# Hydride Development for Hydrogen Storage

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*Livermore, California*

*Combining Fundamental Science,*
*Materials Development and Engineering Science*

# Sandia's Hydrogen Storage R&D Objective

*Practical hydrogen storage using light-weight reversible hydrides*

The lack of a safe and practical means of onboard hydrogen storage is one of the biggest obstacles to the realization of hydrogen powered transportation.

## Goals

- Meet or exceed US-DOE / FreedomCAR Hydrogen storage targets
- Improve performance: capacity, kinetics, thermodynamics, and cycle life
- Expand knowledge of hydrogen sorption phenomena in solid-state media

# Sandia's Hydrogen Storage R&D Capabilities Strong & Expanding

## People

*$H_2$ Storage Research Team (DOE & internally funded)*

- 5 Staff members
- 1 Post-doc
- 3 Technologist
- 2 Students

## Facilities

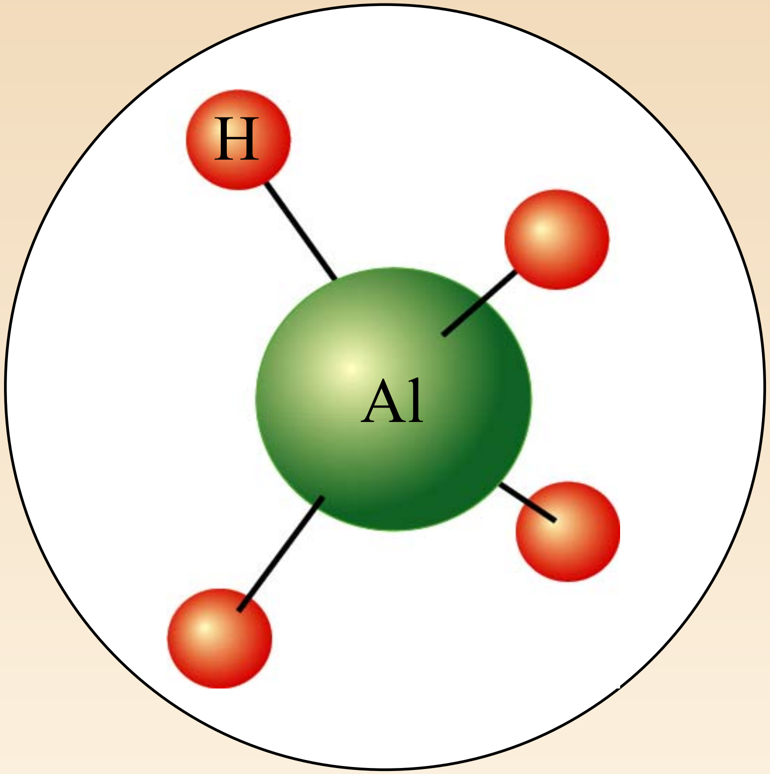
*$H_2$ Storage Materials Synthesis & Characterization*

- 1 Automated PCT instrument
- 3 Manual Kinetics instruments
- 2 Cycle-life instruments
- 2 In situ X-ray diffractometers
- 2 Inert gas prep glove boxes
- SEM, TEM, NMR, XPS, Auger...

# Candidate Solid State Hydrogen Storage Media

## Complex Hydrides

*High Gravimetric Hydrogen Capacities !*




| Examples | Capacity* |
|---|---|
| $Na(AlH_4)$ | 5.6 wt% |
| $Li(AlH_4)$ | 7.9 wt% |
| $Mg(AlH_4)_2$ | 7.0 wt% |
| $Ti(AlH_4)_4$ | 8.1 wt% |
| $Fe(BH_4)_2$ | 9.4 wt% |
| $NaBH_4$ | 7.9 wt% |
| $Ca(BH_4)_2$ | 8.6 wt% |

* *Theoretical Reversible Capacities*

# Sandia's Science-Based Approach

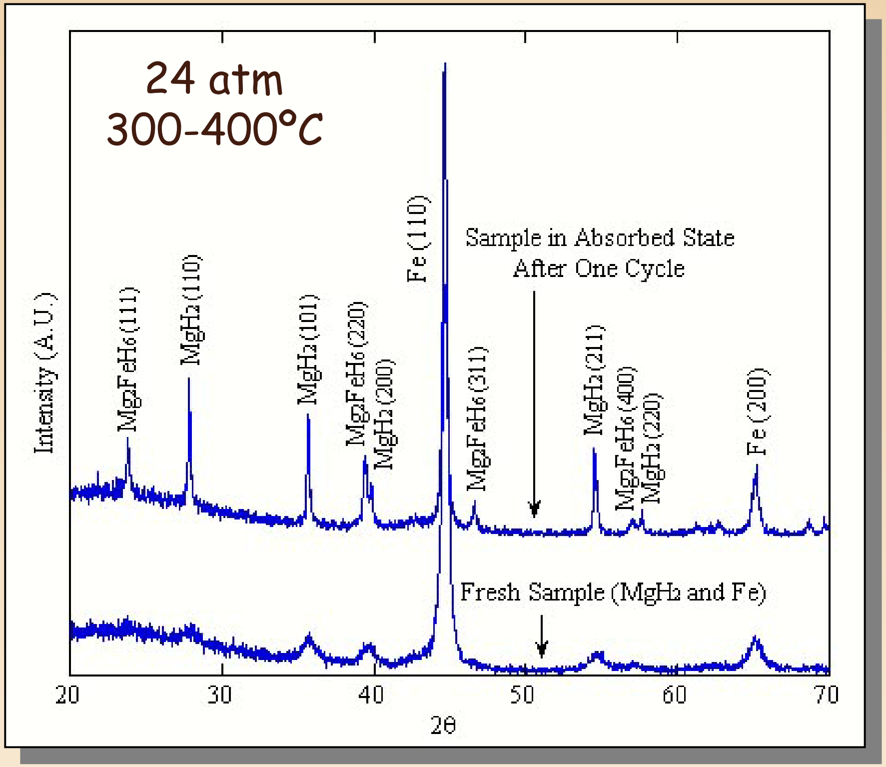
## A) Advanced Complex Hydrides

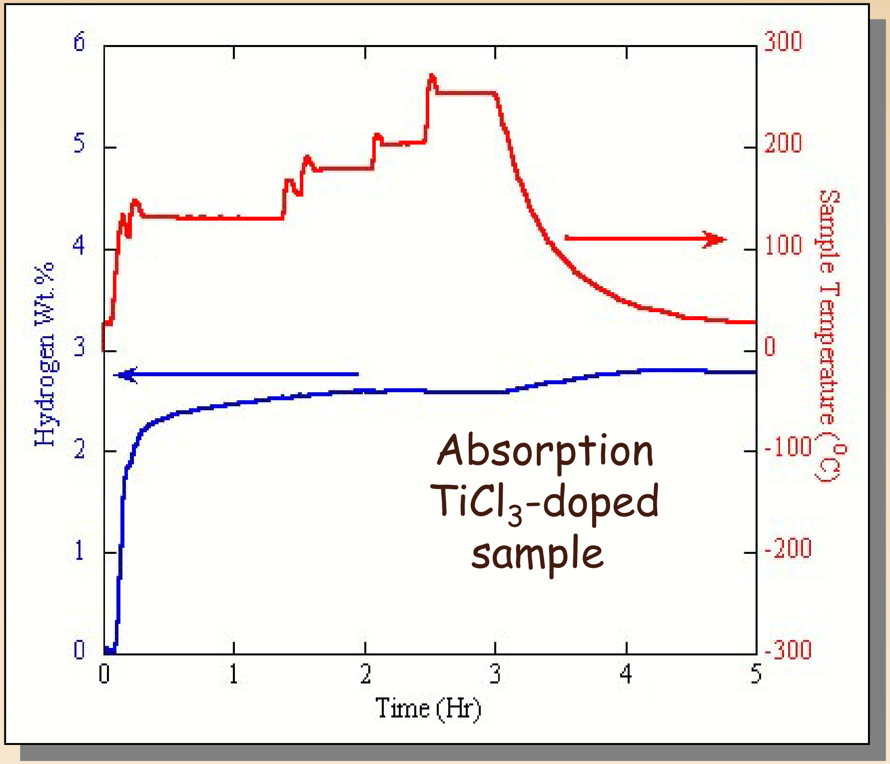
- Improve performance of alanates through modified chemistry.
- Test reversibility and stability of other complex hydrides.
- Demonstrate dopant-enhanced activity of other hydrides.

## B) $NaAlH_4$ as Model System

- Develop synthesis and doping processes to:
  - Improve $H_2$ absorption/desorption properties.
  - Reduce cost and complexity of production.
  - Apply to development of new complex hydrides.
- Determine mechanism of Ti-enhanced Abs/Desorption through experimental analysis and modeling.
- Characterize engineering materials properties.

