High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Complex Compound Hydrides

D.L. Anton
D.A. Mosher
S.M. Opalka
United Technologies Research Center
E. Hartford, CT

F.E. Lynch
HCI, Inc.
Littleton, CO

C. Qiu
G.B. Olsen
QuesTek, LLC
Evanston, IL

Merit Review
Berkeley, CA
May 19-20, 2003

Rev. B

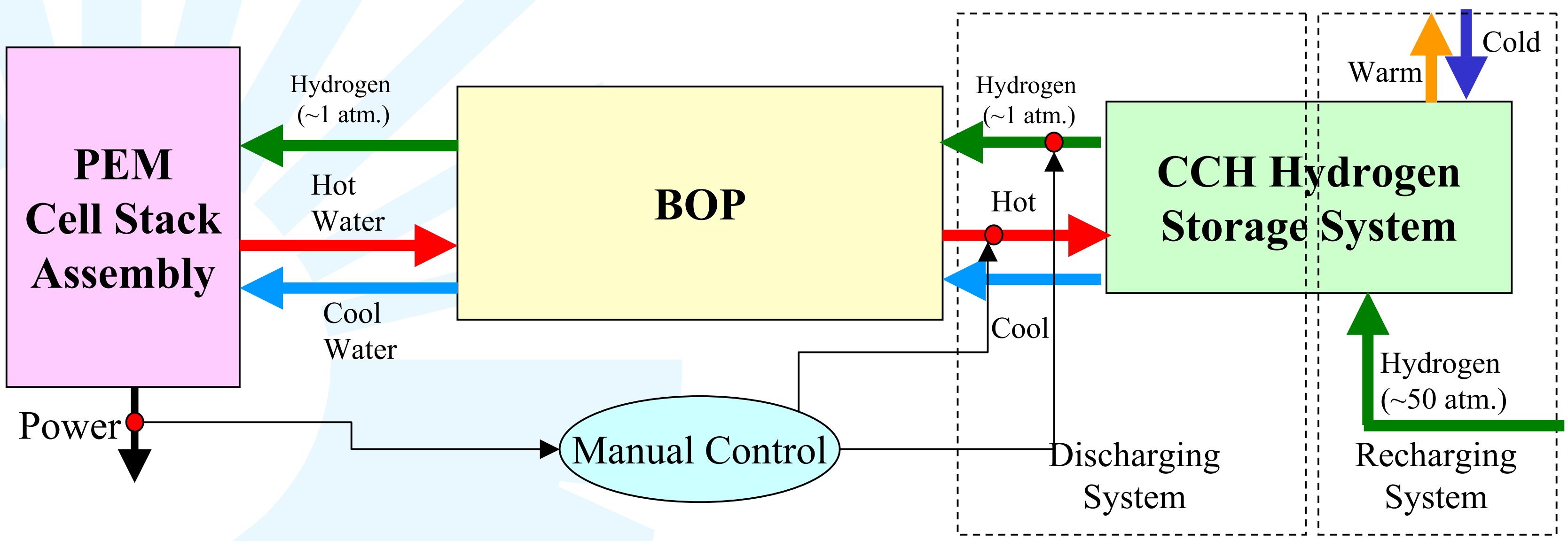
Program Specifics

Objective: Develop, build, bench demonstrate and <u>deliver</u> an *in-situ* rechargeable 5 kg H_2 capacity hydrogen storage system suitable for operation of a PEMFC powered mid-size auto application based.

Approach: Design a low pressure hydrogen storage system initially utilizing catalyzed **$NaAlH_4$**, but capable of being altered to use "*any*" chemical hydride having the higher gravimetric and/or volumetric hydrogen storage densities.

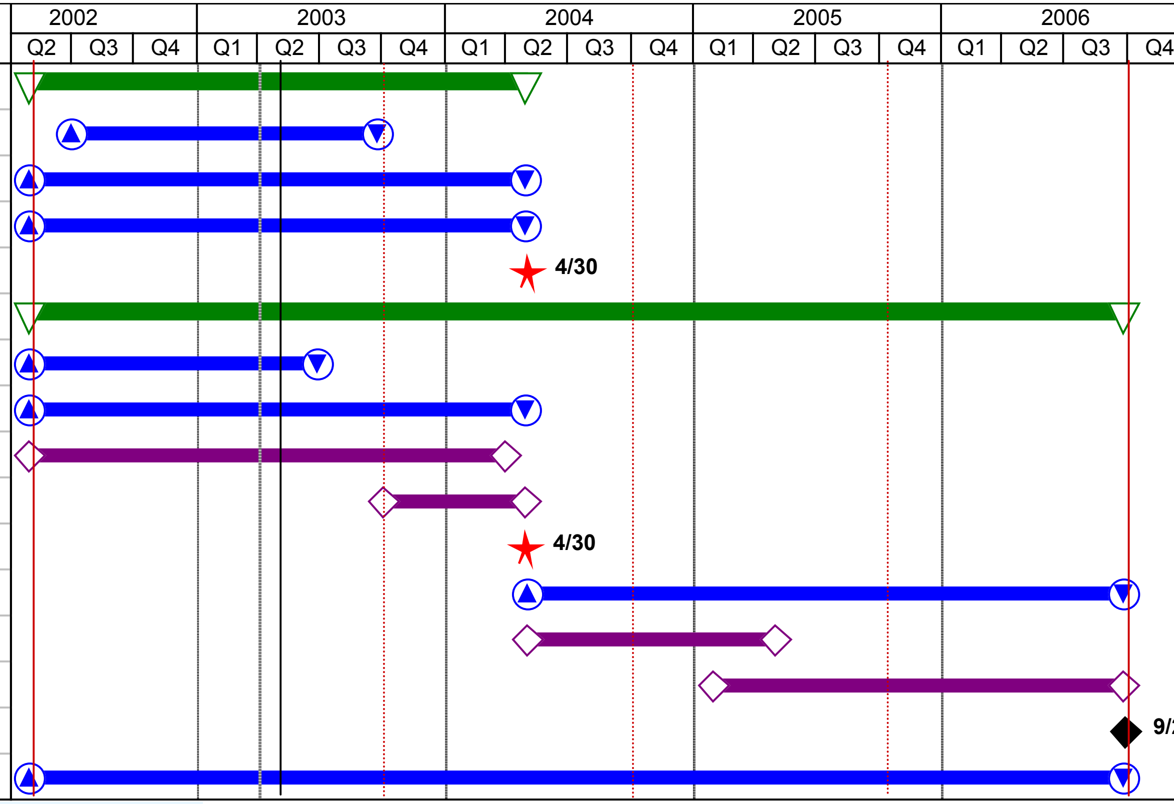
Program Outline

- Safety Analysis
- Atomistic/Thermodynamic Modeling
- 50g H_2 Prototype System
- Media Kinetic Modeling
- Heat/Mass Transfer Analysis
- 1kg H_2 Prototype/Evaluation
- 5kg H_2 Prototype/Evaluation
- 5kg Prototype Delivery



Milestone Chart

ID	WBS	Task Name
1	1	CCH Storage Media Development
2	1.1	50g H2 Sub-System Evaluations
6	1.2	50g Media Evalautions
18	1.3	NaAlH4 Thermodynamic Modeling
29	1.4	GO/NO GO Milestone
30	2	CCH Storage Sys. Demonstration
31	2.1	Safety Analysis
36	2.2	1Kg System Evaluation
37	2.2.1	Design/Fabricate CCHSS#1
45	2.2.2	CCHSS#1 Evaluation
48	2.3	GO/NO GO Milestone
49	2.4	5Kg System Evaluation
50	2.4.1	Design/Fabricate CCHSS#2
58	2.4.2	CCHSS#2 Evaluation
65	2.4.3	Ship CCHSS#2 to DoE
66	2.5	Reporting



