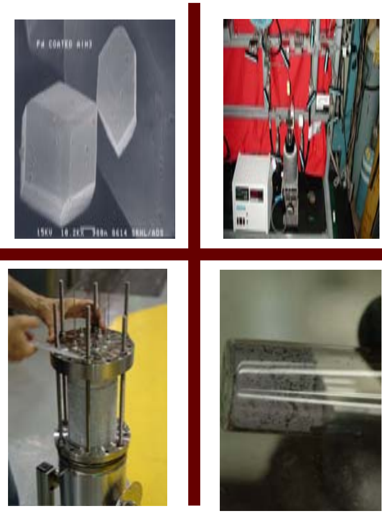
METAL HYDRIDE CENTER OF EXCELLENCE

Development of Reversible Hydrogen Storage Alane



SRNL™
SAVANNAH RIVER NATIONAL LABORATORY
We Put Science To Work

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Savannah River National Laboratory

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This presentation does not contain any proprietary or confidential information

Project ID#: STP20

Overview

Timeline

- Project Start: March 2005
- Project End: TBD
- Percent Complete: <5% new start

Barriers

- General Onboard H2 Storage (A-G)
- Reversible Solid-State Material Storage (M-Q)
- Target is to meet DOE 2007 and 2010 Hydrogen Storage Goals

Budget

- Total Project Funding: $200K/yr
  - DOE Share: 100%
  - Contractor Share: NA
- $0 receive in FY04 (new start)
- $200K received in FY05

Partners

- Brookhaven National Laboratory
- Sandia National Laboratory
- University of Hawaii and other CoE partners as needed