# Reversible Complex Hydride $Mg_2FeH_6$



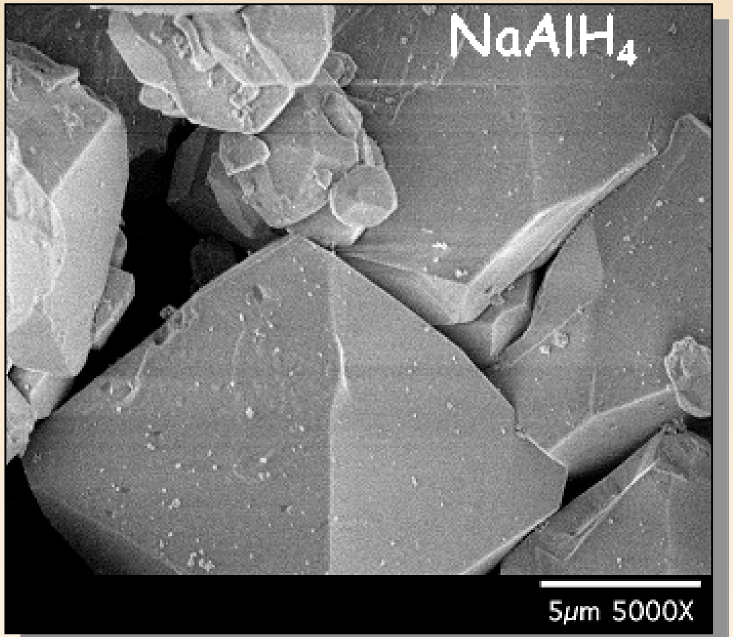

- Used direct synthesis technique starting with $MgH_2$ and Fe
- $MgH_2$ used instead of Mg for ease of milling
- Formation of $Mg_2FeH_6$ under milder conditions than previously reported
- Doping with $TiCl_3$ affects the rehydriding kinetics
- Notable and rapid absorption below 100°C

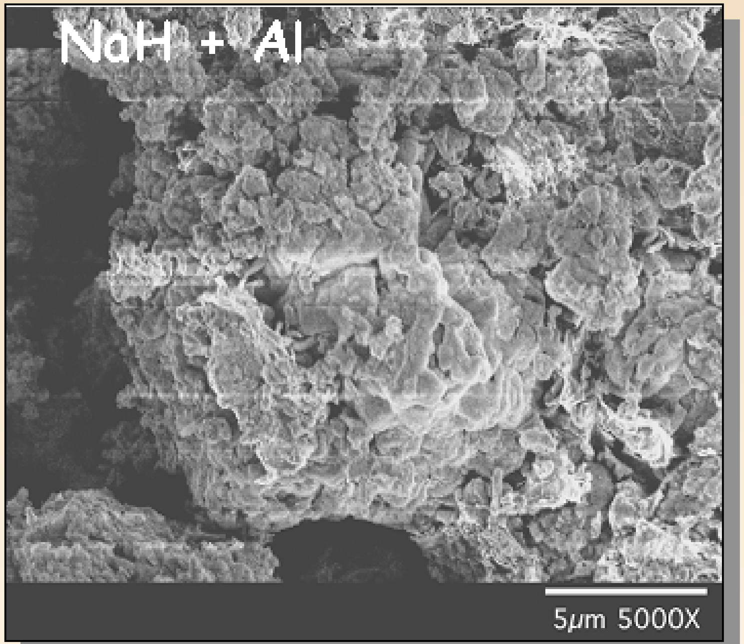
# Hydrogen from Thermal Decomposition of Sodium Alanates

Total Theoretical Capacity = 5.6 wt% hydrogen

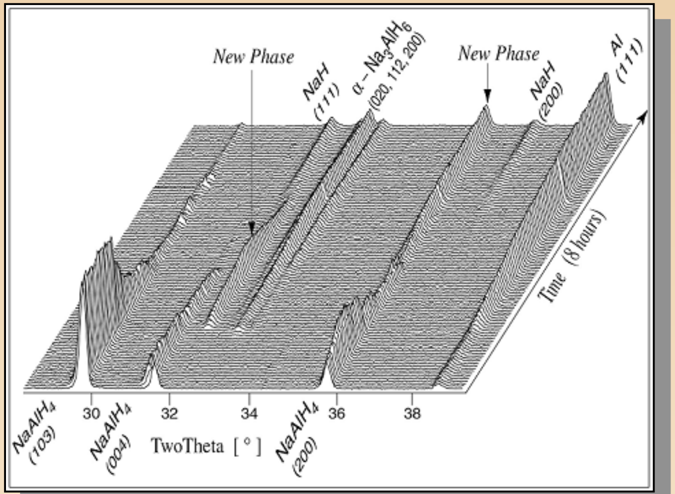
$$NaAlH_4 \Rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \Rightarrow NaH + Al + 3/2H_2$$