Milestones vs. DoE 2005 & 2010 Goals

	Metric	Units	2005 DoE Goal	2010 DoE Goal	UTRC 2003 Estimate	UTRC Prop. GO/NoGo
	Capacity	kg		5		
H_2 Storage Density	Gravimetric	kWh/kg	1.5	2	0.83	1.00
	Volumetric	kWh/l	1.2	1.5	0.40	0.55
Cost	Total life cycle (15 yr/150k miles)	$(03)/kWh	6.00	4.00	16	
	Fuel (gasoline equivilent)	$(01)	3.0	1.3	TBD	
	Marginal Fuel Cost (Ref. $1/kWh for H_2)	$(03)/kg$H_2$	NA	1.5	TBD	
Operating Temperature	Min.	°C	0	-30	TBD	
	Max.	°C	50	50	50	
Cycle Life	Cycle Life (0.25-100%)	N	500	1000	TBD	
	Mean	%	N/A	90	TBD	
	Confidence	%	N/A	90	TBD	

	Metric	Units	2005 DoE Goal	2010 DoE Goal	UTRC 2003 Estimate	UTRC Prop. GO/NoGo
Hydrogen Delivery	Max. H_2 Delivery Temp.	°C	100			
	Min. H_2 Delivery Temp.	°C	-20	-30	TBD	
	Min. Full Flow	g H_2/sec.	3.0	4.0	0.31	0.30
	FC Min. Pressure	kPa/bar	250/2.5	250/2.5	TBD	
	ICE Min. Pressure	kPa/bar	1000/10	3500/35		
	Purity	% (dry)	99.9	99.9	TBD	
Transient Response	0-90% 90-0%	sec.	0.5	0.5	TBD	
	start to full flow @20°C	sec.	4.0	0.5	TBD	
	start to full flow @-20°C	sec.	8.0	4.0		
	Refueling Rate	kg H_2/min.	0.5	1.5	0.30	0.30
	Loss of Useable H_2	g/hr kg H_2	1.0	0.1	TBD	
	Permeation & Leakage	scc/hr	*Federal enclosed-area safety standard*		TBD	
	Toxicity		*Meets or exceeds applicable standards*		TBD	
	Safety		*Meets or exceeds applicable standards*		TBD	

Development Partners

Sandia National Laboratories

HCI

UTC Fuel Cells
A United Technologies Company

University of Hawai'i

Hydrogen Storage
Task XVII
Advanced Fuel Cell Systems
Task XV

QuesTek Innovations LLC

Northwestern University

SRTC
Savannah River Technology Center

ife Institutt for energiteknikk

Albemarle Corporation

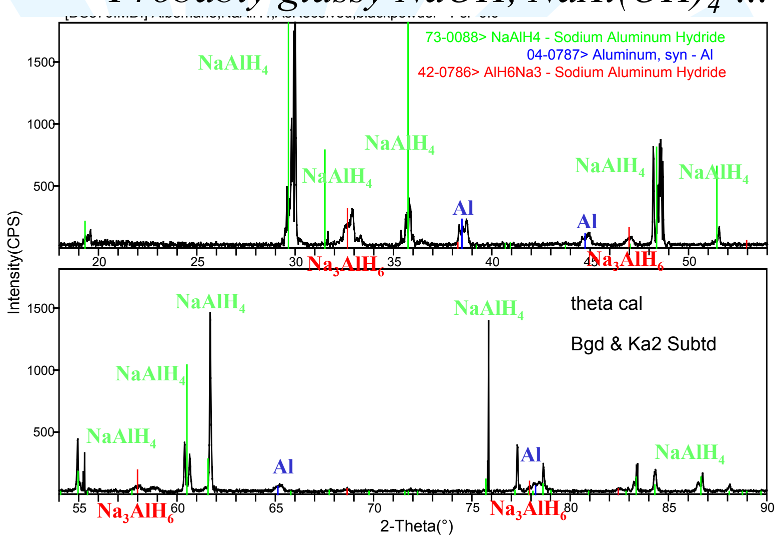
Commercial Materials Characterization

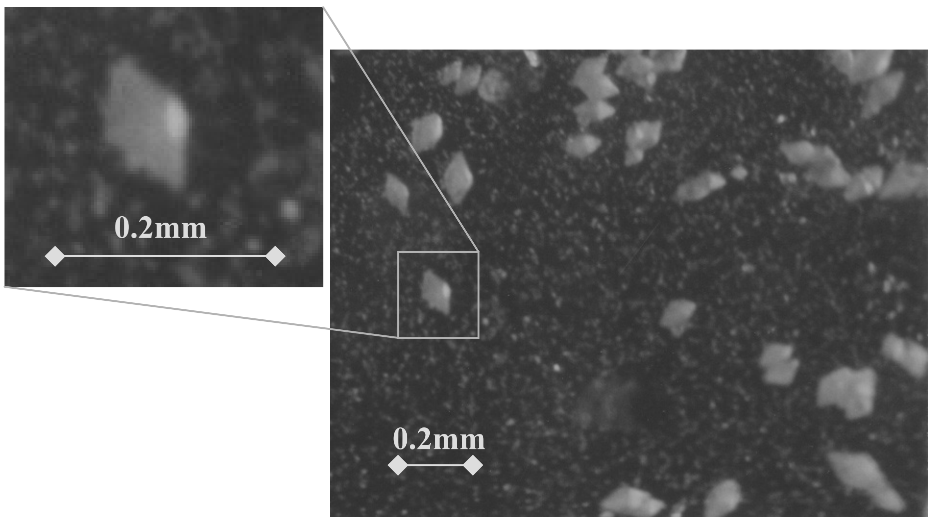
	analytical		x-ray	
	wt%	at%	wt%	at%
$NaAlH_4$	86.3	83.1	87.5	84.8
Na_3AlH_6	4.7	2.4	6.0	2.6
Al^o	7.5	14.5	6.4	12.6
Inert*	1.5			

* *Probably glassy NaOH, $NaAl(OH)_4$ …*

Summary

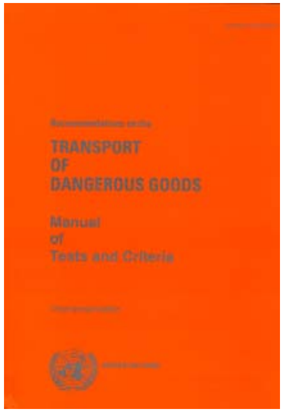
Na:Al	0.9
% Charge	94.7%
Wt%H_2	4.9
Wt% $H_{2\ th}$	5.2





Safety Analysis

DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).



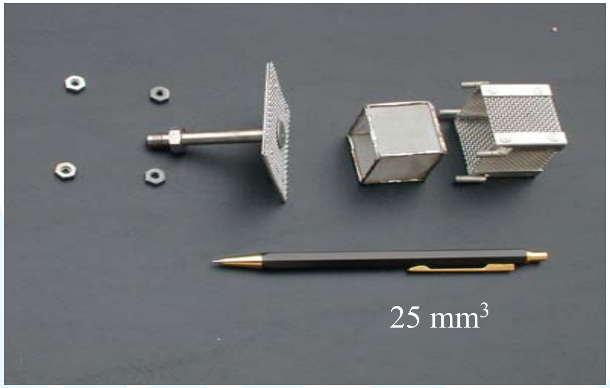
- Flammability
  - *Flammability Test*
  - *Spontaneous Ignition*
  - *Burn Rate*
- Water Contact
  - *Immersion*
  - *Surface Exposure*
  - *Water Drop*
  - *Water Injection*

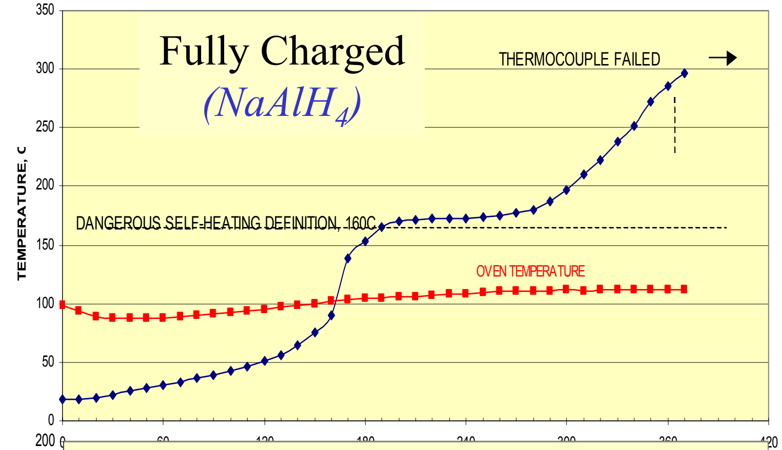
- Dust Explosion (ASTM E1226)
  - P_{max} & $(dP/Dt)_{max}$
  - *Min. Exp. Conc.*
  - *Min. Ignition Energy*
  - *Min. Ignition Temp.*
  - *Min. Dust Layer Ignition Temp.*