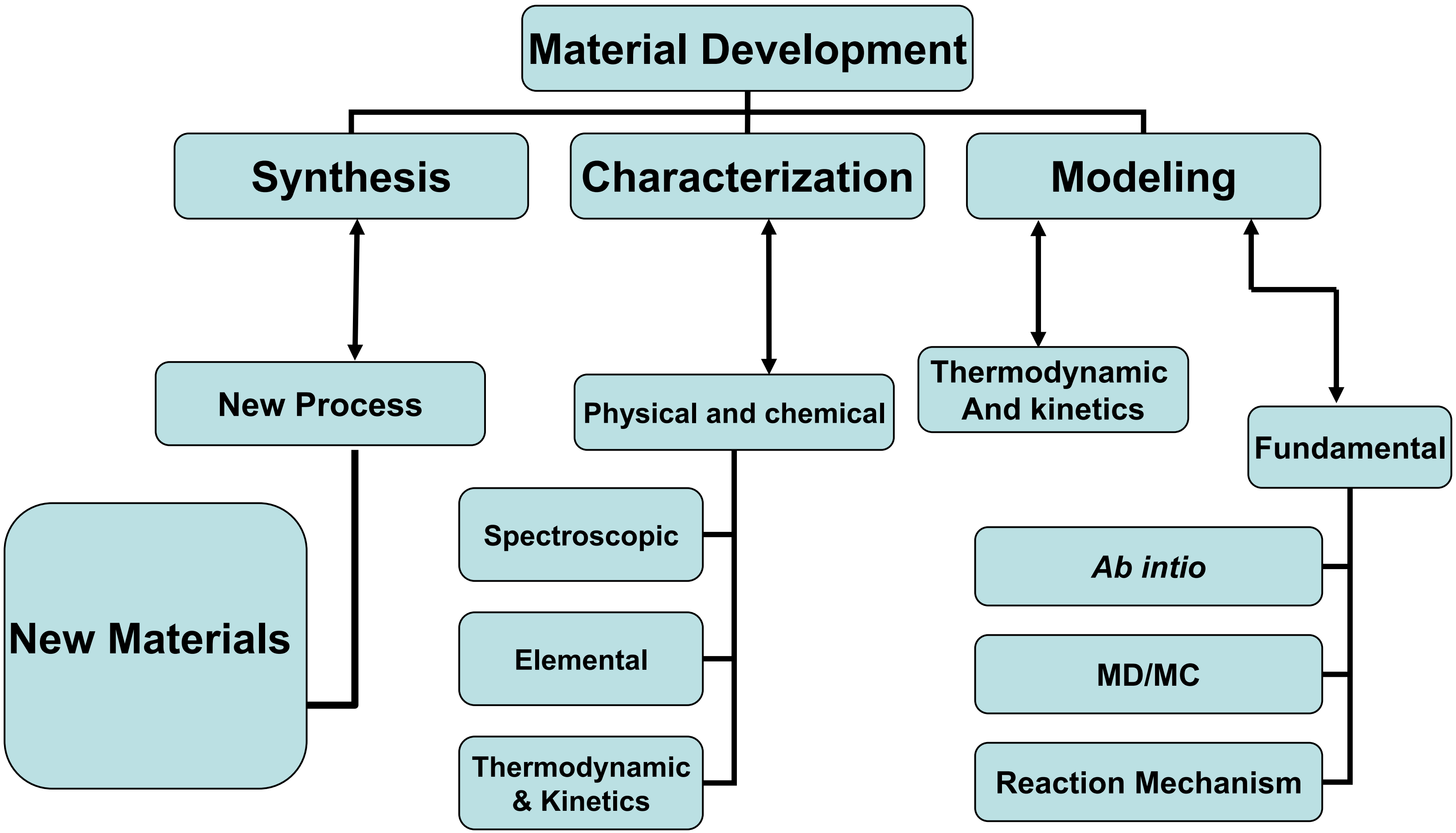
Objective

The ultimate objective of this research is to develop a low-cost hydrogen storage material based on aluminum hydride with high capacity, cyclic stability and possessing favorable thermodynamics and kinetics compatible with the DOE onboard hydrogen transportation goals.

Specific Objectives

- Design and fabricate a novel high pressure cell to efficiently charge aluminum hydride (alane)
- Test and evaluate feasibility of cell for alane charging
- Characterize and analyze charged alane materials for structure, purity and yield

SRNL Approach



Reported High Capacity Al Complexes

Composition	Mol. Wt.	Wt.%H2
$Be(AlH_4)_2$	71.04	8.45
$Mg(AlH_4)_2$	86.33	6.95
$Ca(AlH_4)_2$	102.11	5.88
$Sr(AlH_4)_2$	149.65	4.01
$LiAlH_4$	37.95	7.91
$NaAlH_4$	54.00	5.56
$KAlH_4$	70.10	4.28
$CsAlH_4$	171.13	1.75
$Ti(AlH_4)_4$	171.95	8.14
AlH_3	30.00	10.0

Alane

AlH_3= 10% wt

- Savannah River leads Hydrogen Charging

- Brookhaven leads Hydrogen Discharging

Some sample preparation, exchange and confirmation of structures will be done by others.

Alane Formation

- Alane formation, from the elements, has been reported to occur under very high pressure conditions
- Or plasma Conditions
- Or by non-economical chemical reactions
- Competing reaction can lead to unstable phases
- Innovative methods are needed to recharge

SRNL Program Plan

Alanes

- **Task 1 - High Pressure Cell Design and Fabrication**
  A high pressure cell to synthesize alanes at reasonable operating conditions will be designed and fabricated. The cell will take advantage of a new SRNL design (patent pending).

- **Task 2 – High Pressure Cell Testing and Material Synthesis**
  The new cell will be installed in the SRNL high pressure laboratory and synthesis operations will be initiated. The goal of this task is to demonstrate a new process for producing stable high capacity alanes at reasonable operating conditions. The key to the first year effort is the development of stable alane materials. A GO NO GO decision will be made after the first year with respect to the potential of using this process for developing suitable high capacity hydrogen storage materials.

