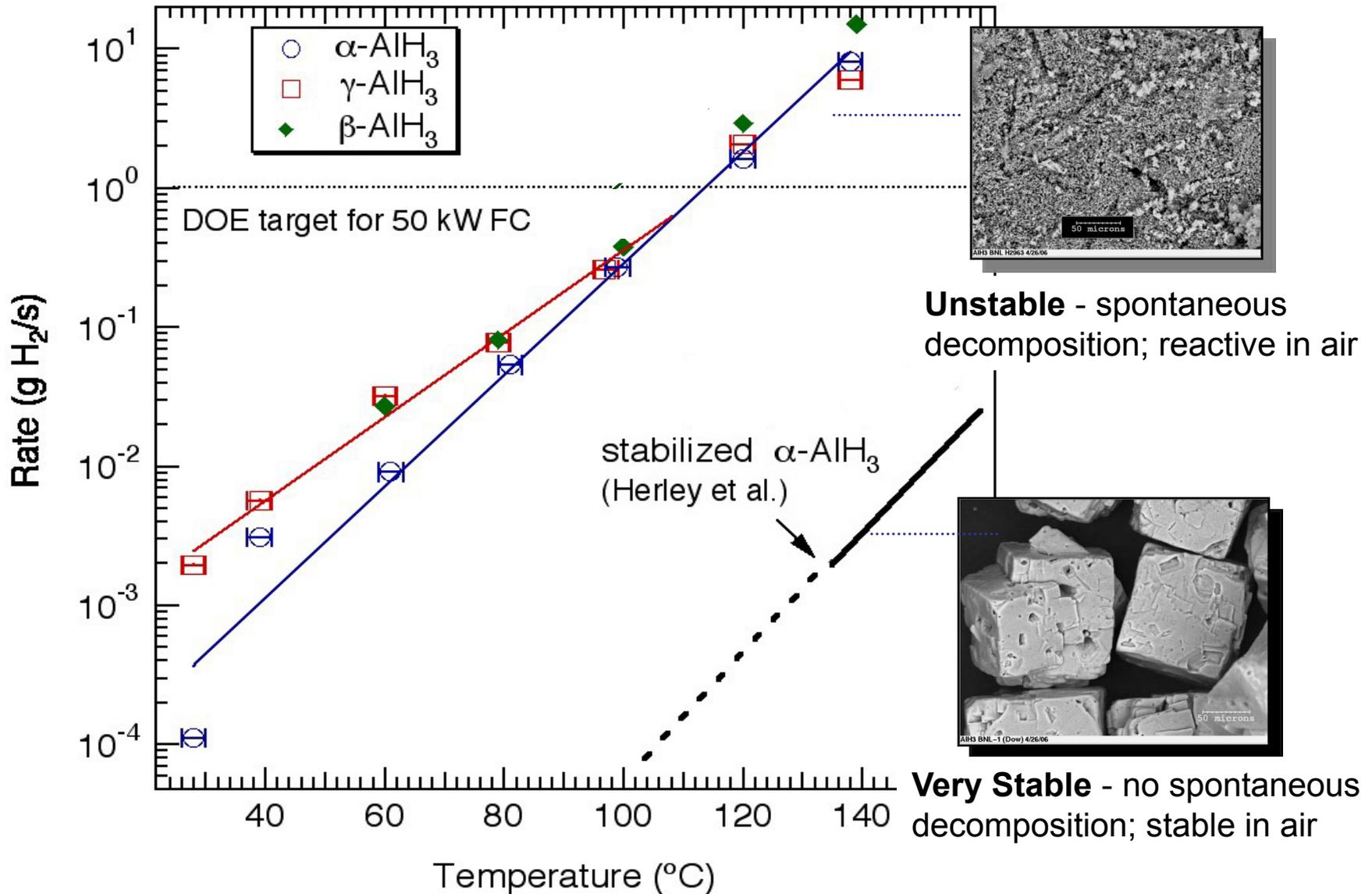
Approach

Objective: Meet DOE technical performance targets using kinetically stabilized aluminum-based hydrides (e.g. LiAlH_4 and AlH_3). Assist the engineering design for an off-board system based on a kinetically stabilized hydride.

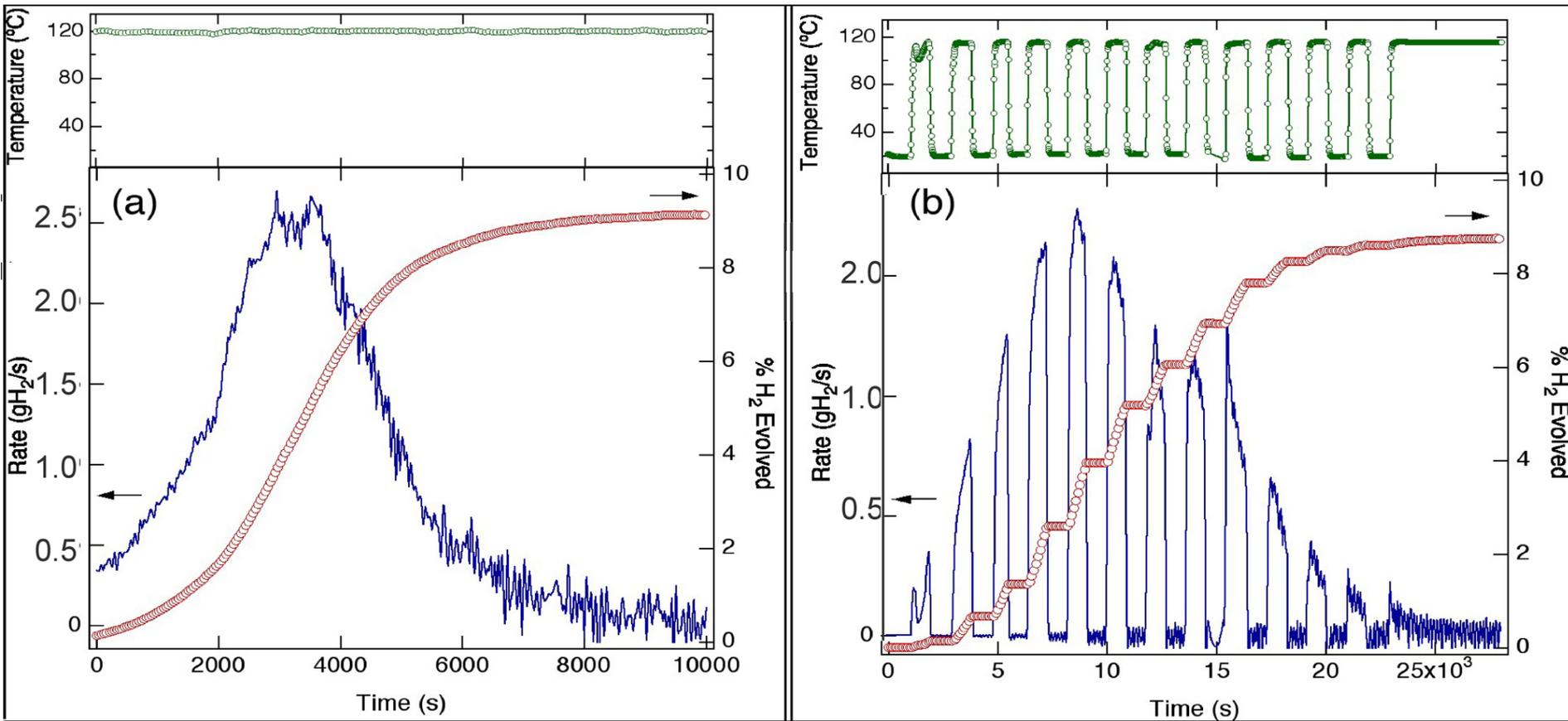
Challenge: Hydrides are thermodynamically unstable at 300K

- 1. System:** How do we control the H_2 evolution? How will a pumpable slurry impact H_2 rates and capacity? Can we tailor hydride properties by altering synthesis conditions?
 - Controlling H_2 evolution rates with temperature
 - Effect of catalysts and slurry media on H_2 rates
 - Preparation of μm -sized AlH_3
 - Rate comparison of AlH_3 powder (nm vs. μm); slurry, and catalyzed slurries
- 2. Regeneration:** How do we reform these hydrides from the spent material using a low cost and low energy process?