3.7 wt.% 1.9 wt.%

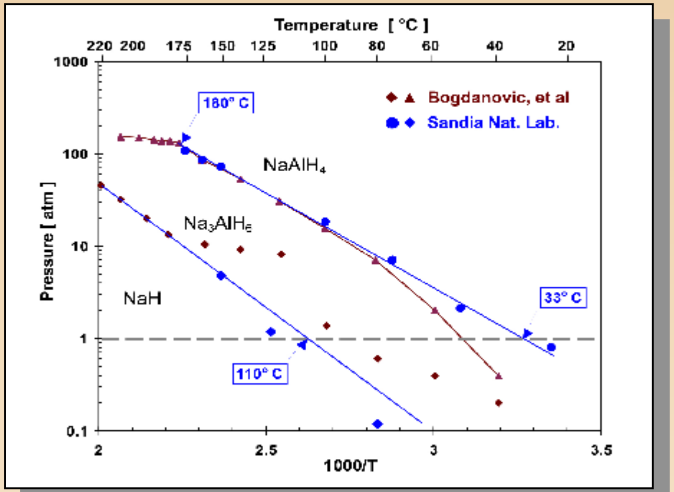


# Past Accomplishments



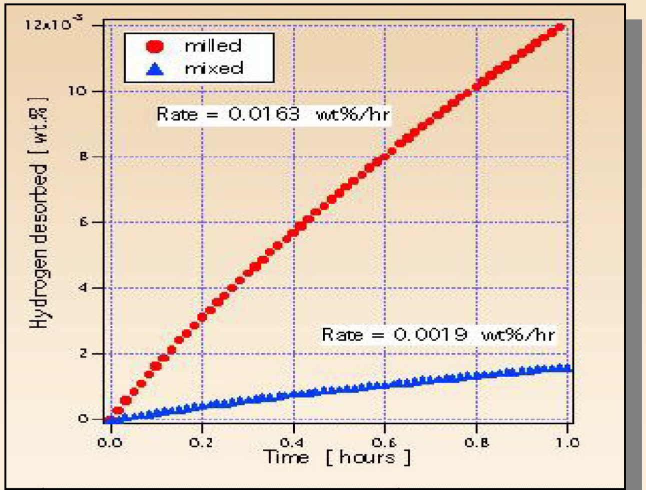

• In situ XRD - Phase Transitions




• Determined Thermodynamics

1999

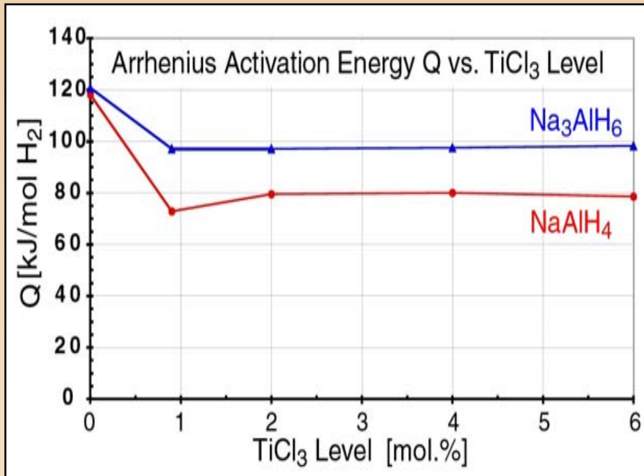
2000



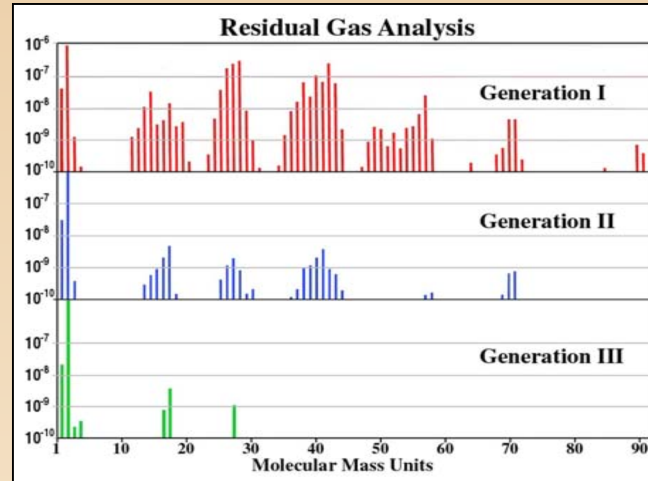

• Milling Synthesis / RT Desorption

• 1st Scaled-up Alanate Tests

# Past Accomplishments Cont.



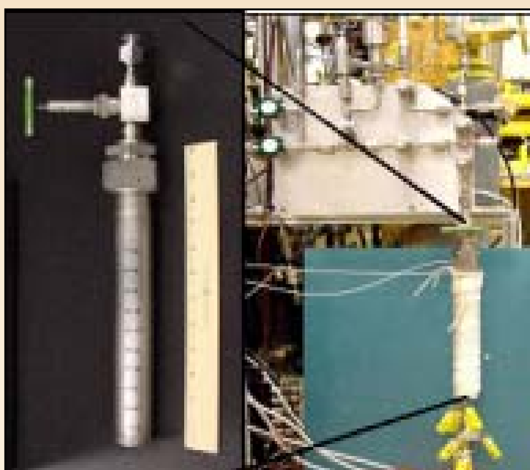

- Kinetics v.s. Level of Ti-Loading



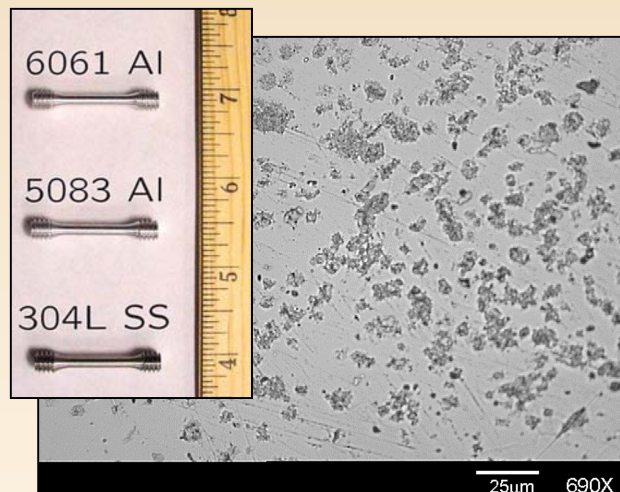

- Direct Synthesis

2001

2002

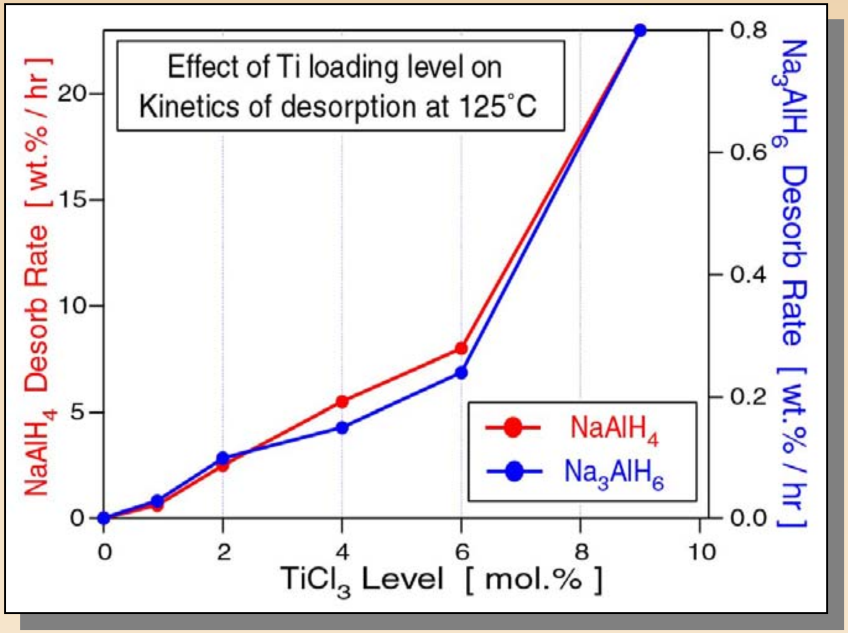


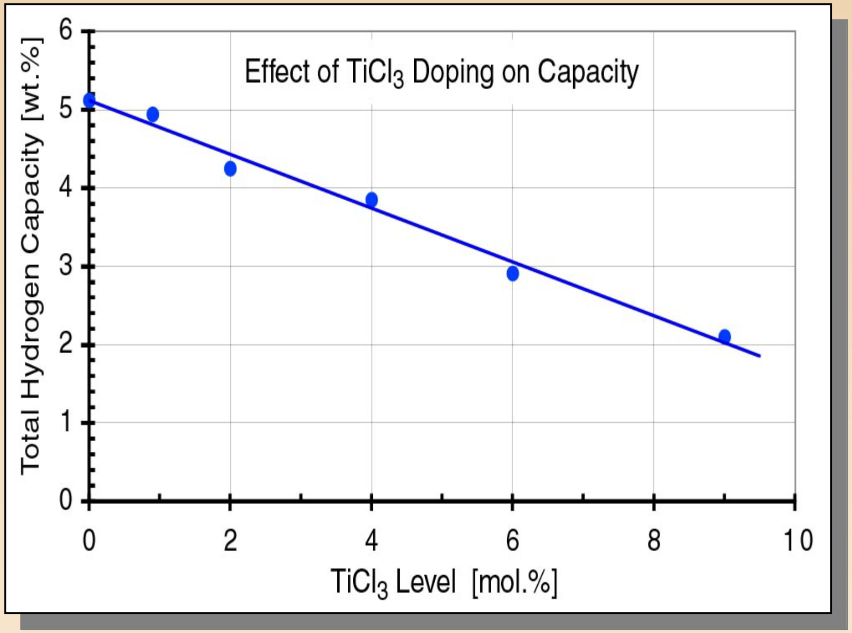
- Instrumented Test Bed




- Safety and Compatibility Testing

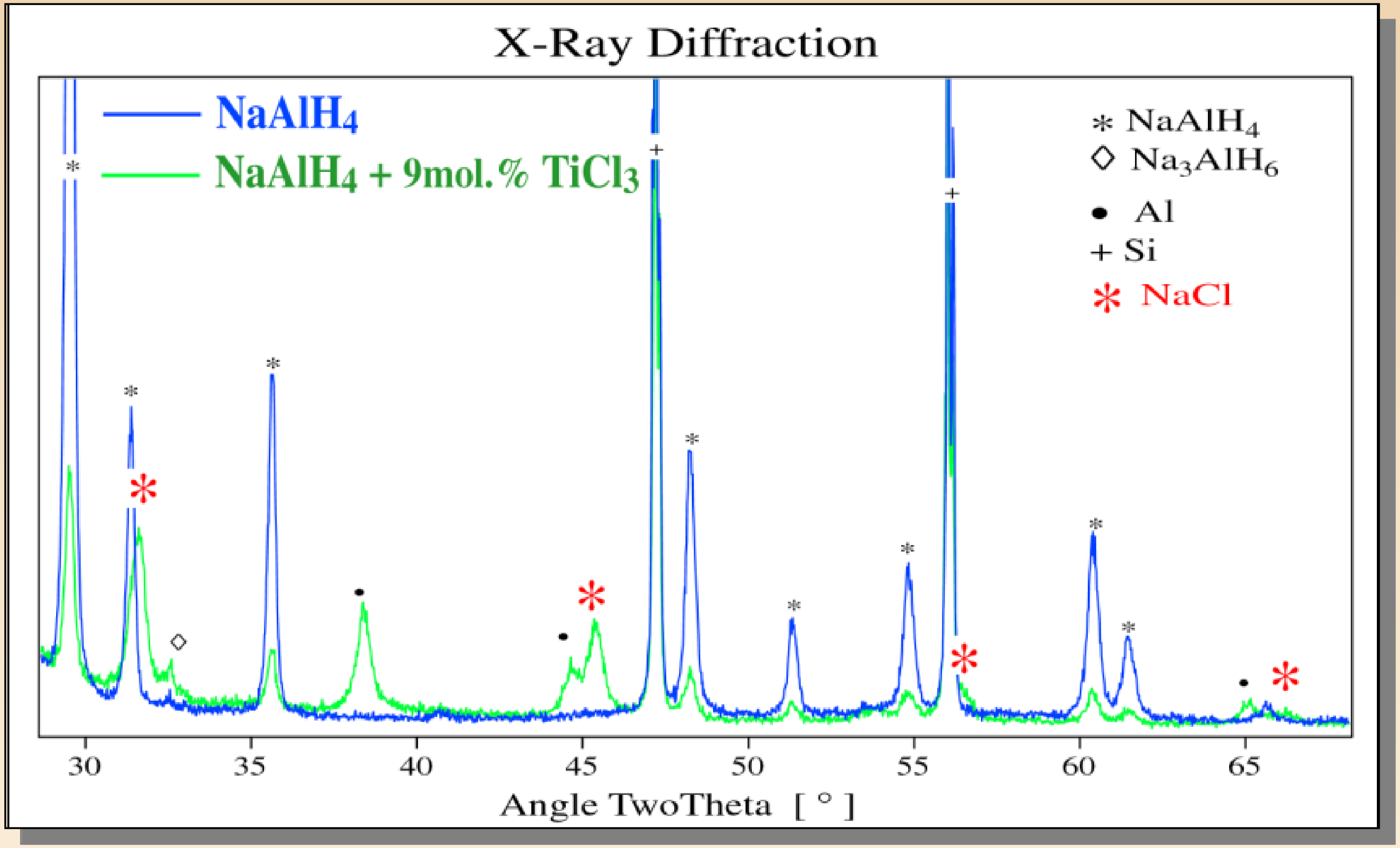
# Motivation
## for Understanding and Improving Doped-$NaAlH_4$




- Desorption (and Absorption) Kinetics increases with $TiCl_3$ doping level
- Reversible Hydrogen Capacity decreases with $TiCl_3$ doping level
- There is a trade-off between improved kinetics and capacity loss
- How can we improve both kinetics and capacity?
- What is the role of doping in the mechanism of enhanced kinetics?