- **Task 3 – Characterization**
  Structural characterizations and physical property analyses will be employed to identify material purity and yield. X-ray diffraction and differential scanning calorimetry (DSC) analyses will be the primary tools. X-ray diffraction will be used to determine phase structure, lattice parameters and a preliminary assessment of the volume fractions of the material produced.

Summary of Progress and Results

- **Basic thermodynamic and diffusion considerations were made and preliminary cell design is under way**
- **Preliminary alane materials were characterized (SEM, XRD)**
- **Preliminary material were evaluated for hydrogen release (TGA, TPD TVA)**
- **High pressure test system capabilities were established**

Basic Thermodynamics

- **Pressure and chemical potential**

$$\Delta G = \Delta H - T\,\Delta S$$

$$RT \ln f = \Delta H - T\,\Delta S$$

$$\ln P = \Delta H / RT - \Delta S / R \text{ (low pressure)}$$

- **Phase and competing reactions**

Dehydrided Phase will be used

Diffusion of Hydrogen

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) = \nabla D.\nabla C + \underline{\underline{D\nabla^2 C}}$$

In one dimension :

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \frac{\partial D}{\partial x}\frac{\partial C}{\partial x}$$

or

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \frac{\partial D}{\partial C}\left(\frac{\partial C}{\partial x}\right)^2$$

Non-linearity hinders rate of diffusion

Diffusion of Hydrogen

Periodic and non-periodic systems

Fraction of occupied state expressed by Fermi - Dirac distrubtion :

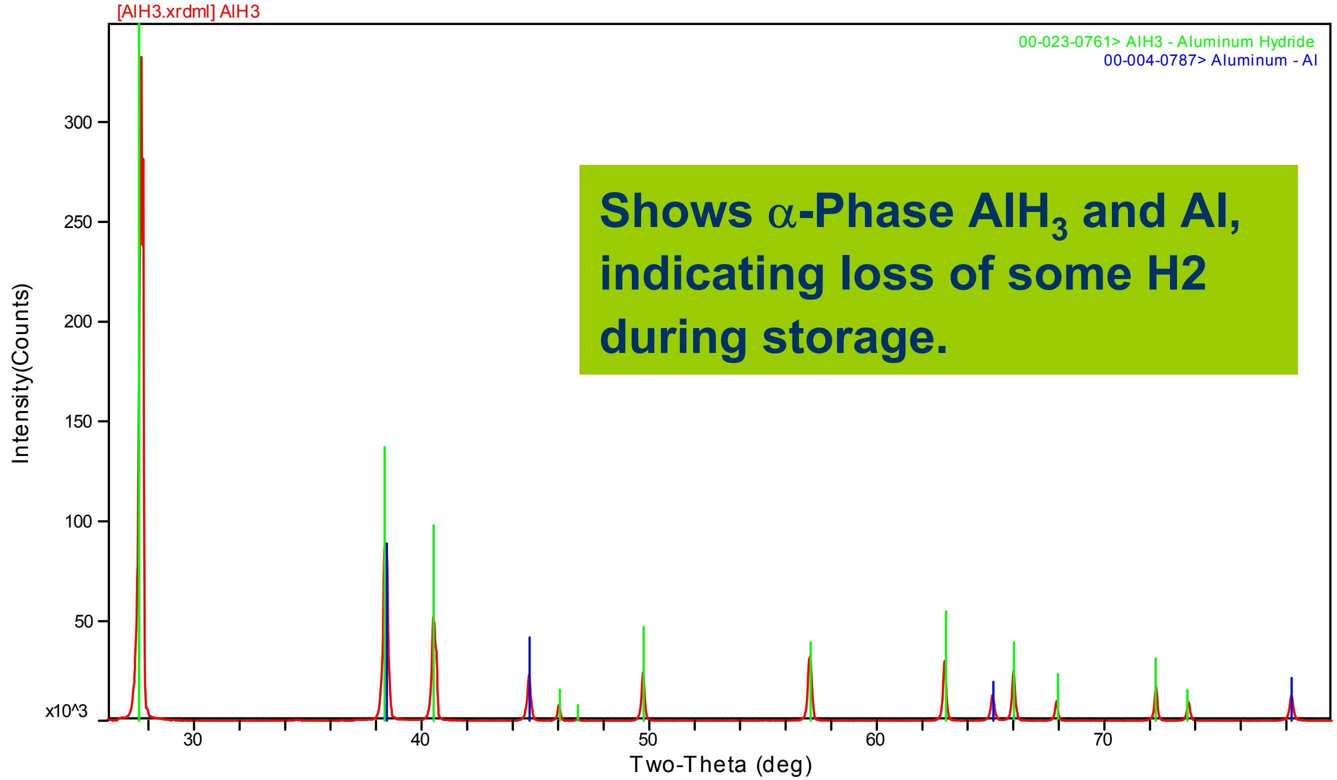
$$C = \sum_i \frac{\delta(E_i - E_m)}{1 + \exp\left(\frac{E_i - \mu}{KT}\right)}$$