AlH₃ decomposition rates

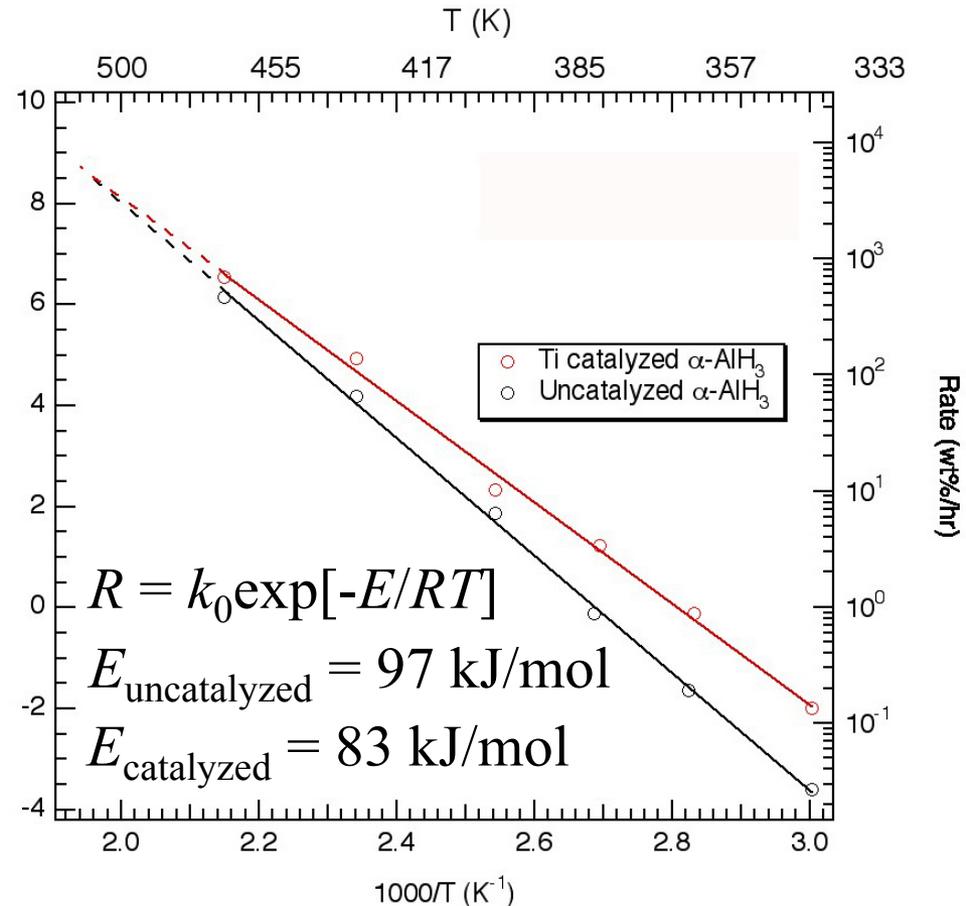
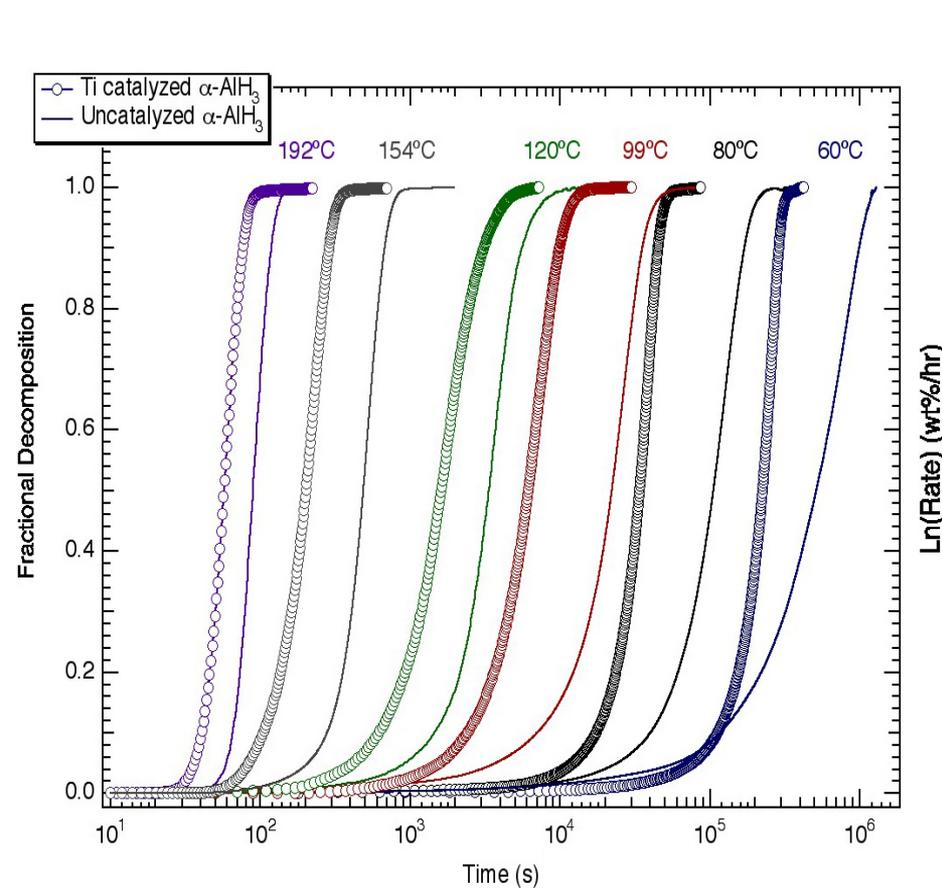


H₂ Release Rates and Thermal Cycling



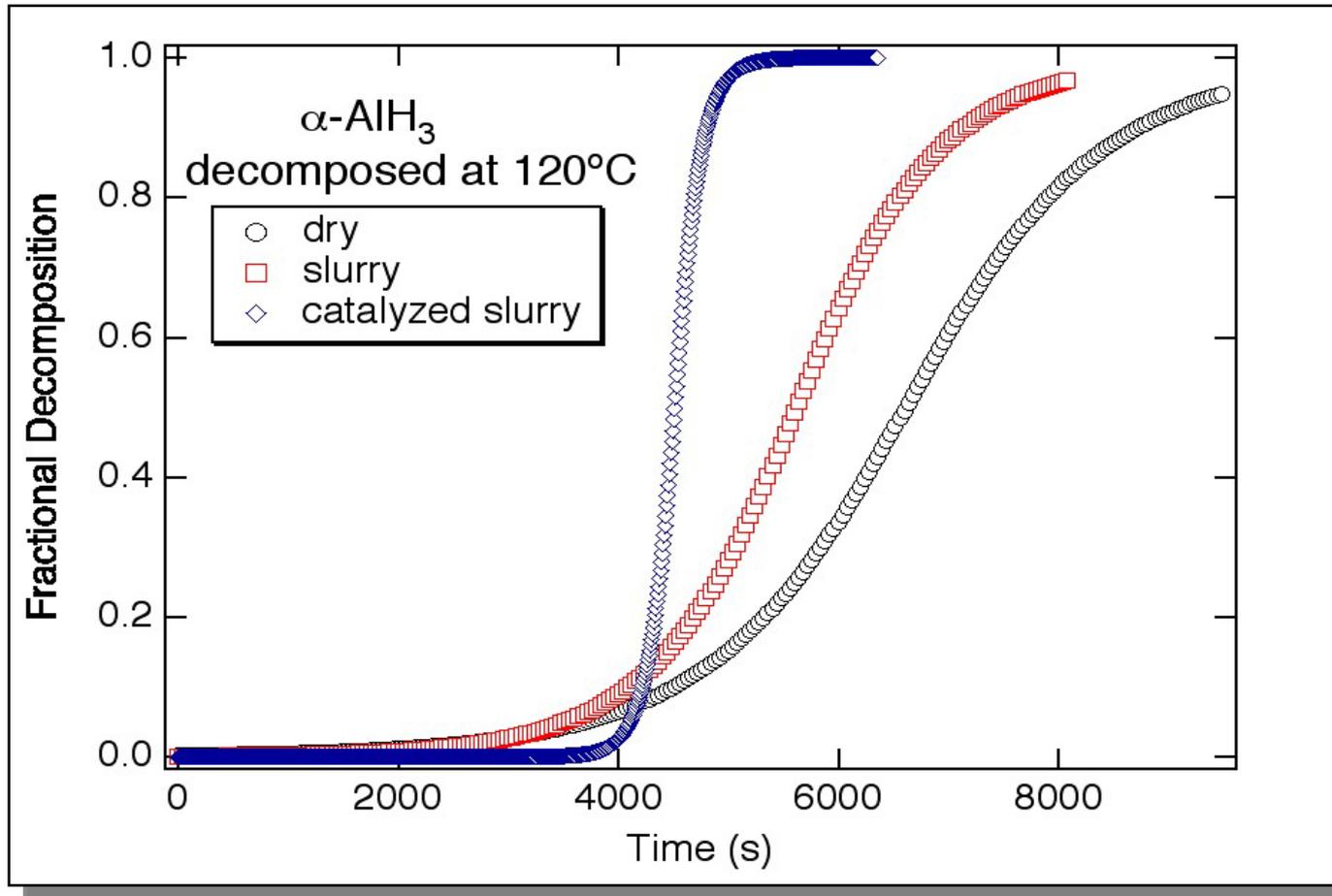
- Decomposition kinetics governed by nucleation and growth of Al with induction (nucleation) and acceleratory (growth) regions
- H₂ release goes to zero as temperature goes to 25°C (On/Off) and rate returns to where it was (before T drop) --> **Rate determined by level of decomposition**