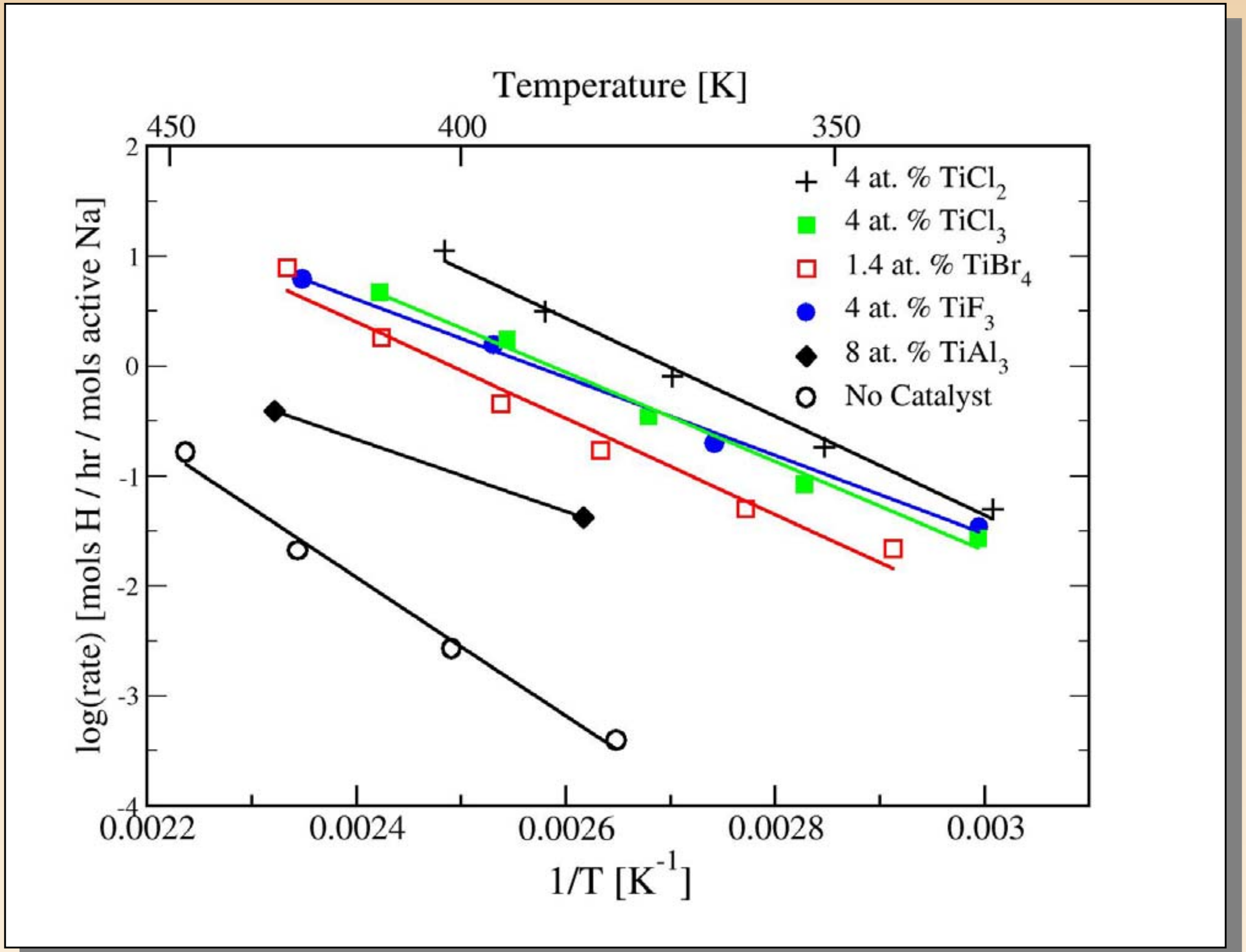
# Cause of the Drop in Capacity




- XRD showed the formation of NaCl through the reaction:

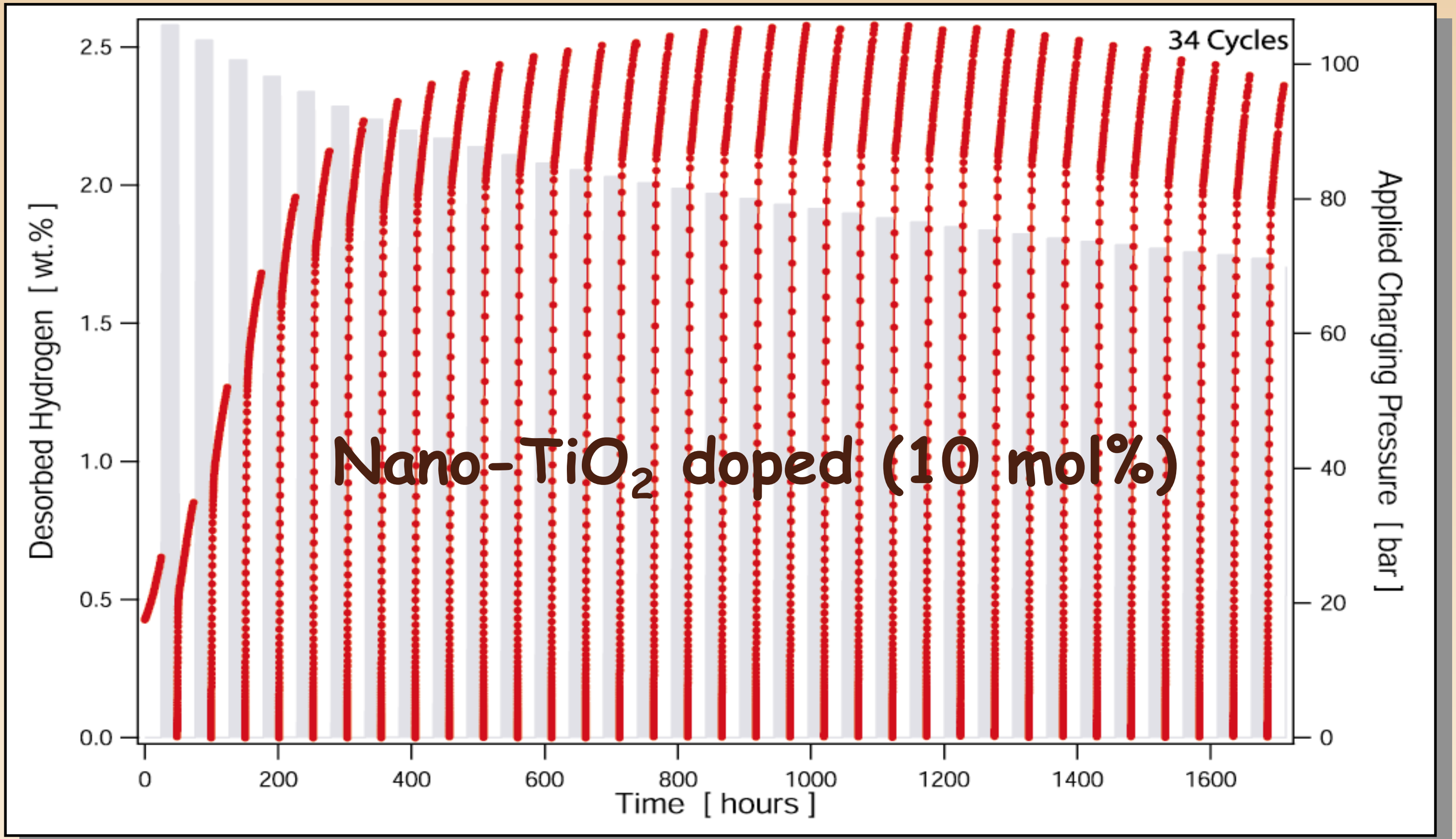
$$3NaAlH_4 + TiCl_3 \Rightarrow Ti + 3NaCl + 3Al + 6H_2$$