$$\delta(E_i - E_m) = \lim_{\sigma \to 0}\left\{\frac{1}{\sqrt{\pi}\sigma}\exp\left(\frac{(E_i - E_m)^2}{\sigma^2}\right)\right\}$$

In general

$$C = \frac{1}{\sqrt{\pi}\sigma}\sum_i \frac{\exp\left(\frac{(E_i - E_m)^2}{\sigma^2}\right)}{1 + \exp\left(\frac{E_i - \mu}{KT}\right)}$$ $\sigma \to 0$ for periodic structure

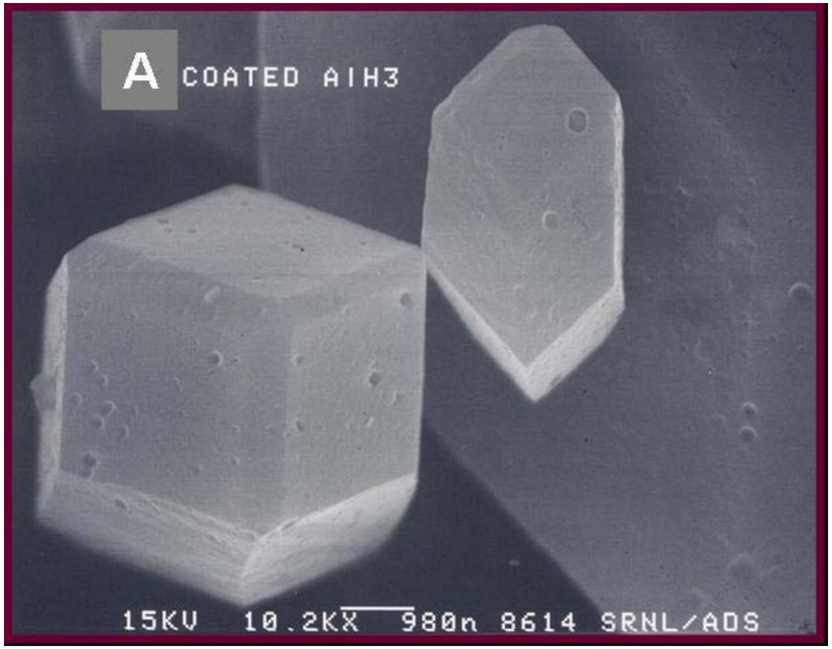
Structure Characterization - XRD

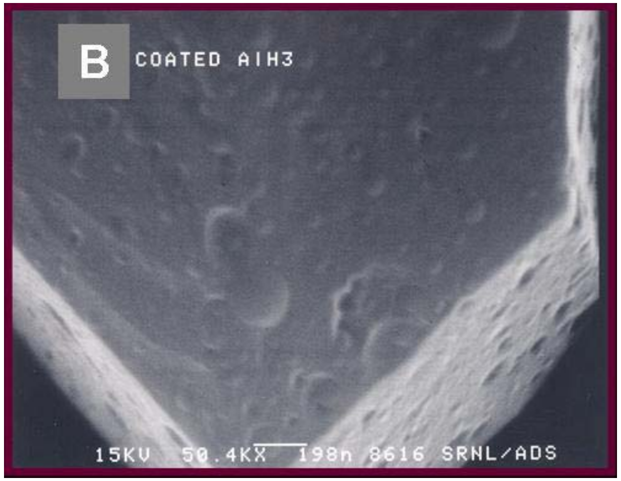


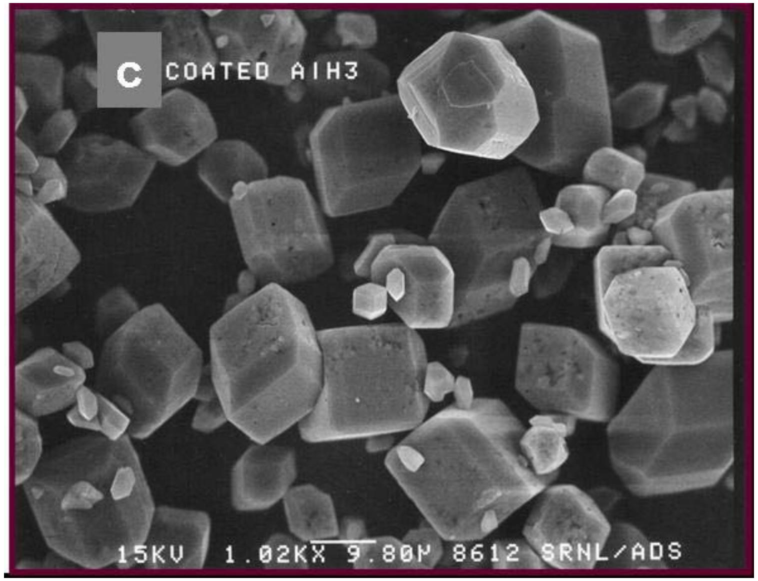
Shows α-Phase AlH_3 and Al, indicating loss of some H2 during storage.

Sample is polymer coated, obtained from United Technology Research Center (UTRC)