Decomposition isotherms of catalyzed AlH_3



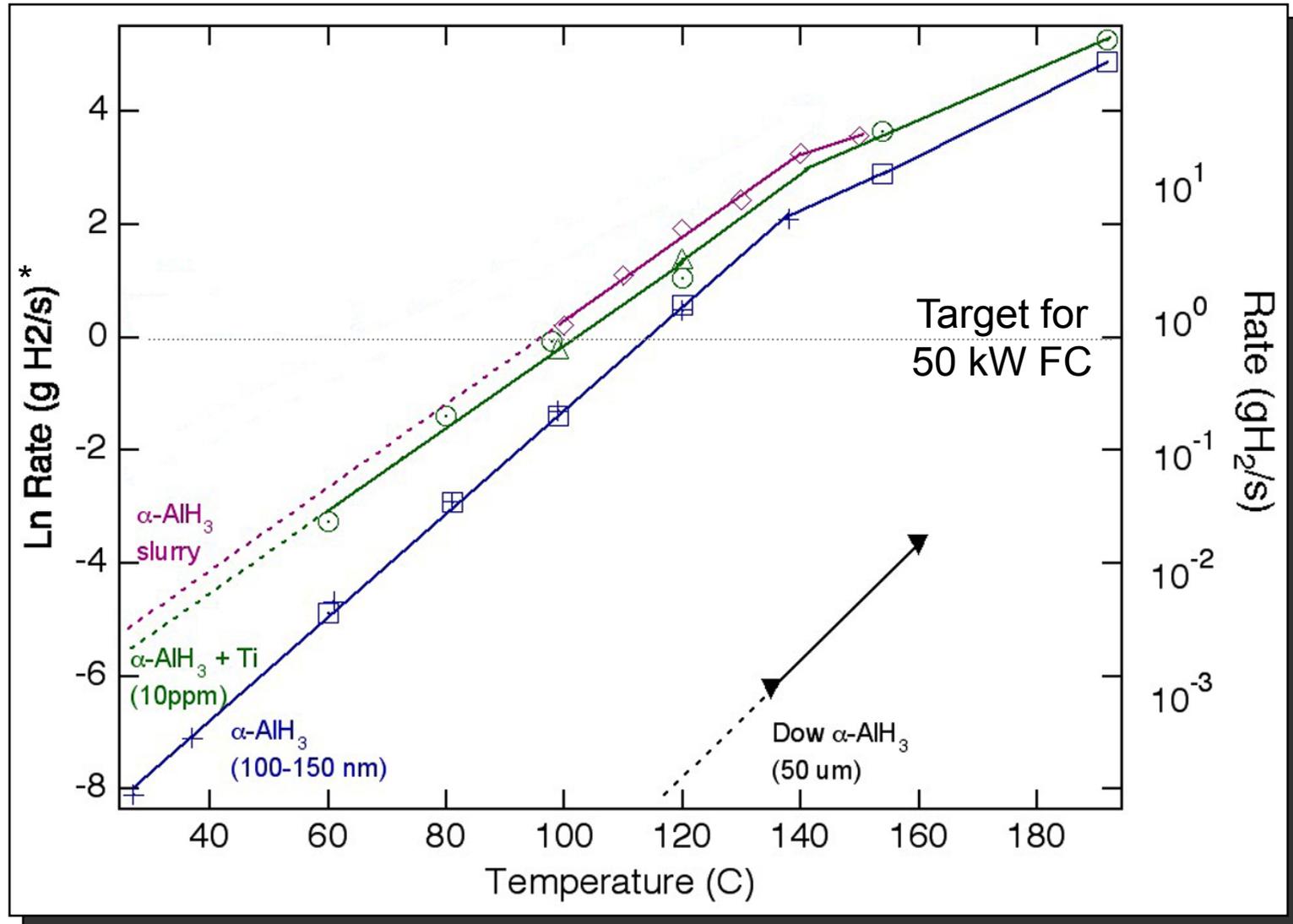
- AlH_3 shows enhanced desorption with 10 ppm Ti
- AlH_3 is completely unstable at Ti concentrations $\geq 0.1 \text{ mol}\%$

Decomposition rates for AlH_3 slurry



- Isothermal decomposition:** (i) pure (dry) $\alpha\text{-AlH}_3$
(ii) $\alpha\text{-AlH}_3$ (60 wt%) in ethylene glycol dibutyl ether (Dibutoxyethane)
(iii) $\alpha\text{-AlH}_3$ (60 wt%) in $\text{C}_{10}\text{H}_{22}\text{O}_2$ with 0.03 mol % Ti as $\{\text{Ti}(\text{OB})_4\}$

Decomposition Rates of α -AlH₃



*based on 100kg AlH₃

Scaling up and increasing crystallite size



Filter

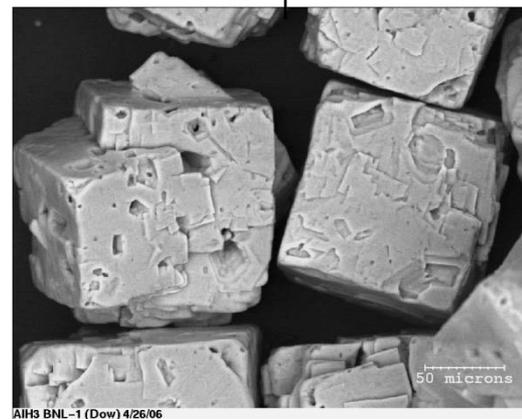
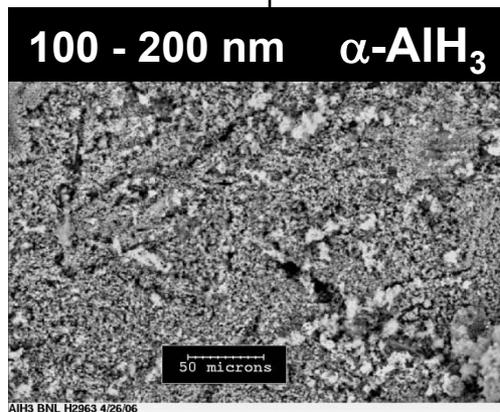
Microcrystallization Reaction

Desolvation

Batch/Continuous Reactions

dry under
vacuum 70°C
with LiAlH_4

4 hrs



$\alpha\text{-AlH}_3$ (Dow) 50-100 μm

- Continuous reaction: desolvation occurs in benzene (or toluene) using a crystallization flask equipped with a fractionation column.
- Etheral AlH_3 solution (w/ $\text{LiAlH}_4 + \text{LiBH}_4$) is added continuously to benzene (or toluene) at $\sim 77^\circ\text{C}$ to distill off Et_2O and precipitate AlH_3 .