# Doping With Other Ti-halides and Alloys



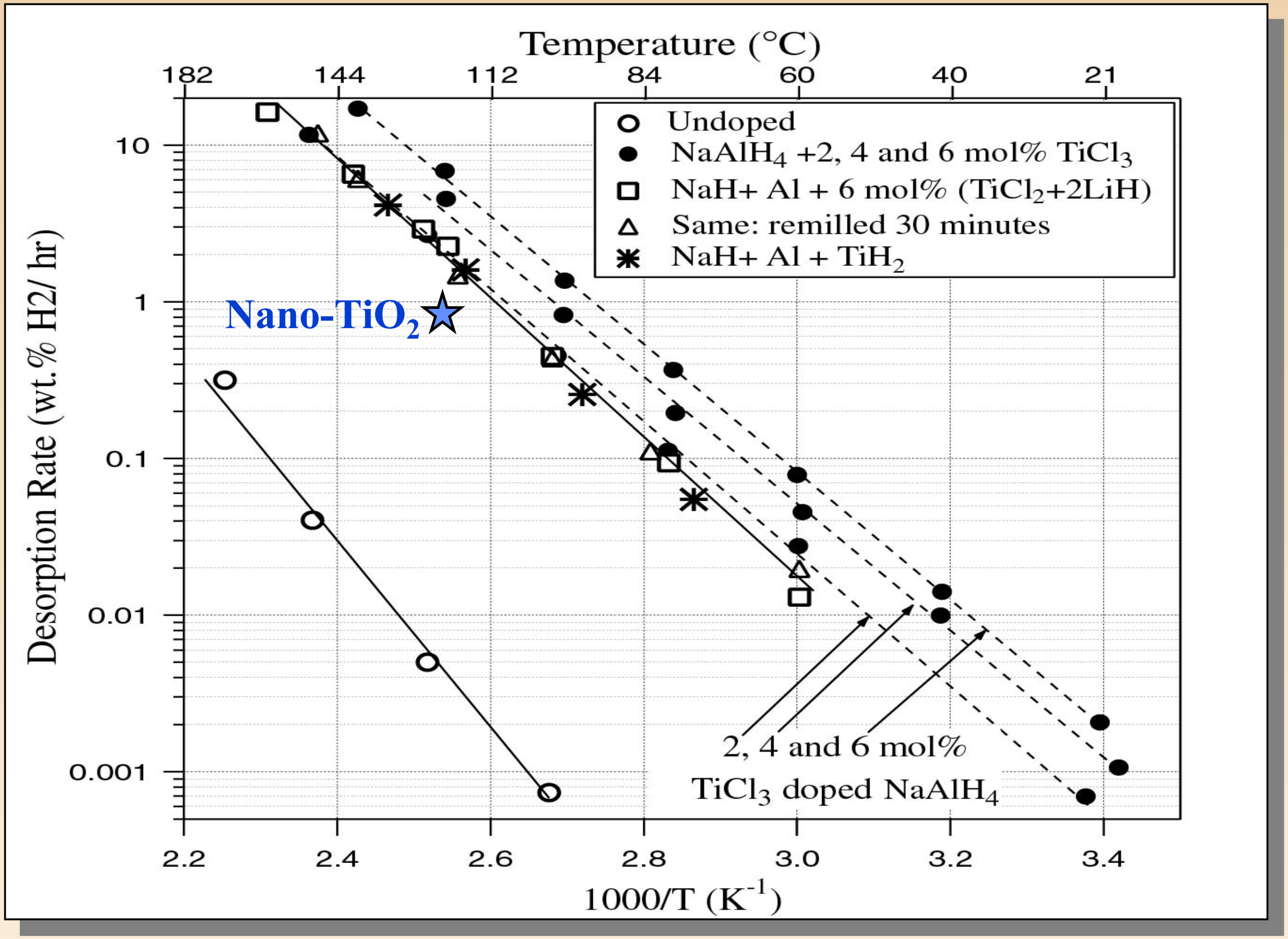

- Activation Energies are identical for $TiCl_3$ and $TiF_3$
- Rates are Independent of Ti-halide precursor

# Reactive Halide-Doping not Required



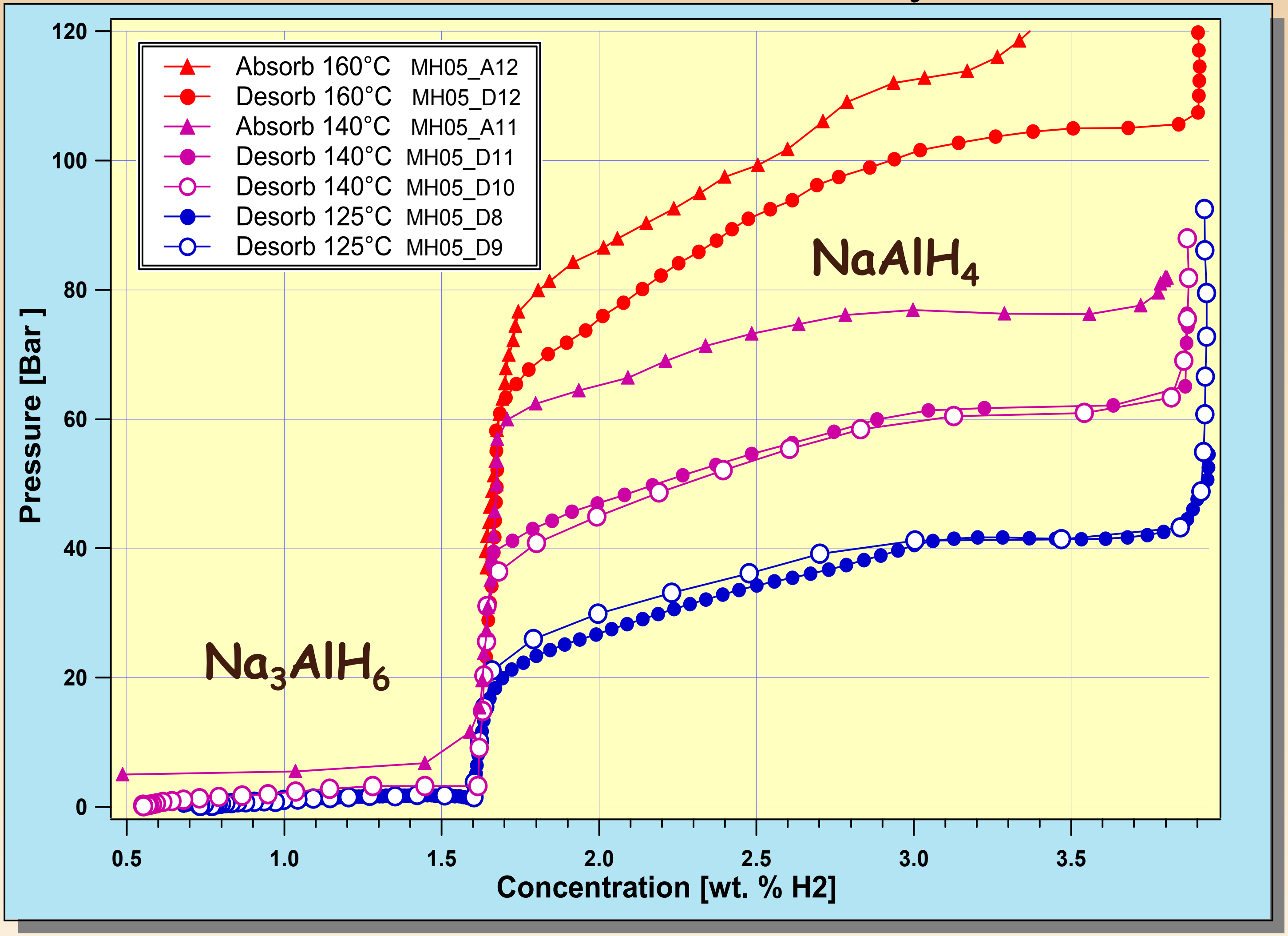

- Activation Process required ~ 8 cycles
- Rates comparable with direct doping of 1 mol% $TiCl_3$
- No capacity loss due to Na-halide reaction (nominal 4 wt.% $H_2$)
- Well dispersed nano-dopant may promote better kinetics