SEM Images of Alane







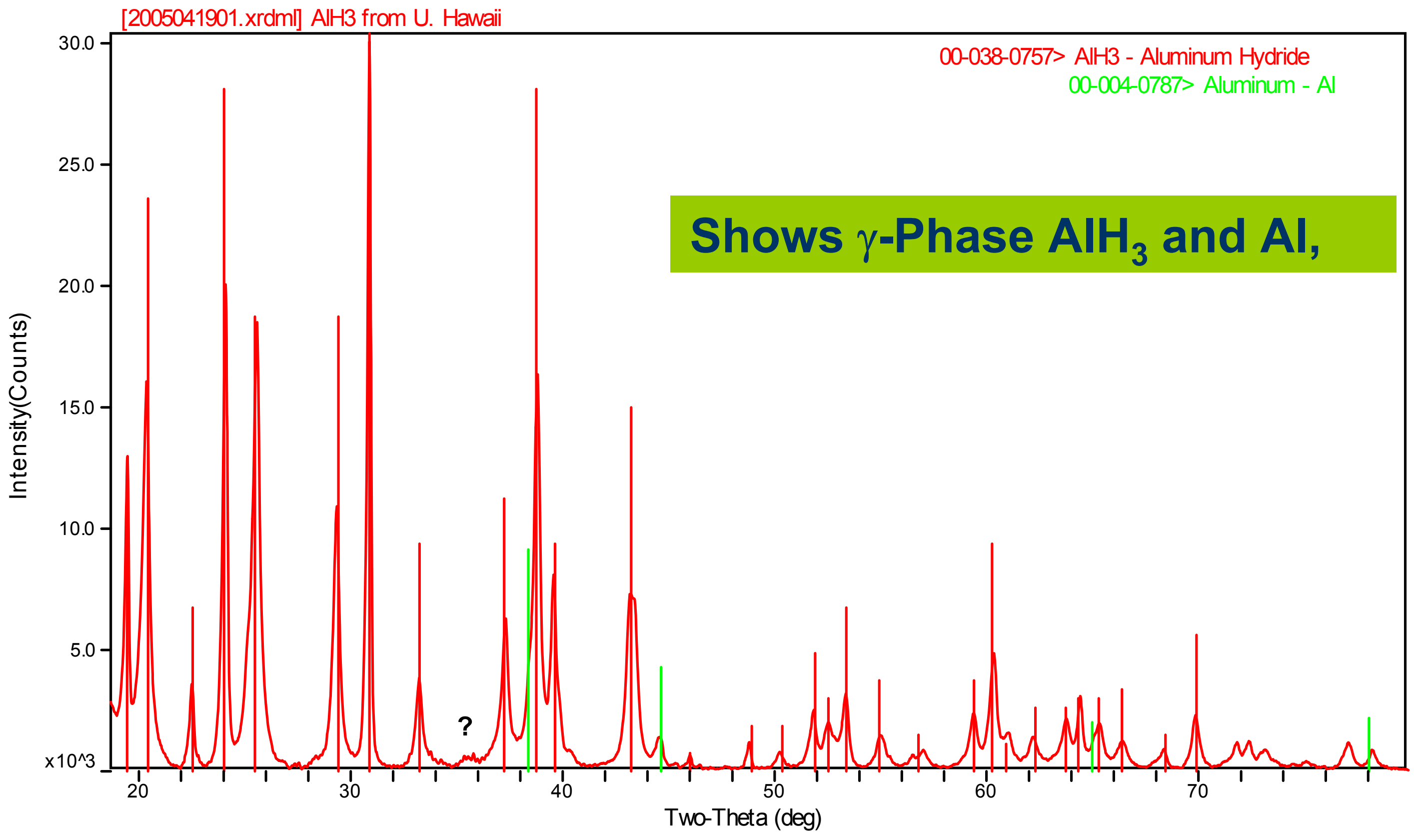
A. **SEM image showing the Crystalline shape of AlH_3**