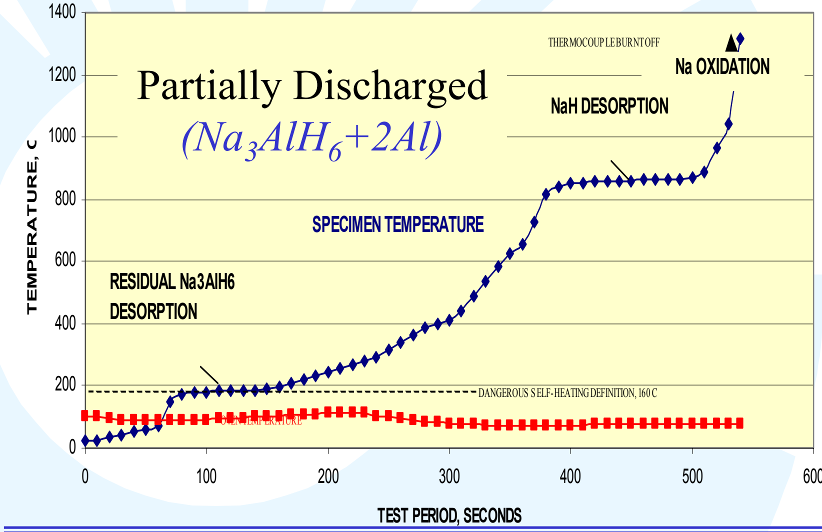
CCH#0: 2m%$TiCl_3$
Fully Charged, CCH#0-100: *($NaAlH_4$)*
Partially Discharged, CCH#0-33: *(Na_3AlH_6+2Al)*
Fully Discharged, CCH#0-0: *(NaH+Al)*

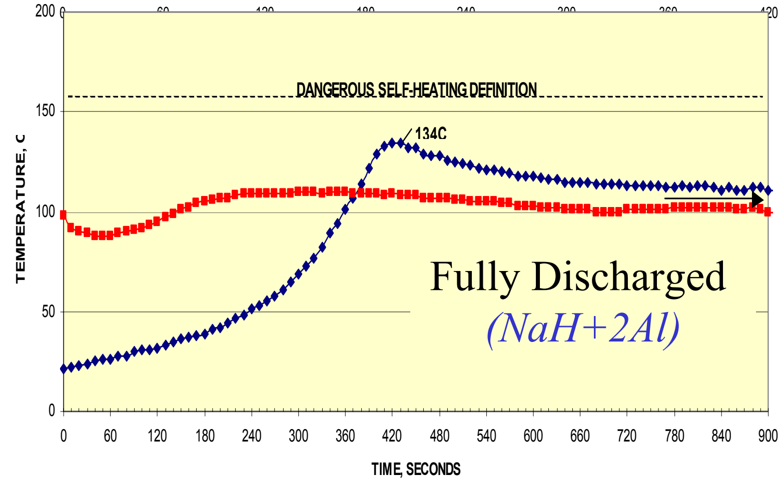
Flammability Test

Objective: To determine if material spontaneously self heats or ignites upon exposure to air at 100°C









Safety Testing Results

Class 4.3, Packing Group II:
No change from uncatalysed material.

SAFETY TESTING TABLE OF RESULTS

Test Method	Ref: UN33.	100%	33%	0%
Prelim. Screening	2.4.3.1	Yes, Flammable Solid	Yes, Flammable Solid	Yes, Flammable Solid
Burning Rate	2.4.3.2	51 mm/sec	222 mm/sec	27 mm/sec
Burning Rate, 80C	Note 1	127 mm/sec	spontanious ignition	40 mm/sec
Spontaneous Ignition, R.T.	3.1.4.3	6 Tries, Not Pyrophoric	6 Tries, Not Pyrophoric	6 Tries, Not Pyrophoric
Spontaneous Ignition, 80C	Note 1	6 Tries, No Ignition	1 Try, Ignited	6 Tries, No Ignition
Dangerous Self-Heat, 100C	3.1.3.3	Yes, Dangerous	Yes, Dangerous	Not Dangerous
Dangerous Self-Heat, 120C	3.1.3.3	Not Tested (Note 2)	Not Tested (Note 2)	Not Dangerous
Dangerous Self-Heat, 140C	3.1.3.3	Not Tested (Note 2)	Not Tested (Note 2)	Yes, Dangerous
Dangerous When Wet	4.1.4.3	Yes, Class 4.3, Pack Gp 1	Yes, Class 4.3, Pack Gp 1	Yes, Class 4.3, Pack Gp 1

Note 1: This is not a UN standard test. We want to know what happens when this material is spilled at operating temperature of 80C. All other details are per UN burn rate and spontaneous ignition test specifications.

Note 2: This test was not necessary, since this material had already shown dangerous self-heating at 100C.

Thermodynamic Modeling

Objective: Combine atomistic and thermodynamic modeling to predict: (i) quaternary phase diagrams and (ii) thermal stability of catalyzed compounds.
Approach: Atomistic calculations used to predict ΔH_f at 0K. Thermodynamic calculations to determine ΔG_f vs T & P

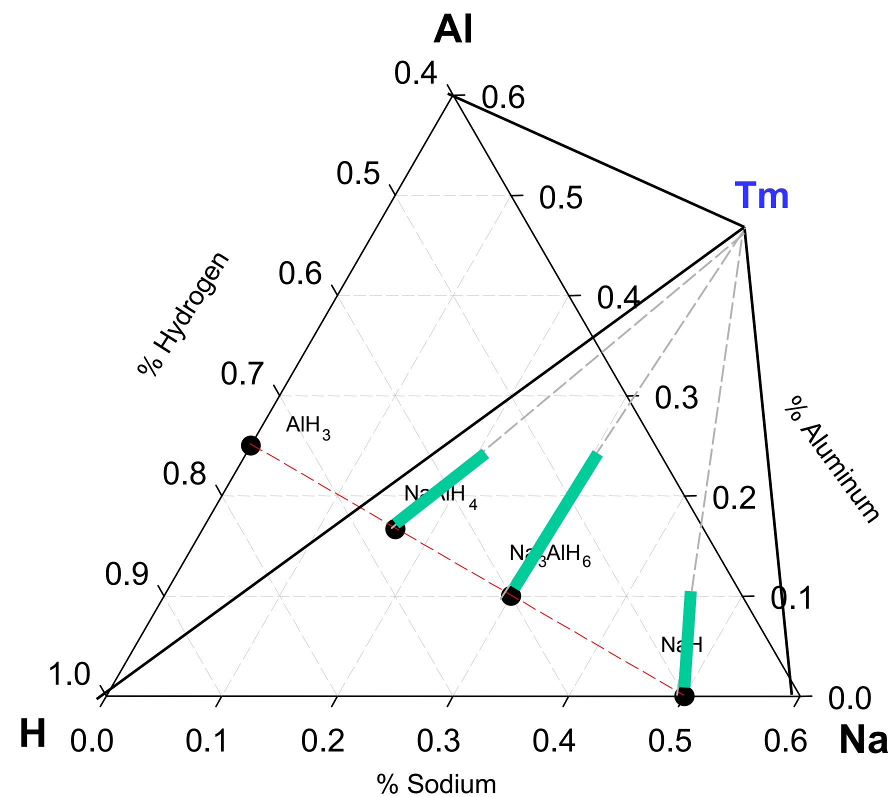
VASP

Atomistic simulations based on Density Functional Theory with pseudo-potentials for core electrons