# *Indirect Doping Processes: $TiO_2$, $TiH_2$, PR-$TiCl_2$*



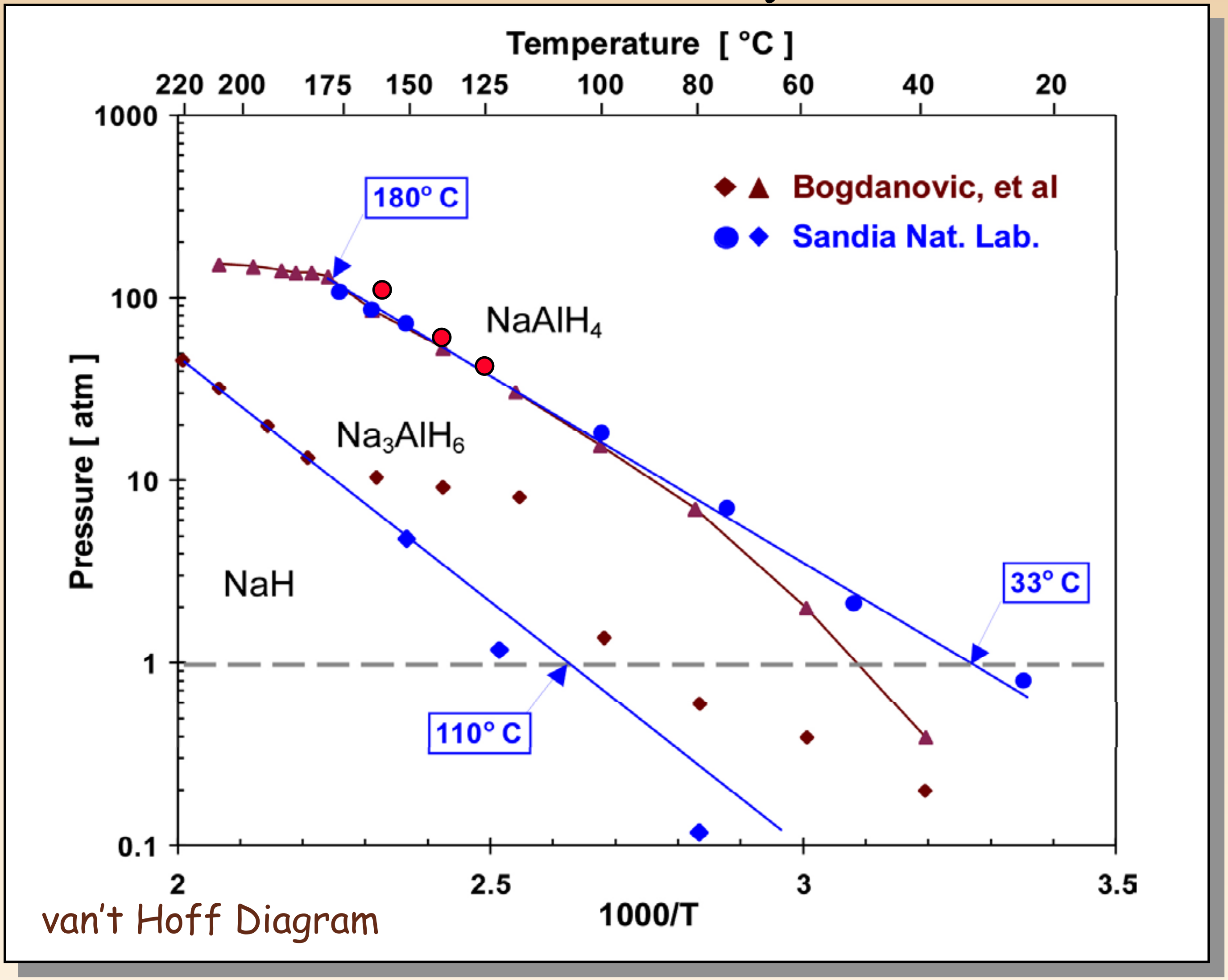

- Rates comparable with direct doping of 1-2 mol% $TiCl_3$
- Activation energies are similar to direct doping
- Potential to improve capacity

# PCT Measurements: Ti-doped $NaAlH_4$




- Two separate components of $NaAlH_4$ phase (Ti distribution?)
- Combination of different kinetics and thermodynamics likely

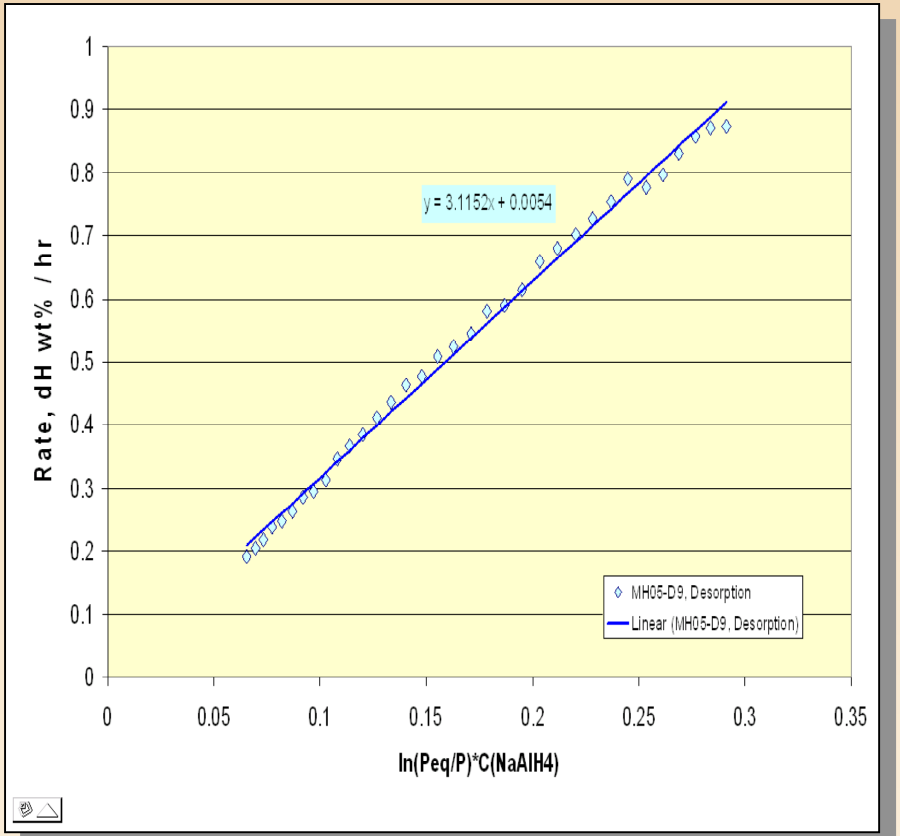
# Modified Thermodynamics ?

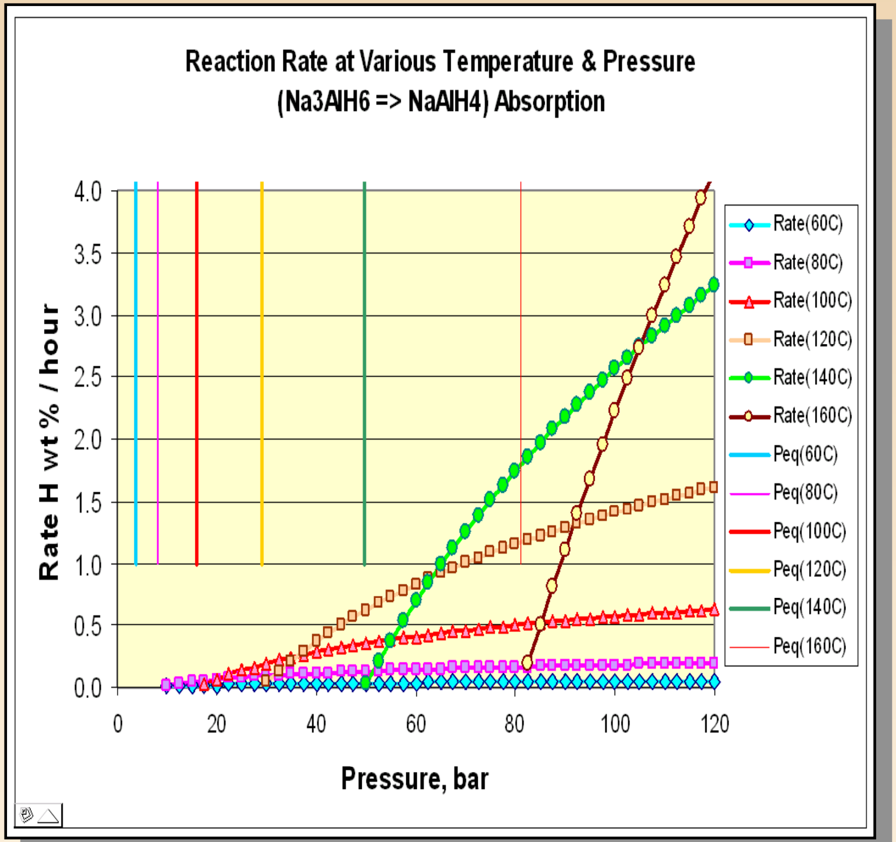



- Slightly less stable than previous data indicates

# Advanced Kinetics Model ⇒ Optimum Conditions

$$dC/dt_{des} = k_o \exp(-Q/RT)\ln(P_{eq}/P)C(NaAlH_4)$$




- Rate dependent on T, ΔP, and phase content C
- Charging alanates at a lower temperature may be advantageous

# Future Plans

## Other Complex Hydrides

- $Mg(AlH_4)_2$ (7 wt.% theoretical)
  - Used direct synthesis technique starting with $MgH_2$ and Al
  - Complex hydride did not form at 100 atm and 350°C
  - Using special facilities to test high-pressure synthesis 10+kpsi
- Looking at other complex hydrides with even higher capacities