B. **The surface of the crystals shows pitted areas, indicating hydrogen leak**

C. **SEM image showing the particle size**

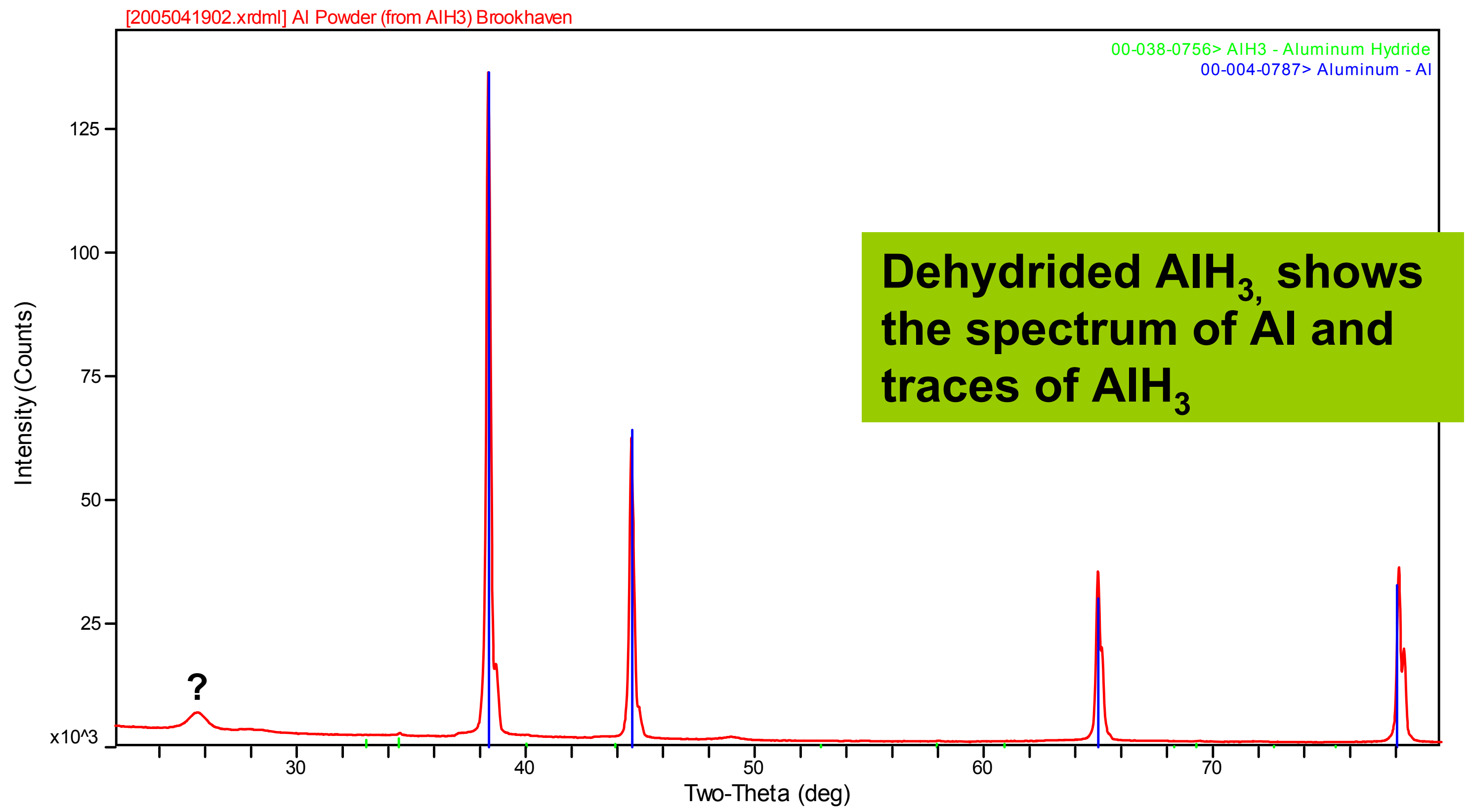
Sample is polymer coated, obtained from United Technology Research Center UTRC

Structure Characterization - XRD