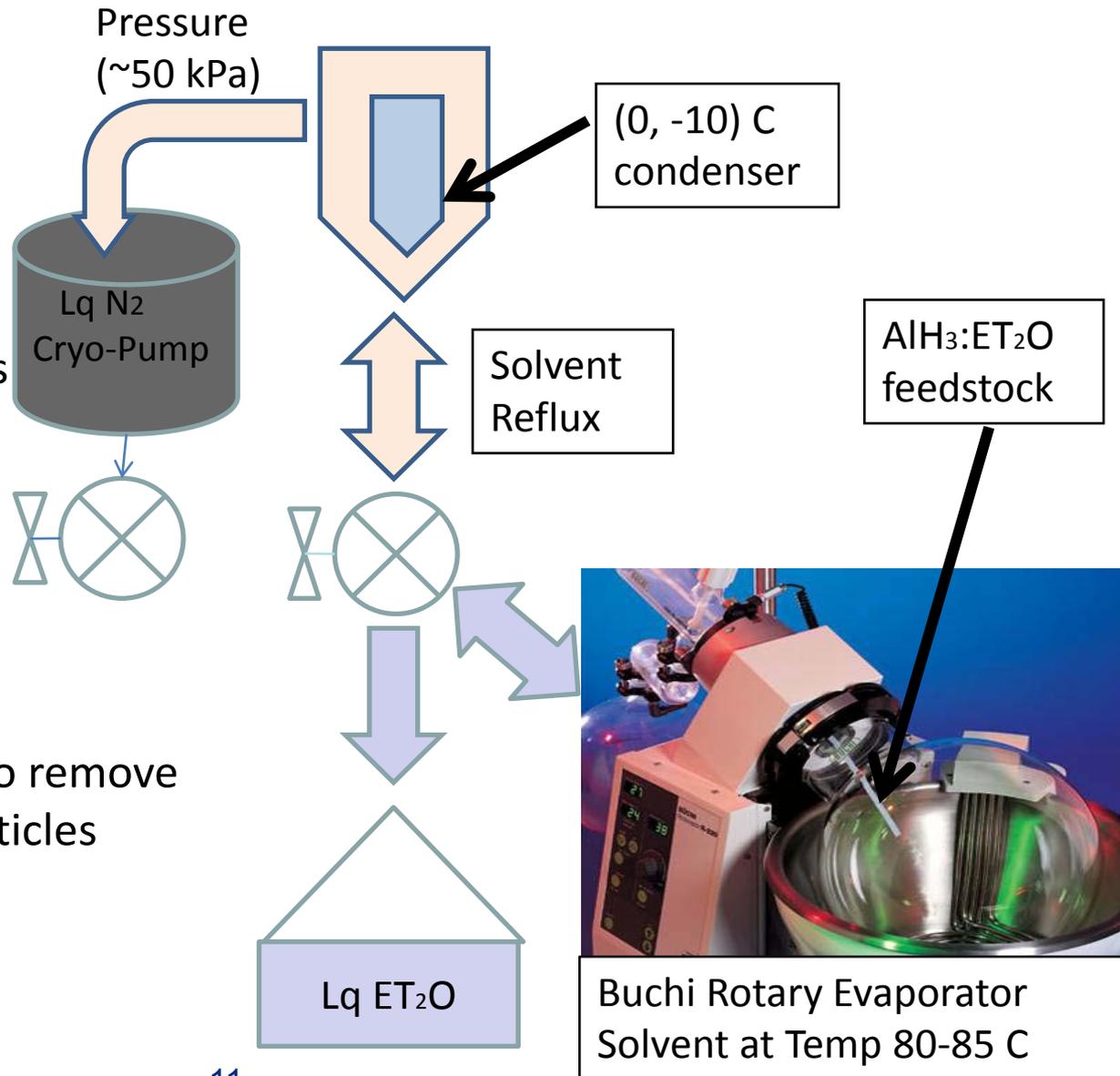
Setup for batch preparation of μm -sized AlH_3

Goal: 6-8 wt% H_2 slurry with viscosities 1000 - 2000 cP

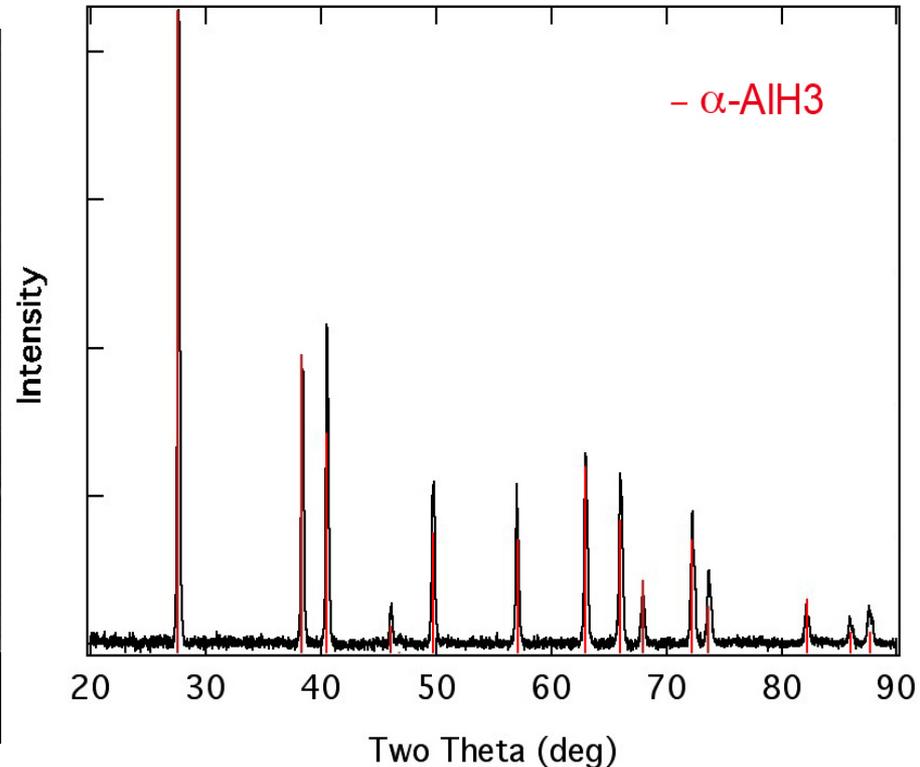
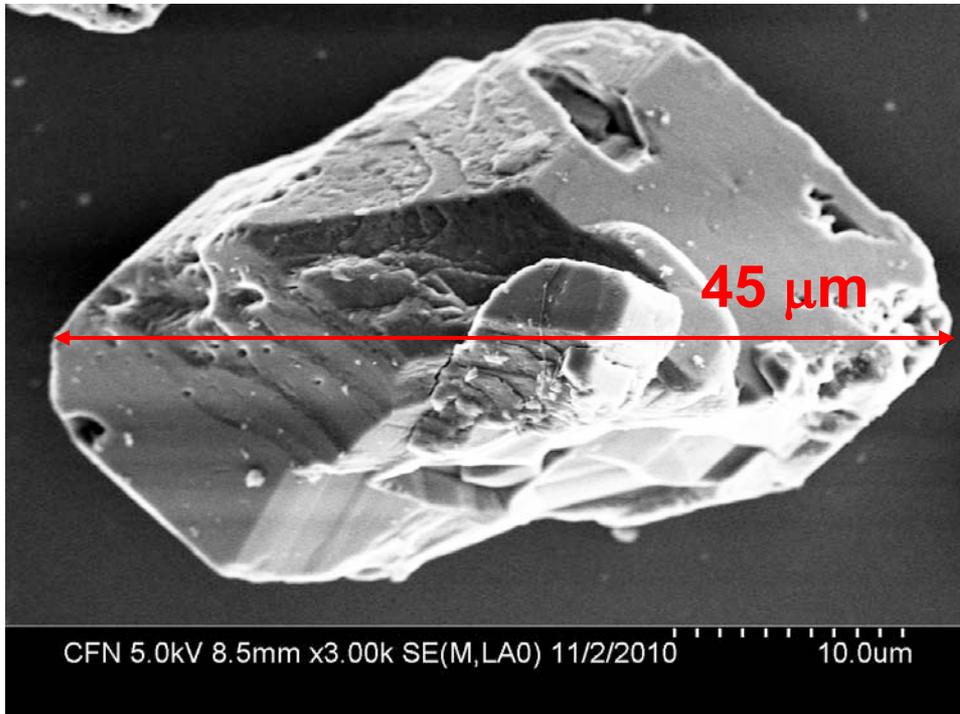
Typical particle size with “dry process” 100-150nm, but we need $\sim 50 \mu\text{m}$ particles for suitable packing/slurry densities

First step is same: $\text{AlCl}_3 + \text{LiAlH}_4$ in Et_2O , but we desolvate in toluene

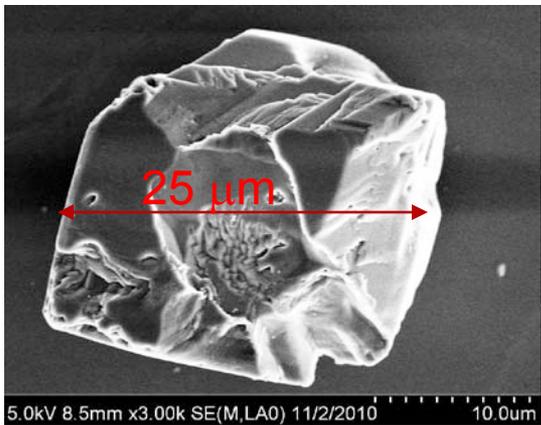
Last step is dilute acid wash to remove impurities and small AlH_3 particles