ThermoCalc

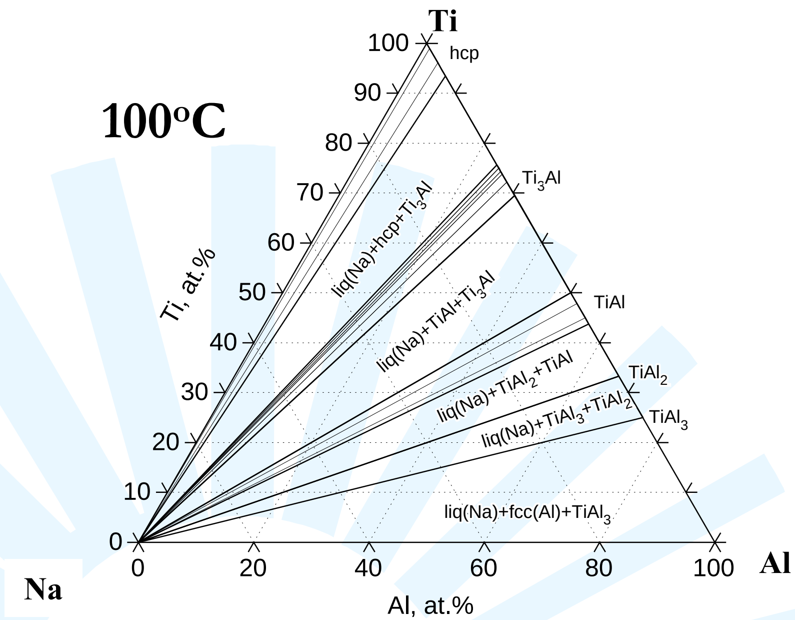
Thermodynamic Simulations of multi component phase diagrams

QuesTek Innovations LLC

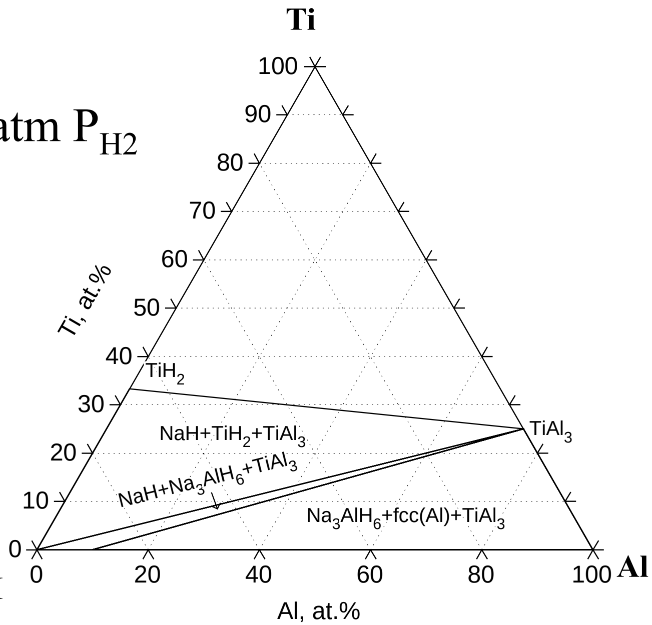


Calculated Na-Al-Ti-H Phase Diagrams

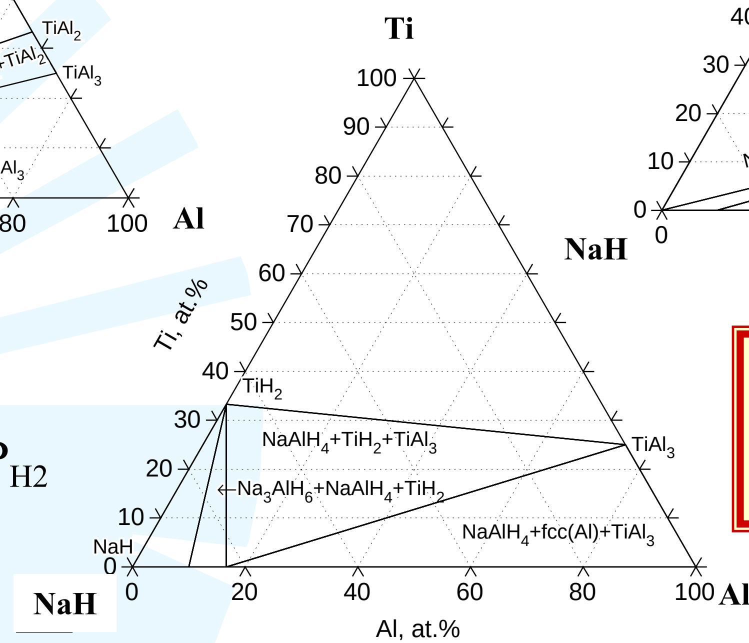
100°C



100°C 1atm P_{H2}



100°C 100atm P_{H2}

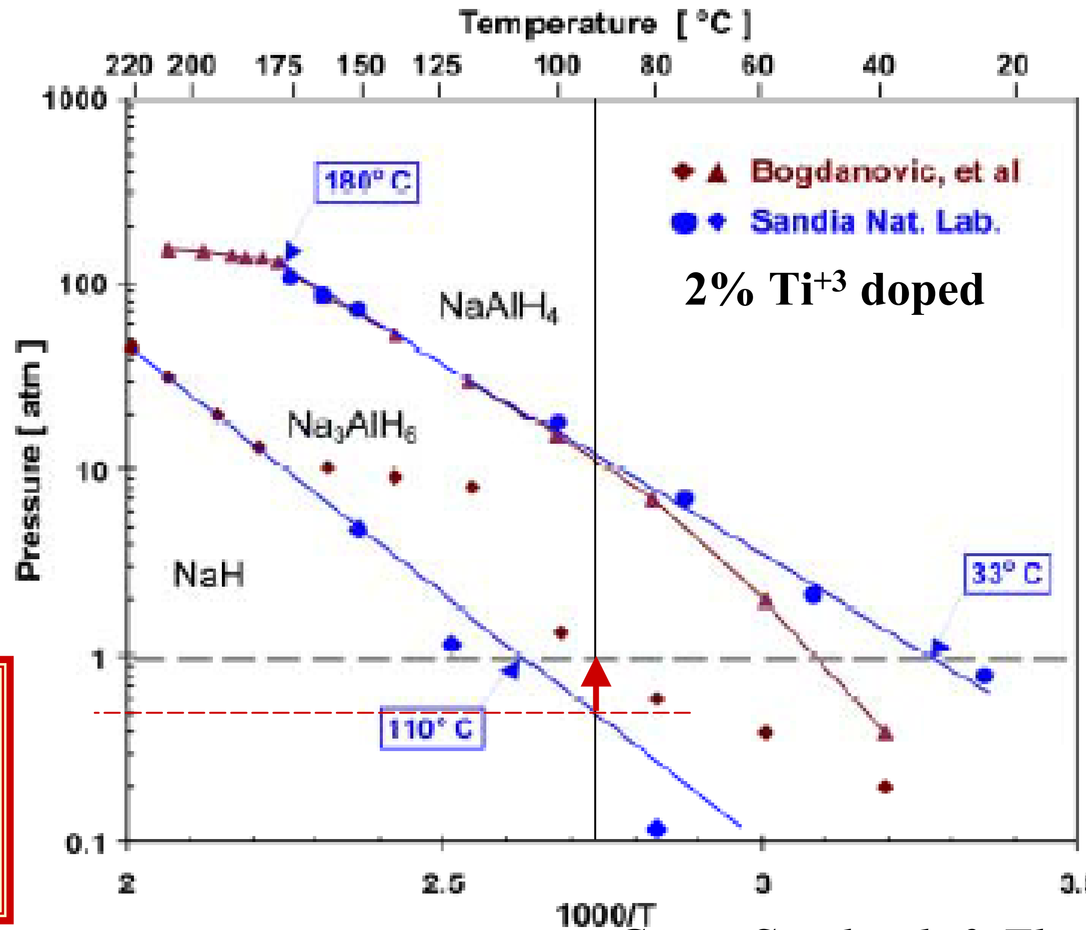


$Na_xAl_yH_z$-TiH_2-Al_3Ti are stable phases of interest

Is transition metal "catalytic" effect in $NaAlH_4$ <u>catalysis</u> or <u>thermodynamics</u>?