Sample was chemically prepared and provided by Professor Craig Jensen from University of Hawaii

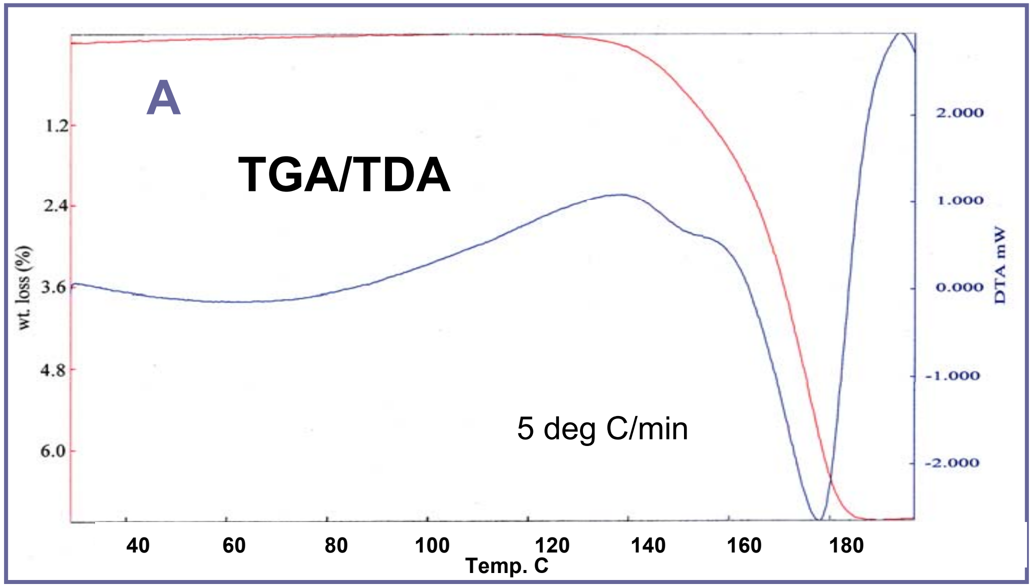
Structure Characterization - XRD



Dehydrided AlH_3, shows the spectrum of Al and traces of AlH_3

Sample was provided by Brookhaven National Laboratory (BNL)