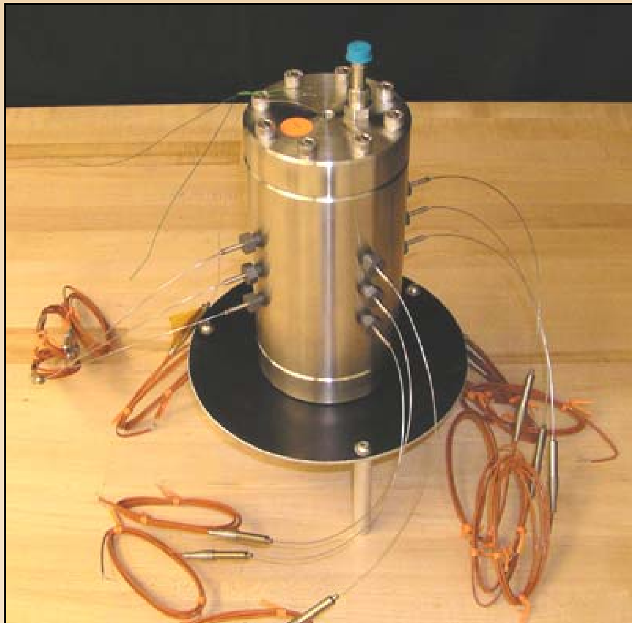
## Na-Alanates

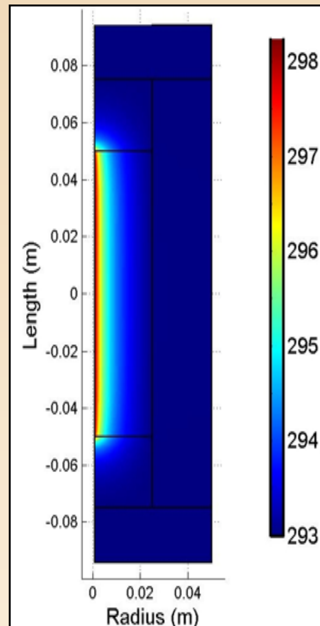
- New non-reactive dopants
- Further PCT analysis
- Structural modifications through substitution (Li,…)

## Materials Engineering Properties of Complex Hydrides

- Thermal Properties
- Volume Expansion & Packing Densities
- Electrical Properties

# Engineering Science: Material Properties of Sodium Alanate

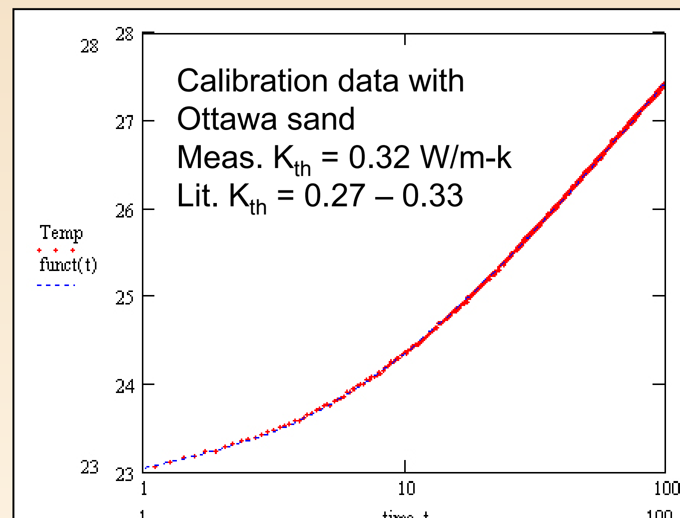





**Instrumented chamber to measure:**

- **Thermal conductivity**
- **Wall resistance**
- **Porosity**

As a function of phase, temperature, cycle, morphology, and pressure.

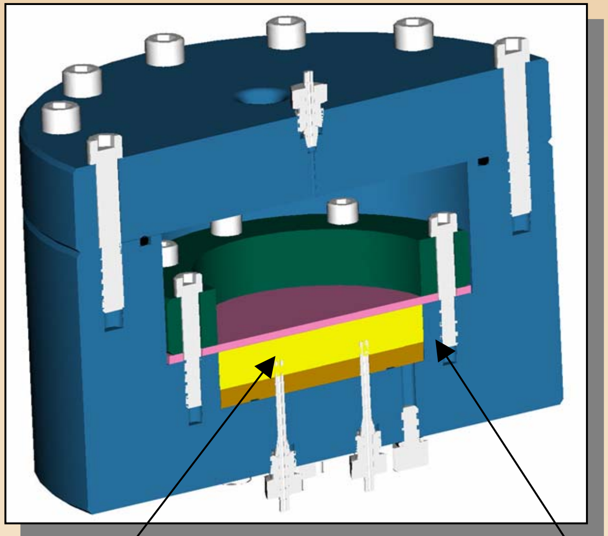



$$T(t) = A \cdot \ln t + B + C \cdot \frac{\ln t}{t} + D \cdot \frac{1}{t}$$

$$K_{th} = \frac{r_P \cdot Q'}{2 \cdot A}$$

$$h_i = \frac{1}{r_P} \cdot \left[ \frac{2 \cdot K_{th}}{\frac{B}{A} - \ln\left(\frac{K_{th}}{\rho \cdot c}\right) + 2 \cdot \ln(r_p) - \ln(4) + 0.8141} \right]$$

# Engineering Science: Material Properties of Sodium Alanate



Alanate

Membrane

**Volumetric Expansion**
**Constrained Force**

Membrane deflection measured to determine pressure exerted by phase induced volume expansion

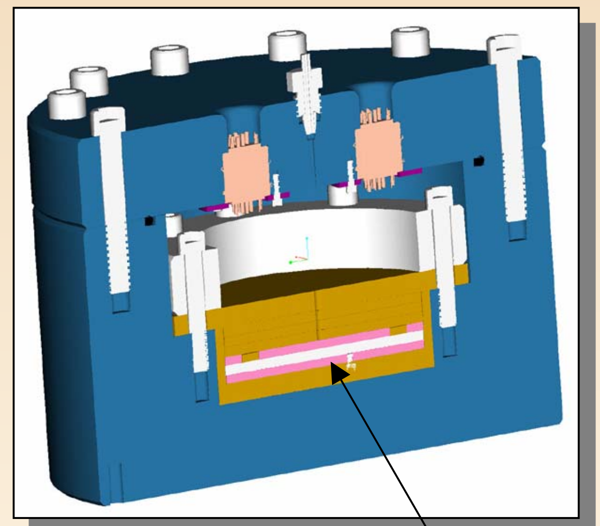
**DC Electrical Properties:**

- Bulk Resistivity

**AC Electrical Properties:**

- Capacitance (permittivity)
- Phase angle
- Power loss

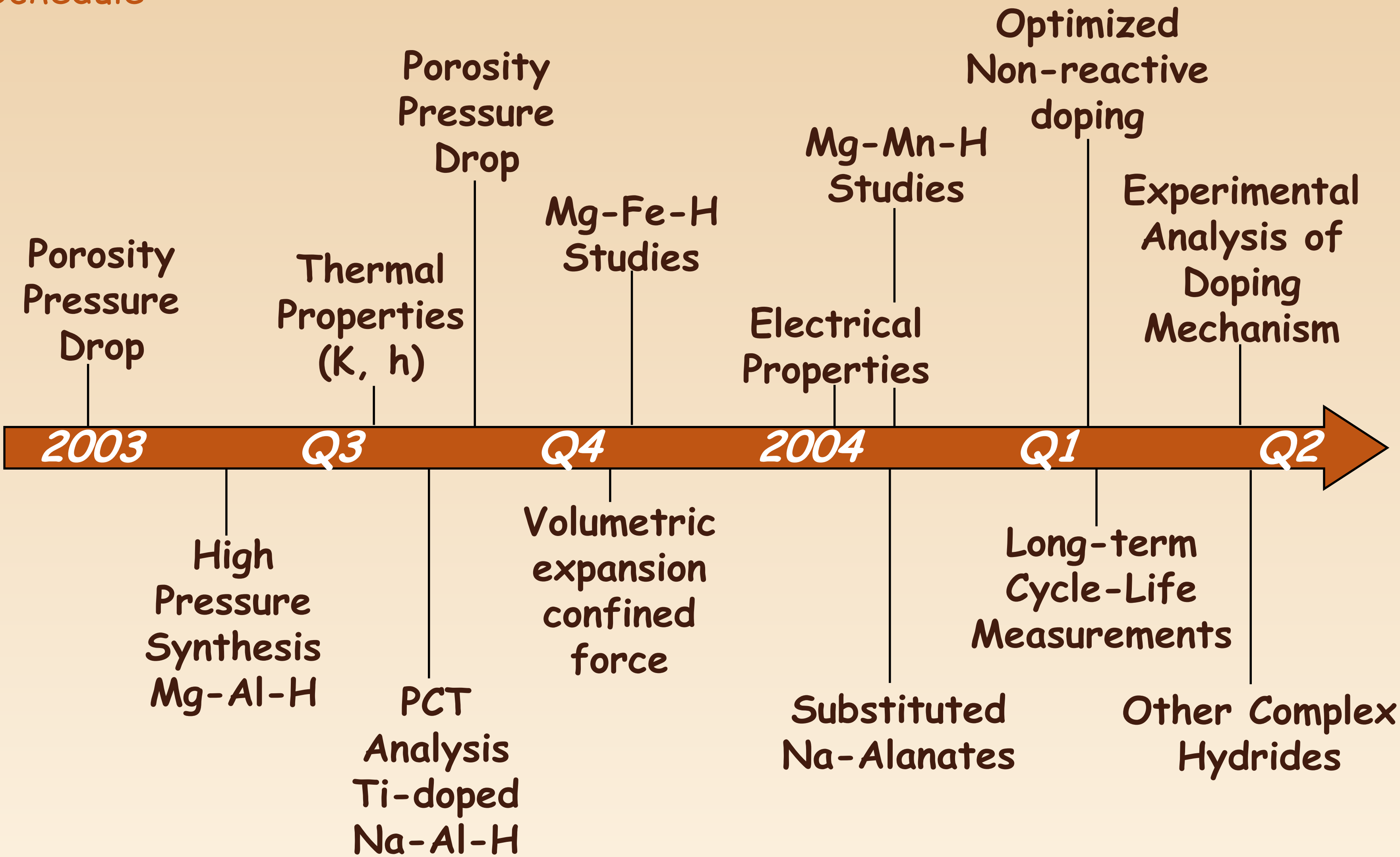
as a function of phase, AC frequency, temperature