At 90°C, Na_3AlH_6 is too stable to access last % H_2
$P_e \sim 0.5$ bar

Urgent requirement to destabilize Na_3AlH_6 by 20°C (0.5bar)!!



Gross, Sandrock & Thomas

Quantum Mechanical Calculations

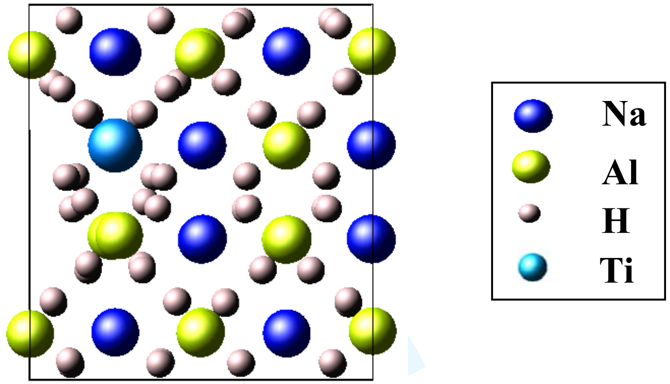
$NaAlH_4$: Enthalpy of Formation at 0K

$(Na_{1-y}Am_y)(Tm_xAl_{x-1})H_4$

$(Na_{1-y}Am_y)_3(Tm_xAl_{x-1})H_6$

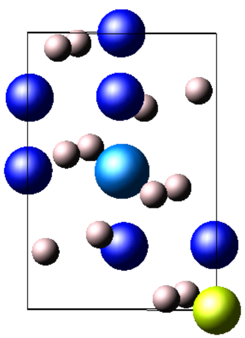
$Na_{16}TiAl_{15}H_{64}$ Supercell

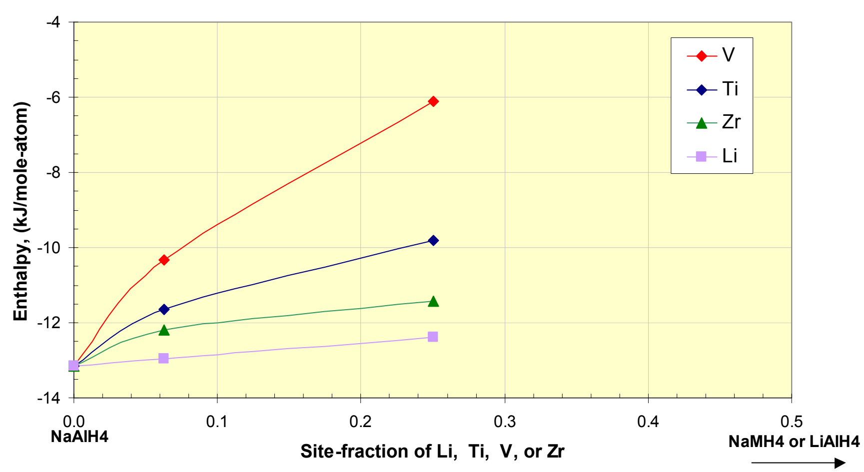
6.25 mole % $NaTiH_4$

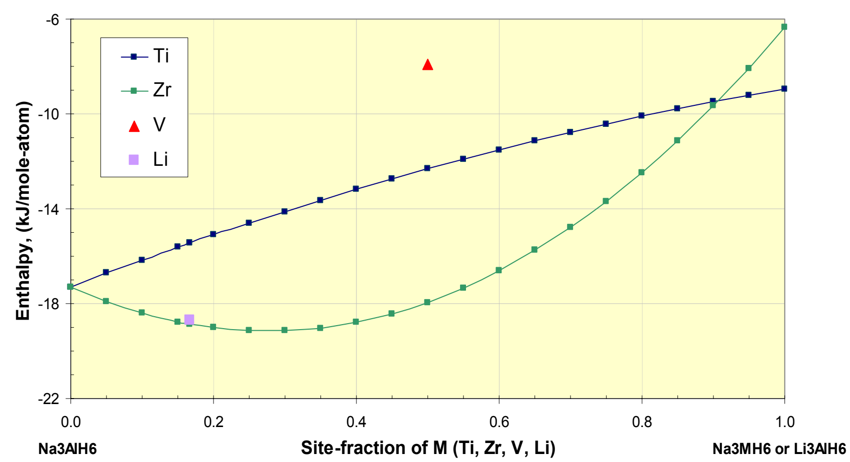


Na_6TiAlH_{12} Supercell

50 mole % Na_3TiH_6







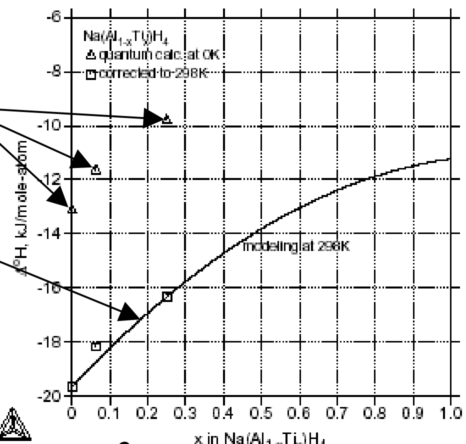
Thermodynamic Calculations

Ti^{+3} Additions

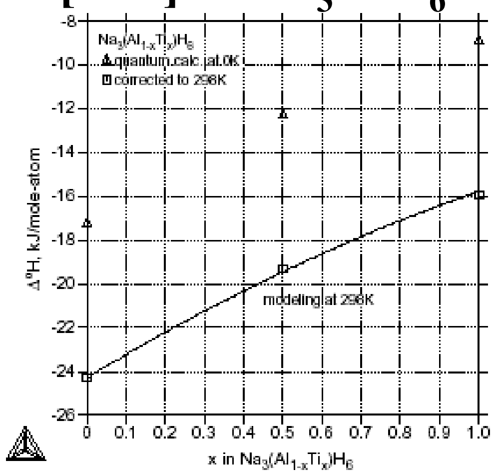
$\Delta^o H$ vs. T & [Ti^{+3}] in $NaAlH_4$

Atomistic Calculations

Thermodynamic Calculations



$\Delta^o H$ vs. T & [Ti^{+3}] in Na_3AlH_6

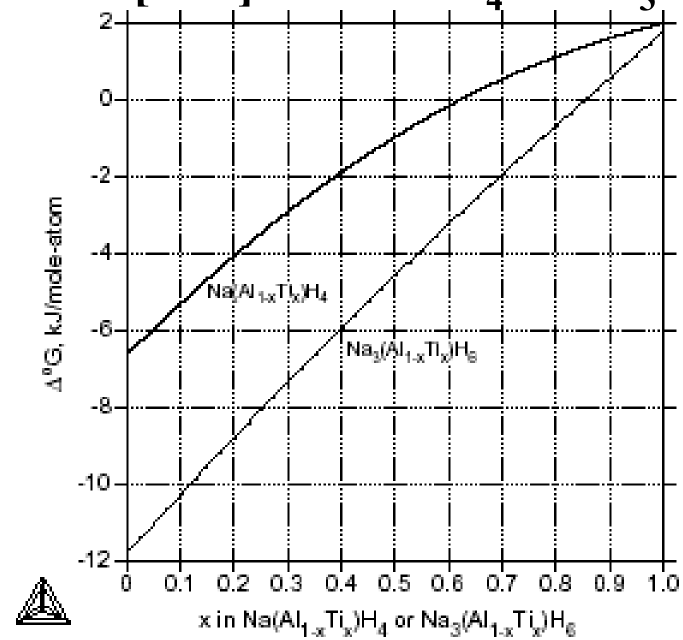


$$^oG_{NaAlH_4} = a_1 + b_1 T + c_1 T \ln T + ^oG_{AlH_3} + ^oG_{NaH}$$

$$^oG_{Na_3AlH_6} = a_2 + b_2 T + c_2 T \ln T + ^oG_{AlH_3} + 3\,^oG_{NaH}$$

a_i, b_i, c_i—constants evaluated from experimental data (ΔH, ΔS, C_P)