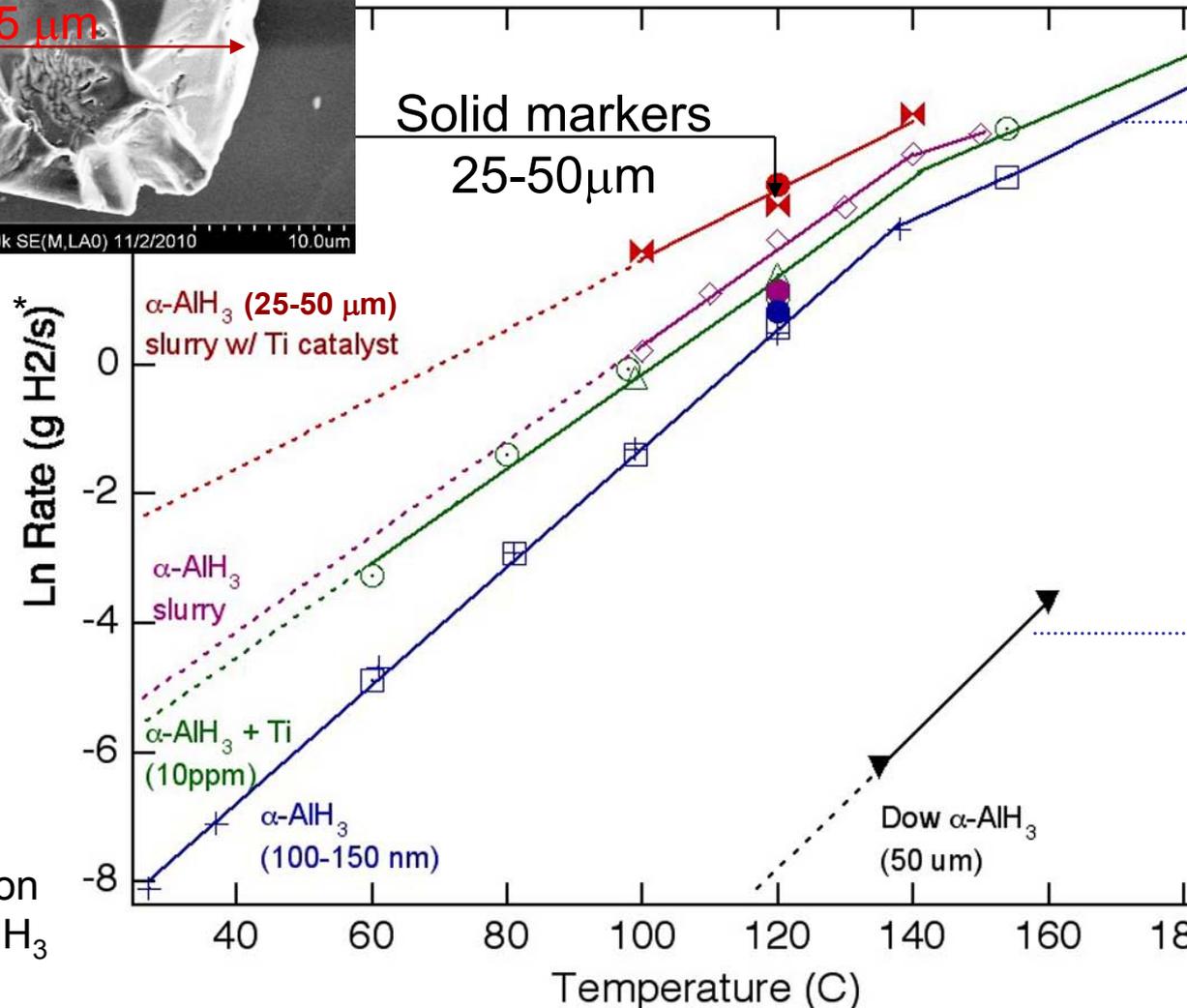
Preparation of μm -sized particles of AlH_3



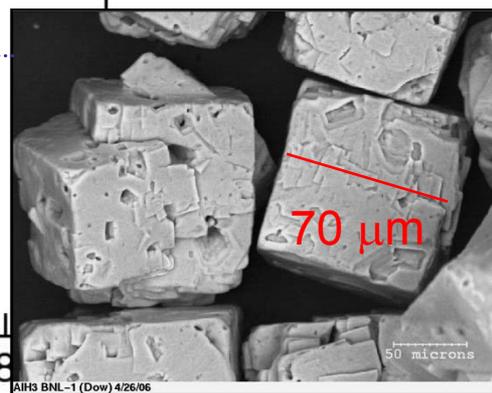
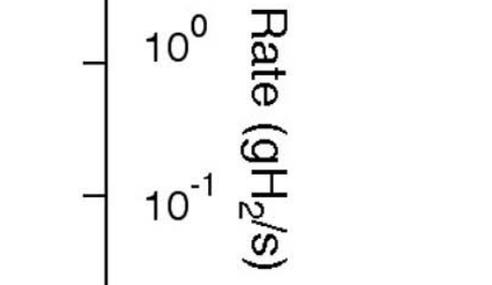
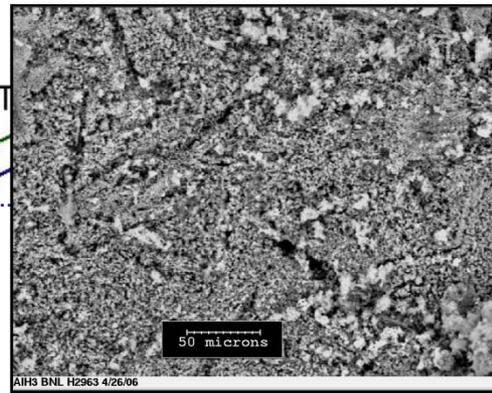
- Large crystallites (20-40 μm) of $\alpha\text{-AlH}_3$ prepared ($\sim 1\text{-}2\ \text{g}$ batch)
 > 9.5wt.% H_2 after dilute acid wash
- Decomposition rate is much faster than DOW alane material



5.0kV 8.5mm x3.00k SE(M,LAO) 11/2/2010 10.0um



*based on 100kg AlH₃



- Particle size **does not** significantly affect kinetics – Stability of Dow AlH₃ likely due to surface coating(s) not crystallite size
- Slurry (60wt% AlH₃) shows rapid decomposition rates <100C

Regeneration of aluminum-based hydrides

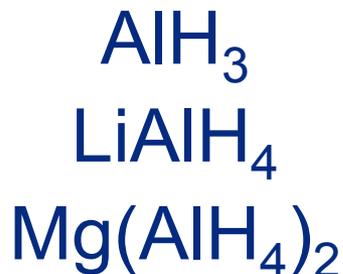
Direct hydronation requires extremely high pressure - can we “regenerate” using a low cost and low energy process?

Two-step approach to regeneration of Al-based hydrides:

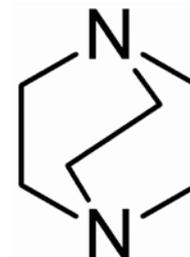
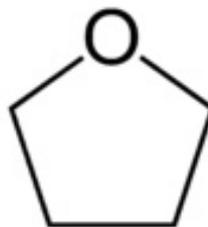
Step I (stabilization): Form stabilized alane or alanate adduct by direct hydrogenation of catalyzed Al and stabilizing molecule (e.g. amine (TEDA, TMA), ethers (THF, Et₂O, Me₂O))

Step II (separation): Remove stabilizing species and recover hydride (alane / alanate)

Metastable hydrides:



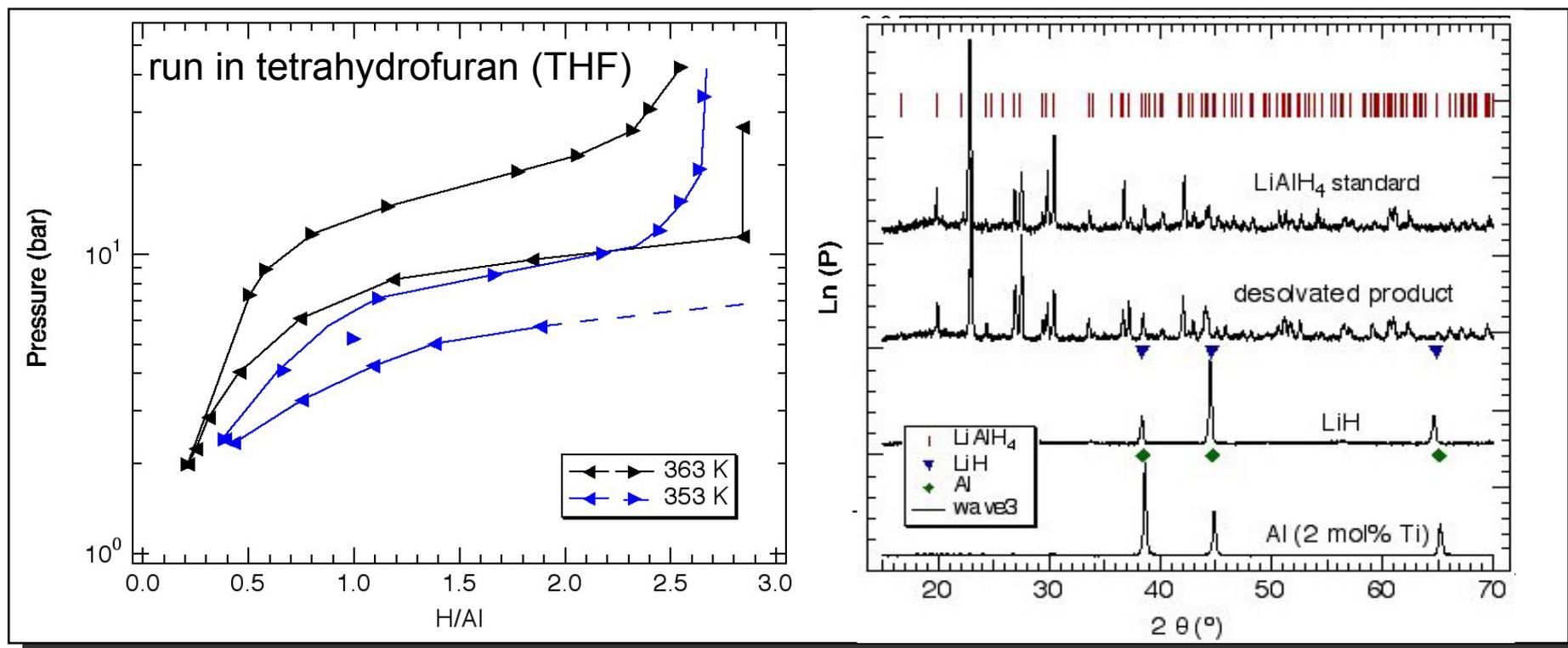
Stabilizers:



ethers (THF) amines (TEDA)

Regeneration of LiAlH_4

LiAlH_4 is considered an “irreversible” complex hydride, but the adduct $\text{LiAlH}_4\text{-THF}$ is formed under relatively mild conditions



Reversible hydrogenation of $\text{LiH} + \text{Al}^*$ in THF at low pressure (~1 bar) and room temperature ($\Delta G_{298\text{K}} = -1.0 \text{ kJ/mol H}_2$)

Regeneration of AlH_3

Step 1: formation of $\text{NR}_3\text{-AlH}_3$ by direct hydrogenation

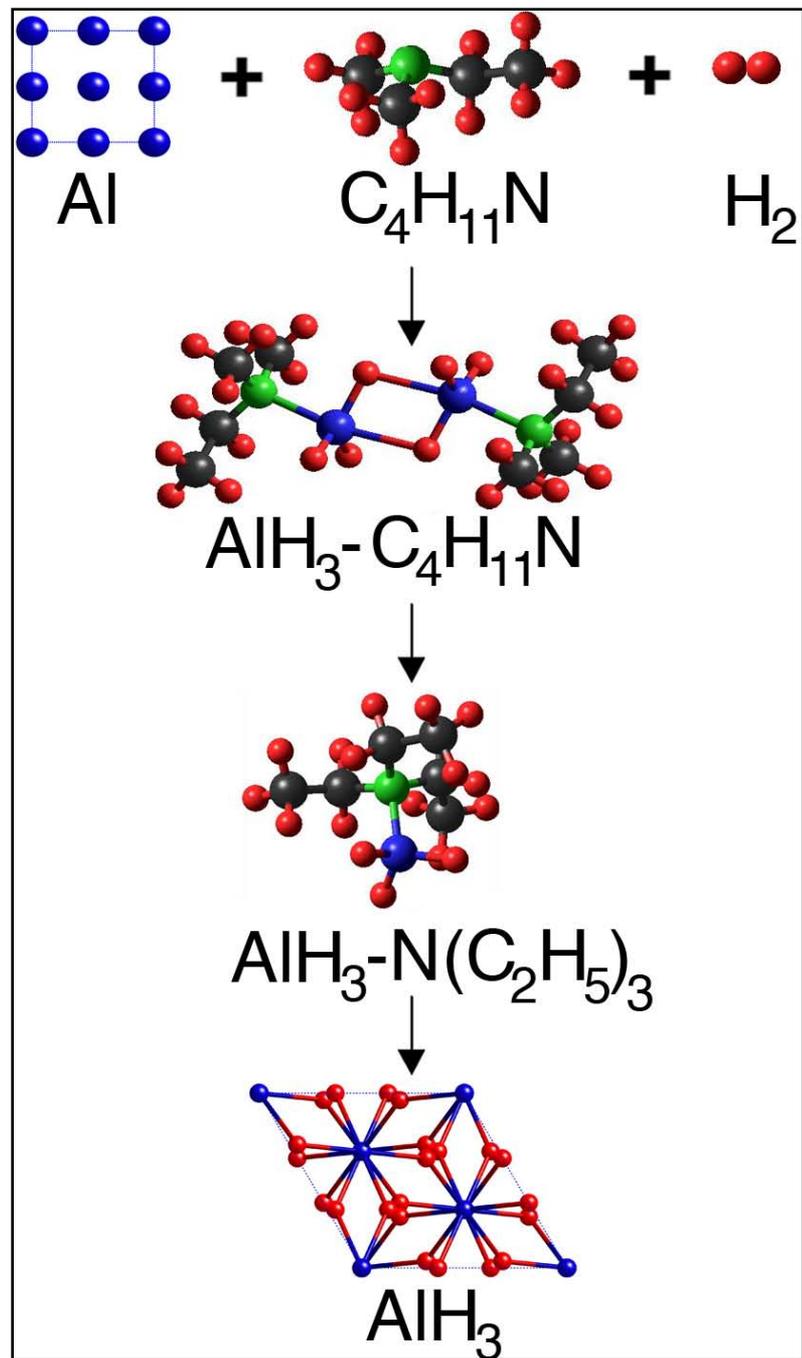
- Five alane adducts formed by direct hydrogenation under mild conditions
- conversion up to 90% (of starting Al)

Step 2: transamination exchange NR_3 for TEA

- Transamination demonstrated starting with DMEA and TMA
- conversion >50% (exact value unknown)

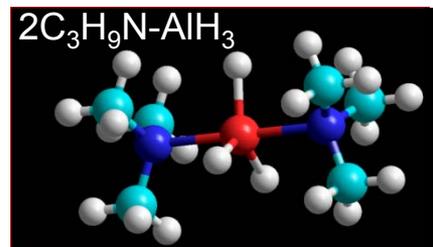
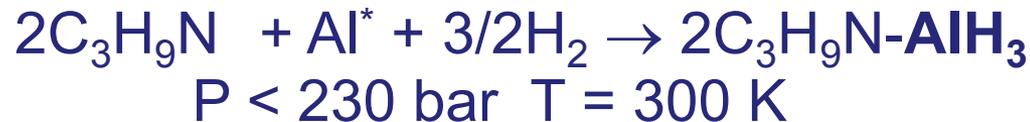
Step 3: separation of TEA-AlH_3

- Separation of TEA-AlH_3 successful
- >90% AlH_3 recovery (<10% Al)
- Well-to-tank efficiency estimates of 40-55% using this route with TMA (WTT target is 70%)

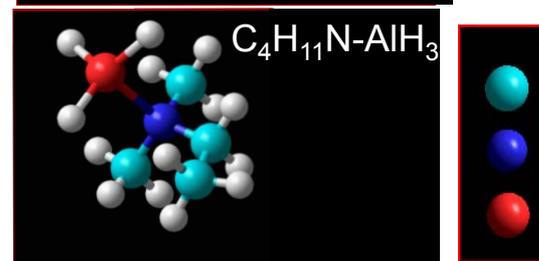
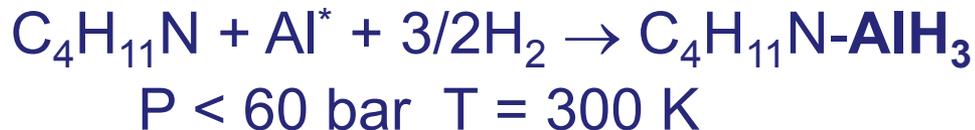