Hydrogen Release from Alane



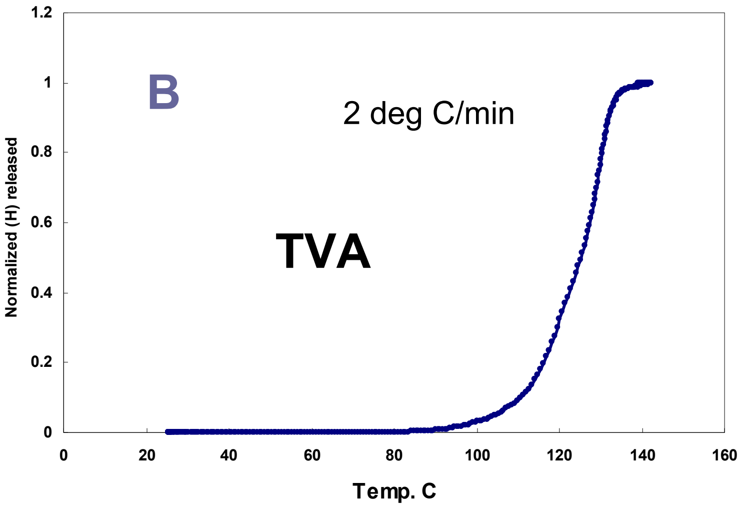
Weight % Released = 7.2 H

Heat of Reactions = -7.6 kJ/mol

Thermal Programmed Desorption (TPD) of hydrogen from AlH_3 Using:

A) Thermogravimetric analyzer (TGA)

B) Thermovolumetric analyzer (TVA)



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High Pressure Characterization System

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Future Work

- Complete cell design & fabrication (SRNL patent pending)
- Install cell in SRNL high pressure laboratory and initiate charging tests.
- Perform structural characterization and physical property analyses to identify material purity and yield (XRD, DSC)
- Arrive at GO NO GO decision after first year on potential of process for producing suitable high hydrogen capacity storage materials
- If successful continue to develop and refine process for future deployment in collaboration with other CoE partners

Recent Publications and Presentations

Publications:

"Synthesis and crystal structure of Na2LiAlD6" ***J. Alloys and Compounds Volume 392, Issues 1-2, 19 April 2005, Pages 27-30,*** **H.W. Brinks, B.C. Hauback, C.M. Jensen and R. Zidan**

"Synergistic effects of co-dopants on the dehydrogenation kinetics of sodium aluminum hydride" ***J. alloys and compounds Volume 391, Issues 1-2, 5 April 2005, Pages 245-255*** **J. Wang, A.D. Ebner, R. Zidan and J.A. Ritter**

"Effect of graphite as a co-dopant on the dehydrogenation and hydrogenation kinetics of Ti-doped sodium aluminum hydride" ***J. Alloys and Compound, in press*****, Jun Wang, Armin D. Ebner, Tanya Prozorov, Ragaiy Zidan and James A. Ritter**

Presentations:

•Hydrogen Economy Workshop, ***Invited Speaker, for the Department of Energy,*** **(1)Hydrogen Storage R&D Key Issues for the Hydrogen Economy, (2)Solid-State Hydrogen Storage Systems Cairo Egypt January 31 – February 2, 2005**

•ASM Material Solution Conference, ***Invited Speaker,*** **Development and Characterization of Complex Hydrides, Columbus, OH Oct. 18- 21 2004**

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