$\Delta^o G$ vs. [Ti^{+3}] in $NaAlH_4$ & Na_3AlH_6

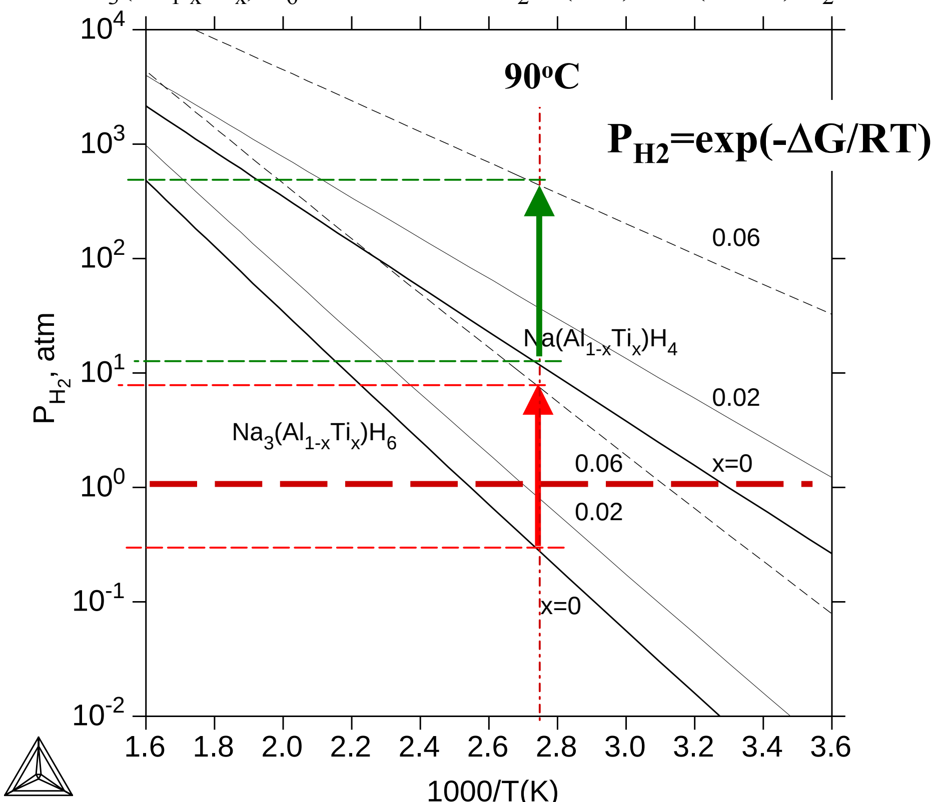


Thermal Stability of Ti^{+3} doped $NaAlH_4$ & Na_3AlH_6

$Na(Al_{1-x}Ti_x)H_4 = 1/3Na_3AlH_6 + xTiH_2 + (2/3-x)Al + (1-x)H_2$

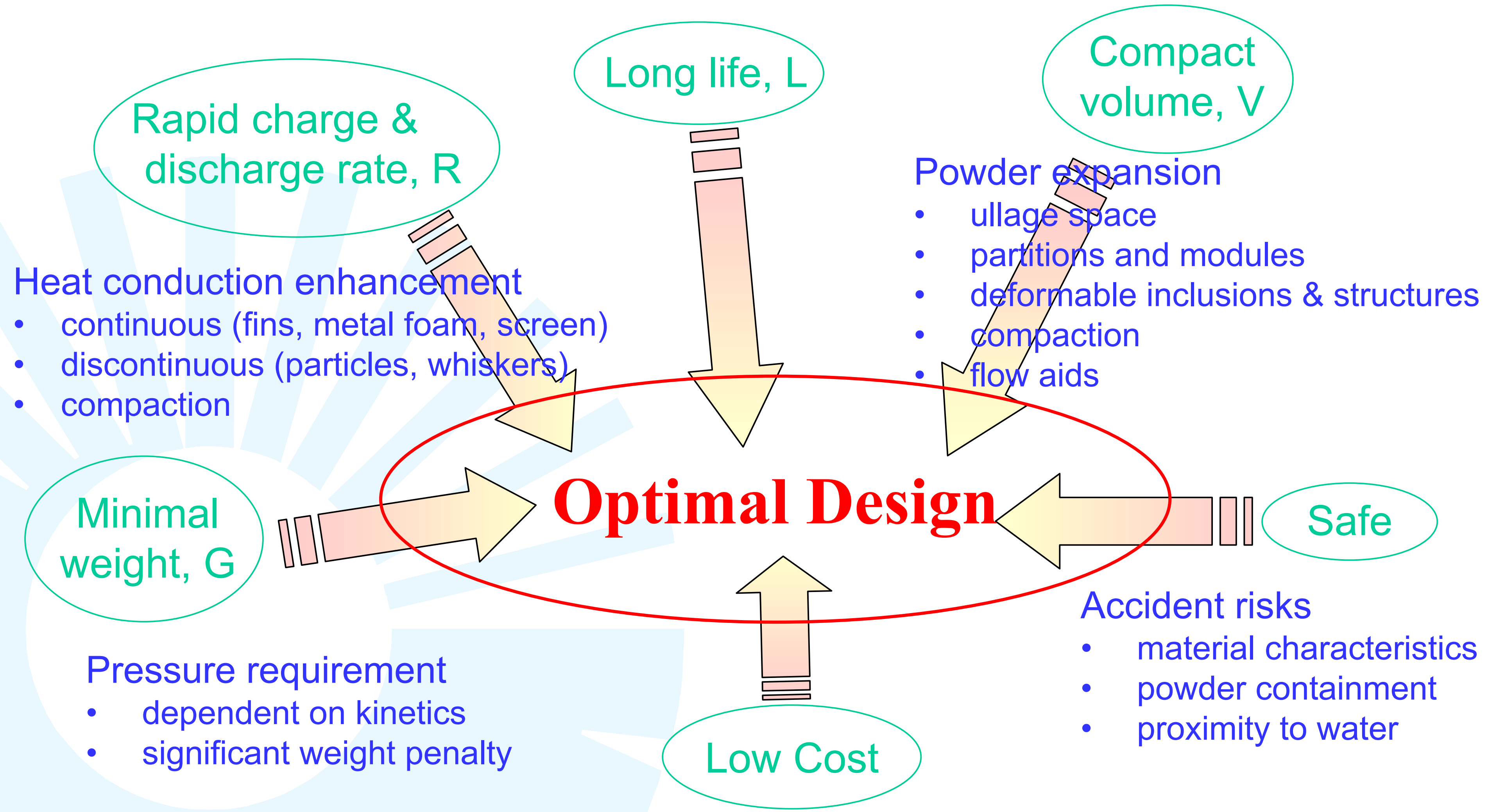
$Na_3(Al_{1-x}Ti_x)H_6 = 3NaH + xTiH_2 + (1-x)Al + (1.5-x)H_2$

- Both $NaAlH_4$ & Na_3AlH_6 destabilized with $[Ti^{+3}]$ additions (~50°C @ $[Ti^{+3}]=0.06$)
- Isothermal plateau pressures predicted as a function of $[Ti^{+3}]$
- **$Na_3Al_{0.94}Ti_{0.06}H_6$ plateau pressure raised from 0.3 bar to 7 bar at 90°C**
- $NaAl_{0.94}Ti_{0.06}H_4$ plateau pressure raised from 10 bar to 400 bar at 90°C

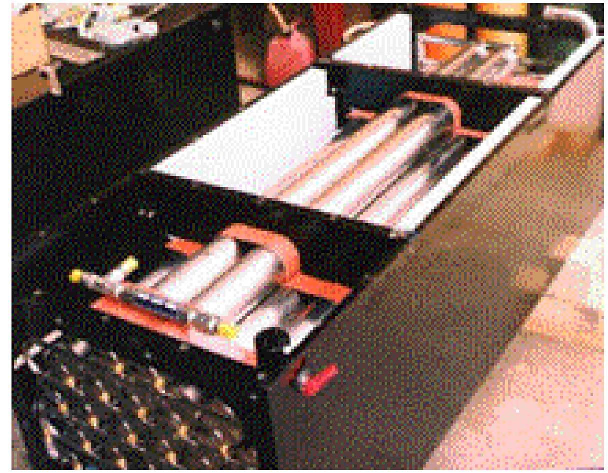


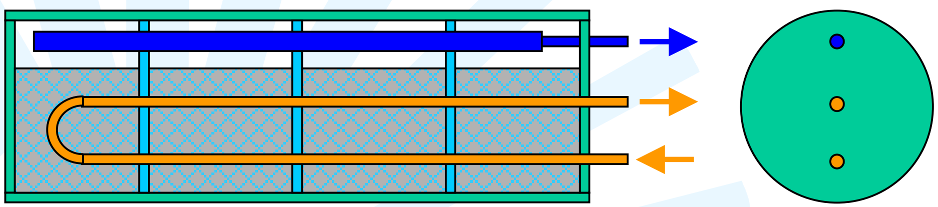
Predicts accessibility of full 5.5wt% H_2 above 1 bar pressure!!