Three electrode system, measurement plus guard

# Milestones

Completion Schedule



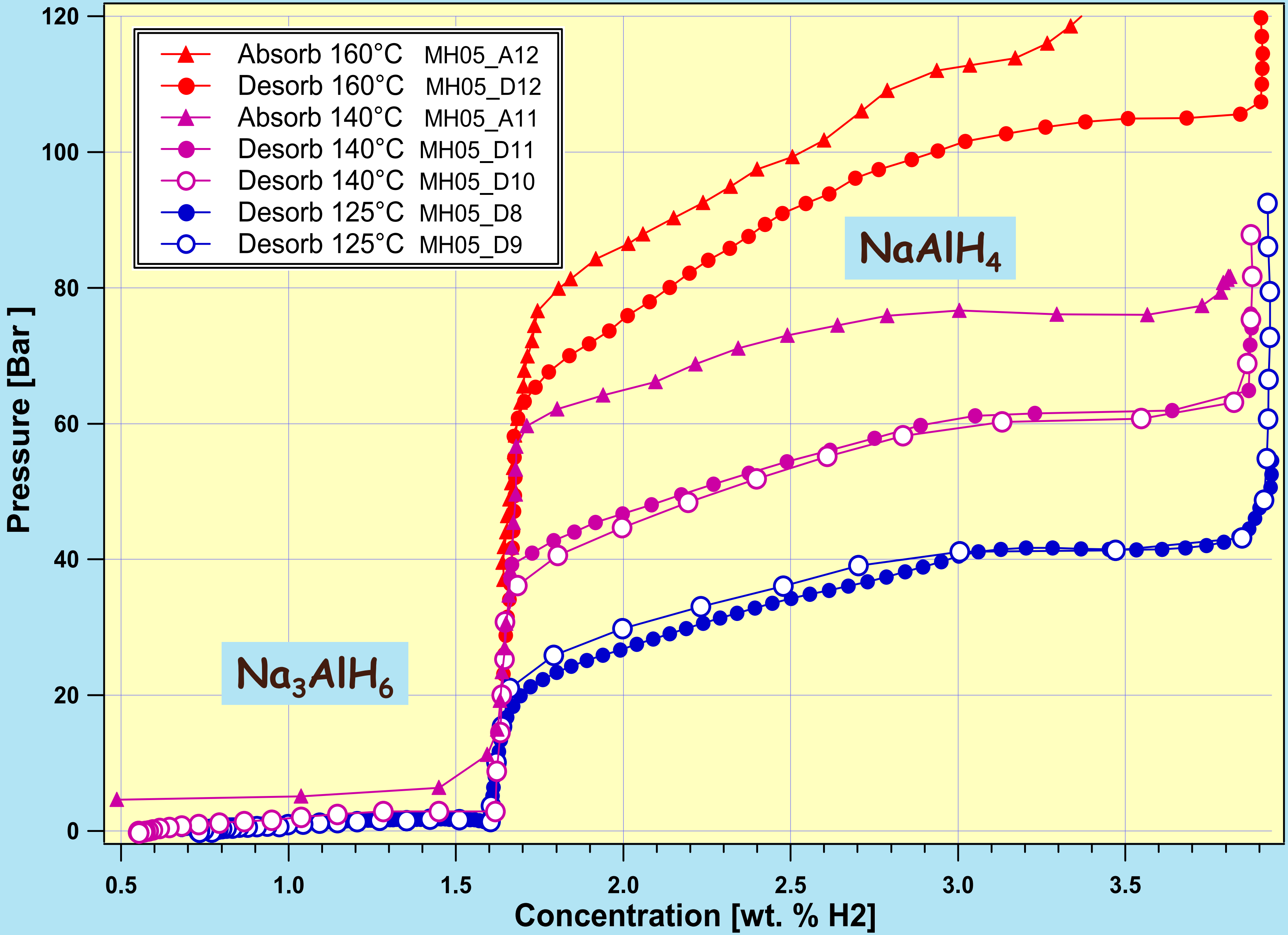
# Collaborations

- University of Hawaii: Mechanisms of Ti-doping enhanced kinetics
- University of Geneva: New Complex Hydrides
- Florida Solar Energy Center: New Complex Hydrides
- Denver University: Electron Spin Resonance measurements
- NIST: Neutron Diffraction and Scattering
- UCLA: Ab Initio Calculations
- UTRC: Materials Purity Issues and Safety Testing

# Publications


- "The effects of titanium precursors on hydriding properties of alanates", K.J. Gross, E.H. Majzoub, S.W. Spangler Submitted J. Alloys and Comps 2002
- "Catalyzed alanates for hydrogen storage", Gross, KJ; Thomas, GJ; Jensen, J. Alloys and Comps, 2002; v.330, p.683-690
- "Titanium-halide catalyst-precursors in sodium aluminum hydrides", E.H. Majzoub, K.J. Gross, Submitted J. Alloys and Comps 2002
- "Rietveld Refinement and Ab Initio Calculations of $NaAlD_4$", E.H. Majzoub and V. Ozolins, In preparation.
- "EPR Studies of Titanium Doped $NaAlH_4$: Fundamental Insight to a Promising New Hydrogen Storage Material", Sandra Eaton, Karl Gross, Eric Majzoub, Keeley Murphy, and Craig M. Jensen, submitted Chemical Communications, 2003
- "Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates", Sandrock, G; Gross, K; Thomas, G, J. Alloys and Comps 2002; v.339, no.1-2, p.299-308
- "Microstructural characterization of catalyzed $NaAlH_4$", Thomas, GJ; Gross, KJ; Yang, NYC; Jensen, C, J. Alloys and Comps, 2002; v.330, p.702-707
- "Interactions Between Sodium Aluminum Hydride and Candidate Containment Materials", E.H. Majzoub, B.P. Somerday, S.H. Goods, K.J. Gross, Proceedings Conf."Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions, to be published.
- "Engineering considerations in the use of catalyzed sodium alanates for hydrogen storage", Sandrock, G; Gross, K; Thomas, G; Jensen, C; Meeker, D; Takara, S, J. Alloys and Comps, 2002; v.330, p.696-701
- "Dynamic in situ X-ray diffraction of catalyzed alanates", Gross, KJ; Sandrock, G; Thomas, GJ, J. Alloys and Comps, 2002; v.330, p.691

# Sandia's Hydrogen Powered Data



# Special Acknowledgement


| | |
|---|---|
| Jennifer Chan | - Systems Integration |
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| Steve Goods | - Hydrogen Materials interaction |
| Weifang Luo | - Hydrogen Storage Materials |
| Joshua Lamb | - Summer Student |
| Steve Karim | - Experimental Setup |
| Eric Majzoub | - Fundamental Studies |
| Andres Orozco | - Summer Student |
| Vidvuds Ozolins | - Fundamental Studies |
| Greg Roberts | - Hydrogen Storage Materials |
| Brian Somerday | - Hydrogen Materials interaction |
| Gary Sandrock | - Hydrogen Storage Materials |
| Scott Spangler | - XRD, Materials Synthesis |
| Ken Stewart | - Laboratory and Experimental Setup |
| George Thomas | - Hydrogen Storage Materials |
| Nancy Yang | - Microscopy |


**Thank you!**