Step 1: Low pressure AlH₃ formation

Trimethylamine (TMA) alane:

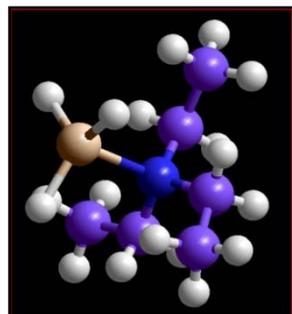
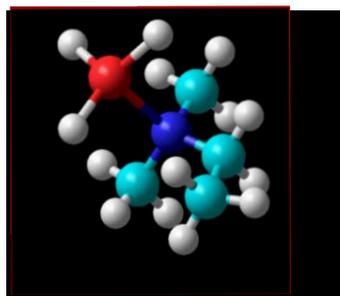


Dimethylethylamine (DMEA) alane:



Carbon
Nitrogen
Aluminum

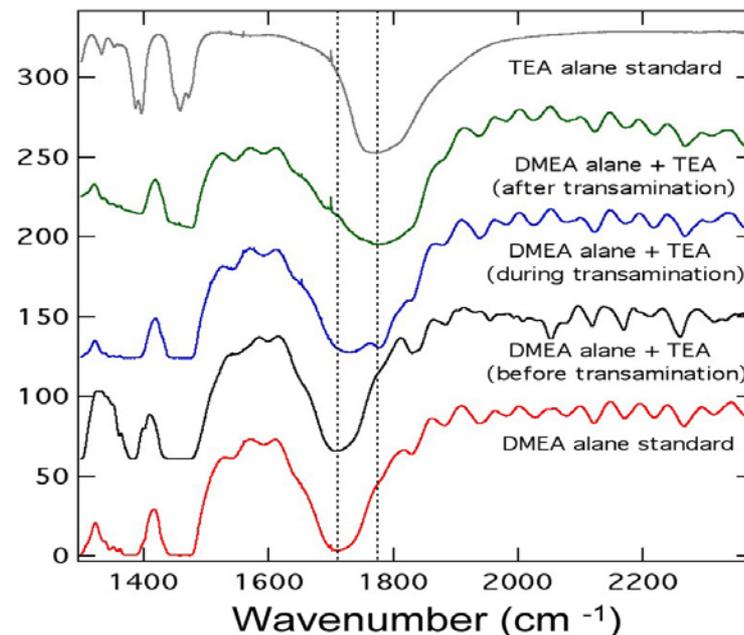
Step 2: Amine exchange (transamination)



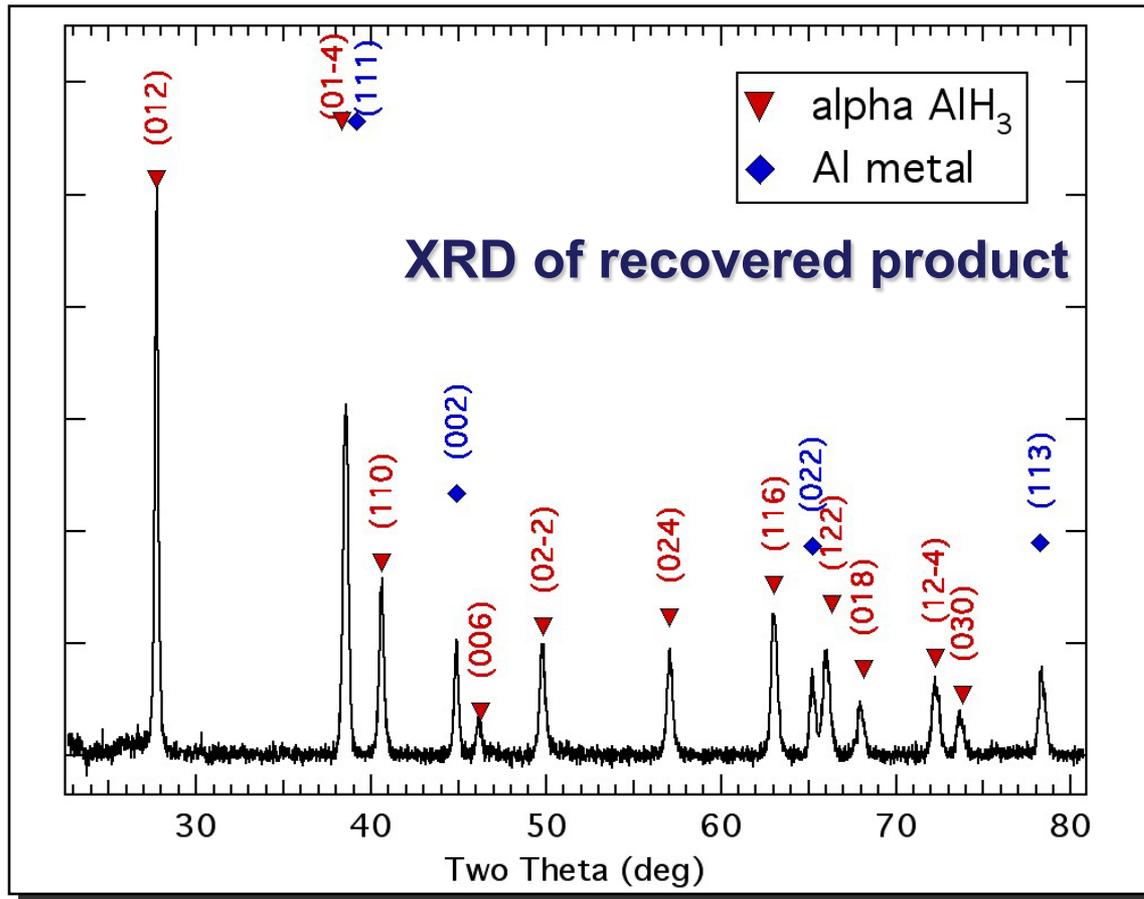
DMEA-AlH₃

TEA-AlH₃

DMEA-AlH₃ + 4TEA
T = 50°C, P_i = 1 bar
P_f = 26 mbar, 4.5 hrs



Step 3: Separation of TEA-AlH₃



- TEA-AlH₃ successfully separated at 70°C under vacuum (<100 mbar)
- Analysis of recovered AlH₃ suggests >80% AlH₃ with <20% Al
- With recent improvements in separation >90% AlH₃ (<10% Al)

Summary of accomplishments and future work

- Demonstrated thermal control over H₂ evolution rates - H₂ rate determined by level of decomposition
- Slurries of 60wt% AlH₃ (40wt% dibutoxyethane) showed enhanced H₂ rates compared to dry powder; fastest rates w/ catalyzed AlH₃ slurry
 - Continue to develop alane slurries and explore use of nonionic dispersants: **Goal:** 6-8 wt% H₂ with viscosity 1000-2000 cP
- Preparation of 20-50 μm AlH₃ - showed rates similar to 100 nm AlH₃
 - Improve large particle synthesis and increase batch size
 - Work with Engineering Center to develop AlH₃ system
- **Low cost regeneration remains the critical challenge:** Promising pathways identified, but we need to improve and optimize process:
 - Pathway 1: **Al + H₂ + TMA → AlH₃-TMA $\xrightarrow{\text{TEA}}$ AlH₃-TEA → AlH₃**
 - Pathway 2: **Al + H₂ + DMEA → AlH₃-DMEA $\xrightarrow{\text{TEA}}$ AlH₃-TEA → AlH₃**
 - How does cycling affect the “activity” of the Ti-Al catalyst?
 - Need to combine steps 1-3 and optimize yield and efficiency and continue work with ANL to determine mass balance & energy cost

Supplemental Slides

Energy consumption for AlH₃ regeneration (per kg H₂ in AlH₃)

Process (TMA route)	Operating Conditions			Q, MJ	E, kWh
	T, °C	P, bar	Reflux ratio		
Compress H ₂ from SMR to 30 bar	70	30			0.3
Compress circulating H ₂ to 30 bar	70	30			0.6
Distill trimethylamine	65	5	1.0	28.6	
Distill ether	25	0.3	0.3	22.9	1.1
Decompose triethylamine alane	50	0.2		20.2	1.4
Vacuum dry alane product	50	10 ⁻⁴ - 10 ⁻¹		0.2	0.2
Total				71.9	3.6

- Without using wasted heat, well-to-tank (WTT) efficiency is 40.5%
- Using wasted heat for thermal energy increases WTT to 55%
- **Target is 70%** - improvements possible by reducing excess H₂, TMA and TEA, switching to gas flow (rather than vacuum) and using DMEA

Efficiencies based on 100% conversion during hydrogenation, 75% conversion during transamination and 75% recovery from separation.