Design Goals & System Elements



Metal Hydride Systems





- Inner pipe
- Particle filter
- Hydride material
- Heat transfer enhancement
- Partitions
- Outer pipe & end caps

SRTC design serves as a baseline

- Elements common to many designs
- Efficient pressure containment
- 280 Wh/kg (1.0 MJ / kg)
- 420 WH/L (1.5 MJ / L)

Modifications for $NaAlH_4$

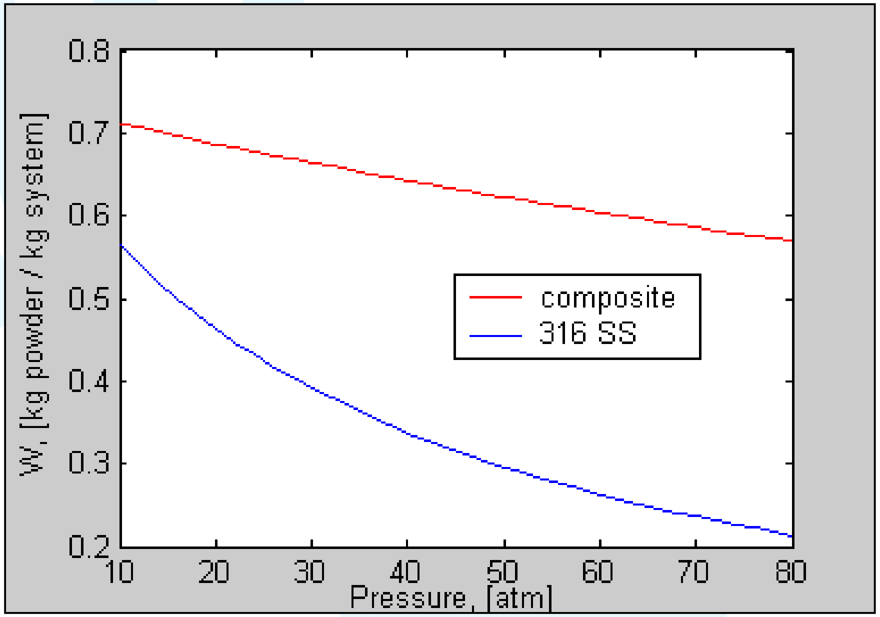
- Higher pressures
- Weight reduction
- Powder expansion differences

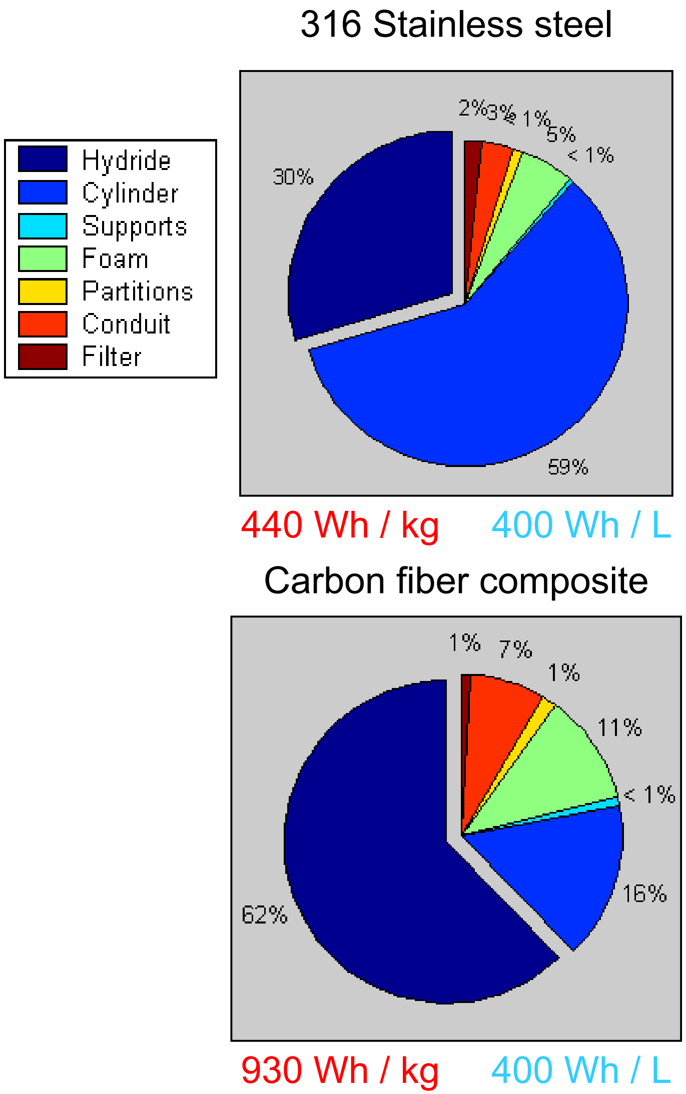
Design Comparisons

Gravimetrics vs. Pressure

<u>System Comparison</u>

- 4.5 wt% material
- 47% powder relative density
- 50 atm charging pressure





Composite tank necessary to achieve gravimetric goals!

Kinetics Modeling

Current approach tracks weight fraction of each composition

$$\underset{C_1}{NaH + Al + 3/2\ H_2} \leftrightarrow \underset{C_2}{1/3\ Na_3AlH_6 + 2/3\ Al + H_2} \leftrightarrow \underset{C_3}{NaAlH_4}$$

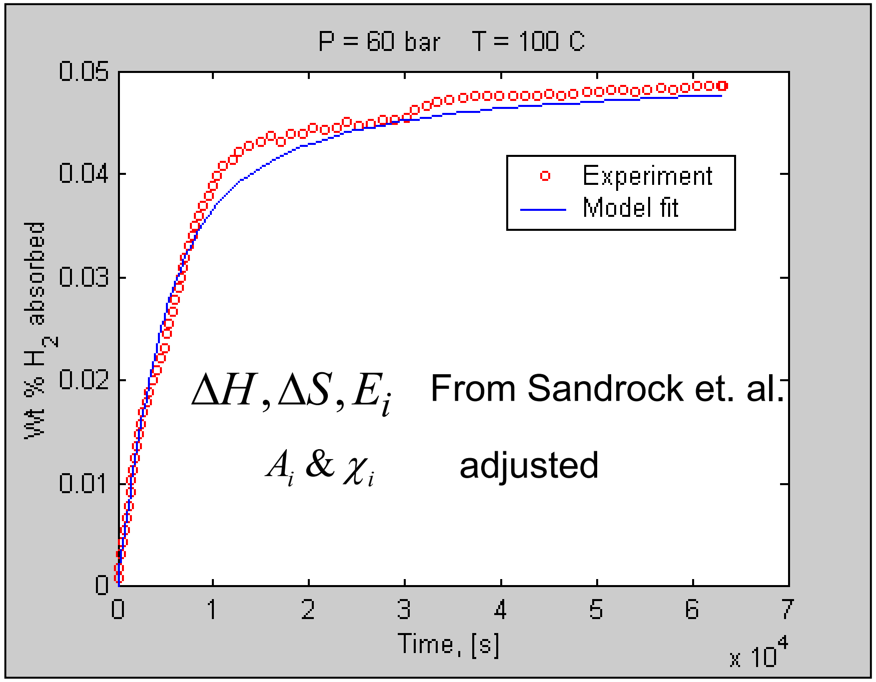
$$\left(\frac{dC_i}{dt}\right)_{ri} = f(T) * g(P) * h(C_i)$$