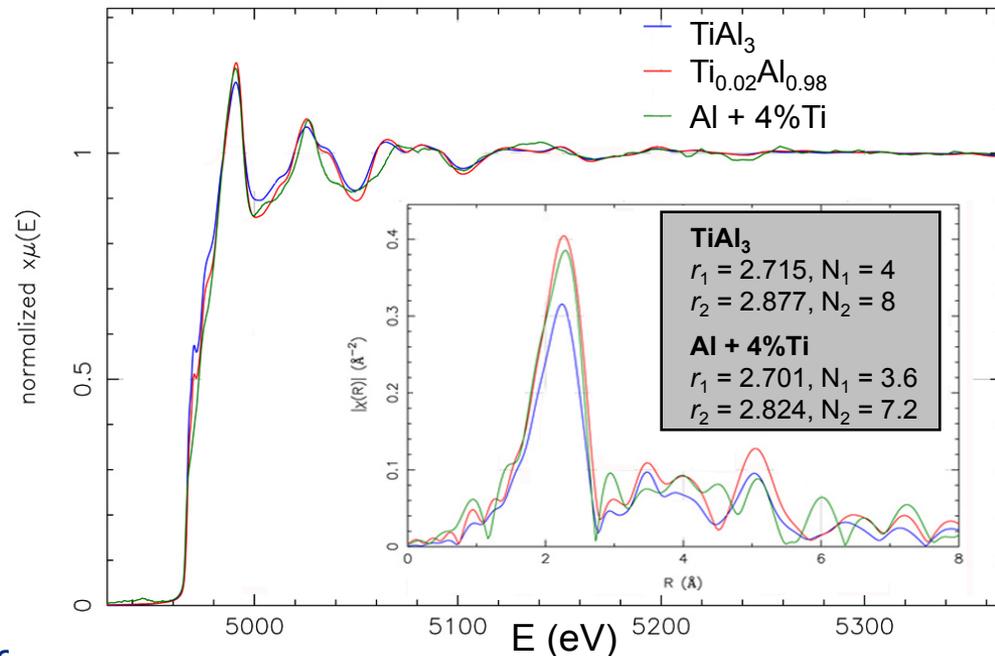
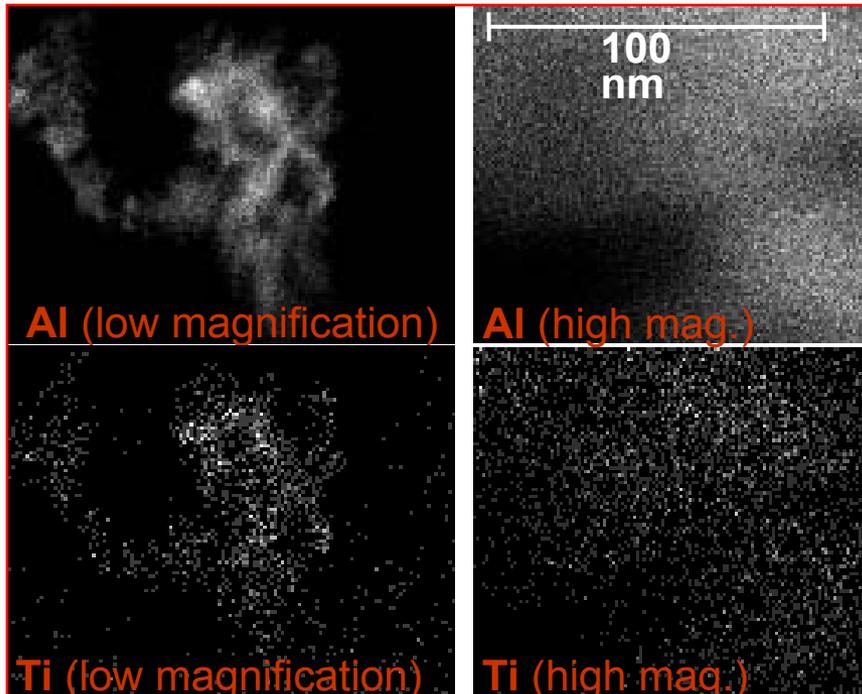


Preparation of catalyzed Al

- Ti catalyzed Al (Al*) prepared by first making AlH_3 with TiCl_3 in ether and then decomposing the ether adduct

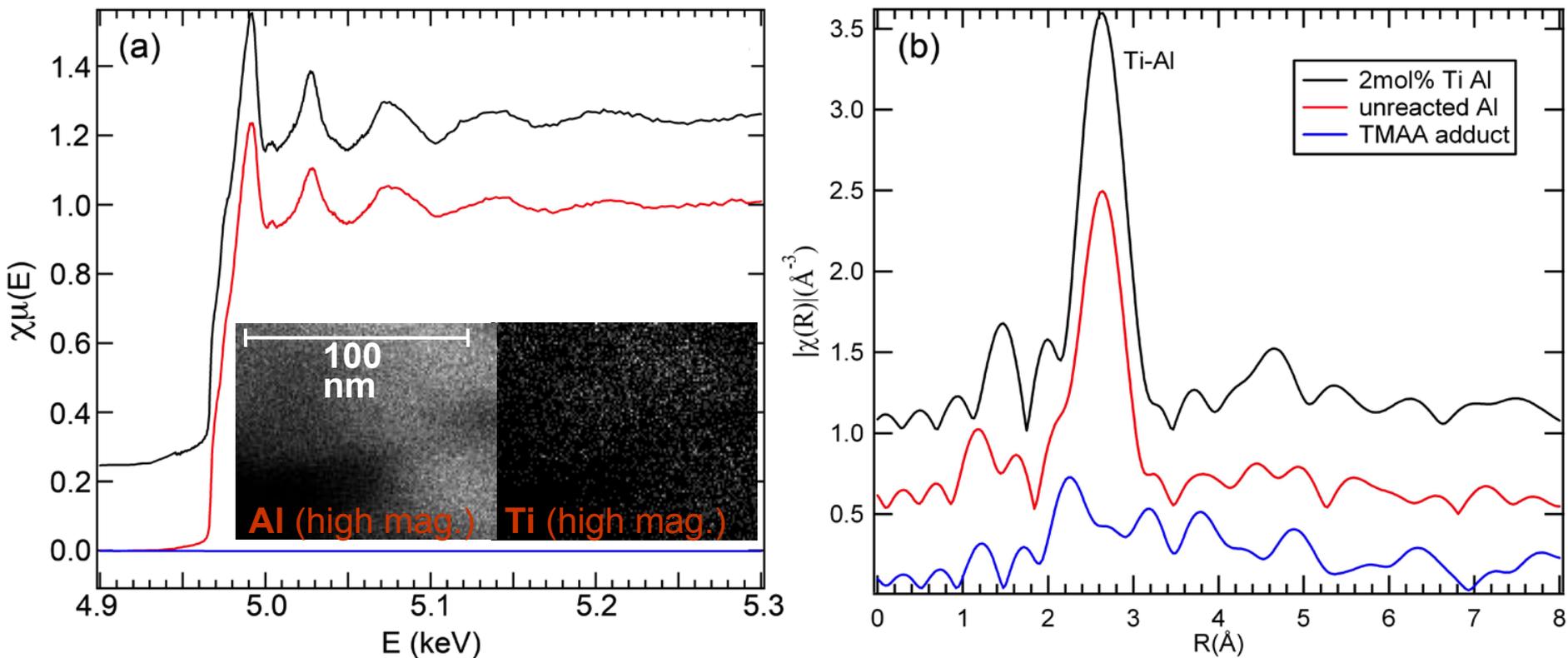


- grain size = 165 nm; Ti well-dispersed throughout Al



Location of Ti after adduct formation

Ti necessary for hydrogenation, but Ti destabilizes LiAlH_4 and AlH_3 and must be removed in the final product - where is Ti after hydrogenation?



- In initial Al^* the Ti is well-dispersed throughout Al
- After hydrogenation Ti concentrated in unreacted Al
- **No detectable Ti in recovered solid alane/alanate adducts**

AlH₃ temperature-pressure phase diagram