For C_1:

$$\left(\frac{dC_1}{dt}\right)_{r1} = A_1 \exp\left(-\frac{E_1}{RT}\right) * \left(\frac{P_{e,1} - P}{P_{e,1}}\right) * (C_2)^{\chi_1}$$

$$\left(\frac{dC_2}{dt}\right)_{r1} = -\left(\frac{dC_1}{dt}\right)_{r1}$$

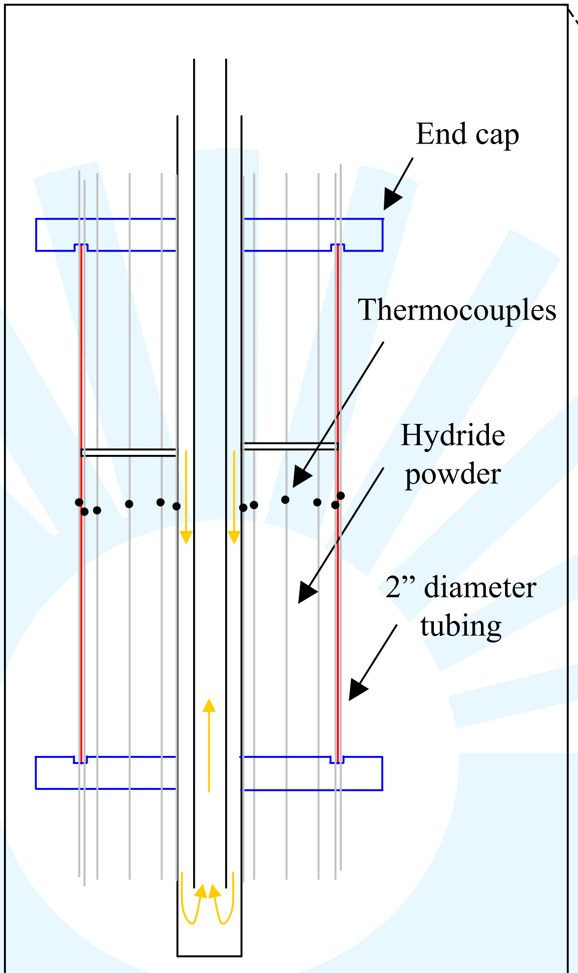
El Osery, 1993



$\Delta H, \Delta S, E_i$ From Sandrock et. al.

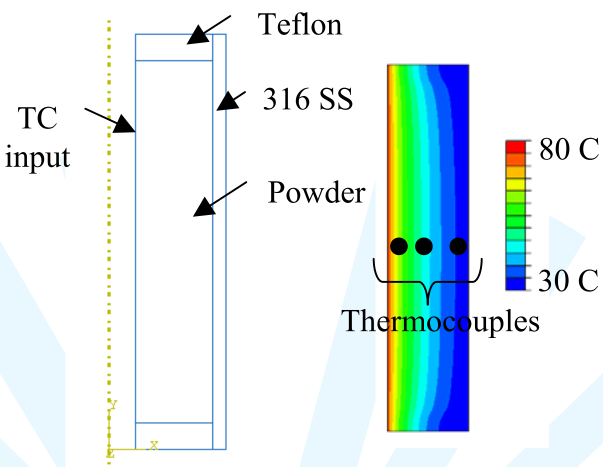
A_i & χ_i adjusted

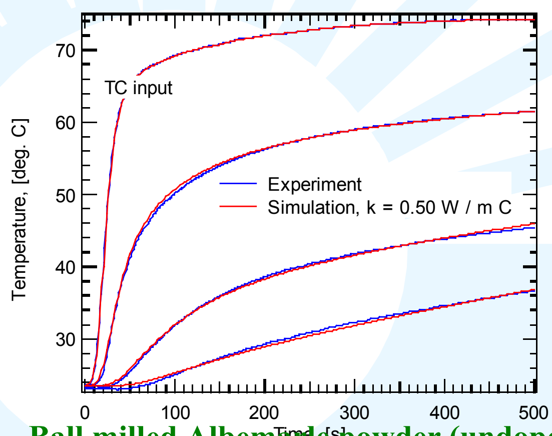
50g sub-scale system



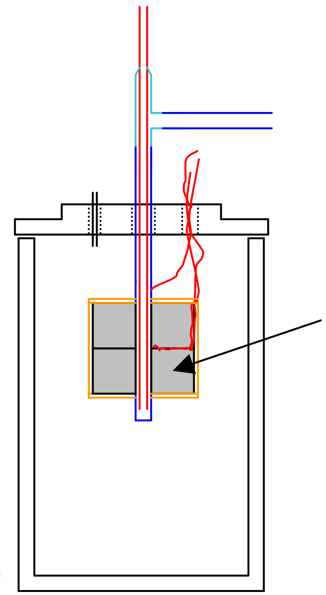
Thermal Conductivity/Enhancement

ABAQUS simulation





Ball milled Albemarle powder (undoped):
k = 0.35 to 0.50 W / m °C



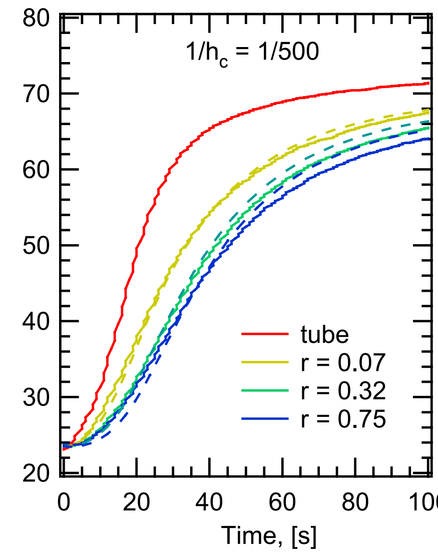
Unfilled contact resistance

$$\frac{1}{h_c} = \frac{1}{500\ \mathrm{W/m^2\ ^oC}}$$

Filled with $NaAlH_4$

$$\frac{1}{h_c} = \frac{1}{1000\ \mathrm{W/m^2\ ^oC}}$$

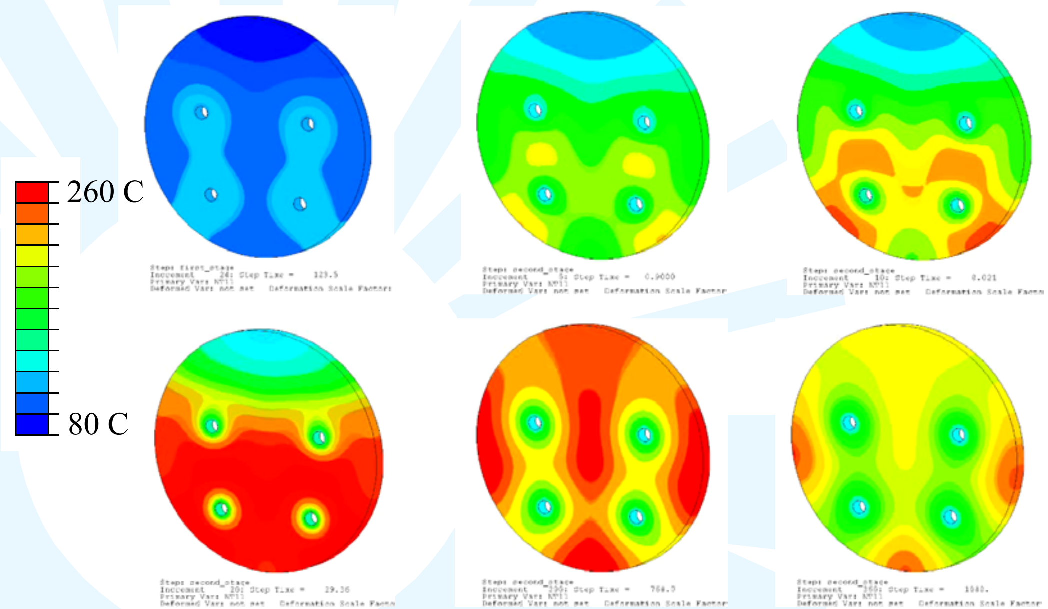
Unfilled contact resistance results

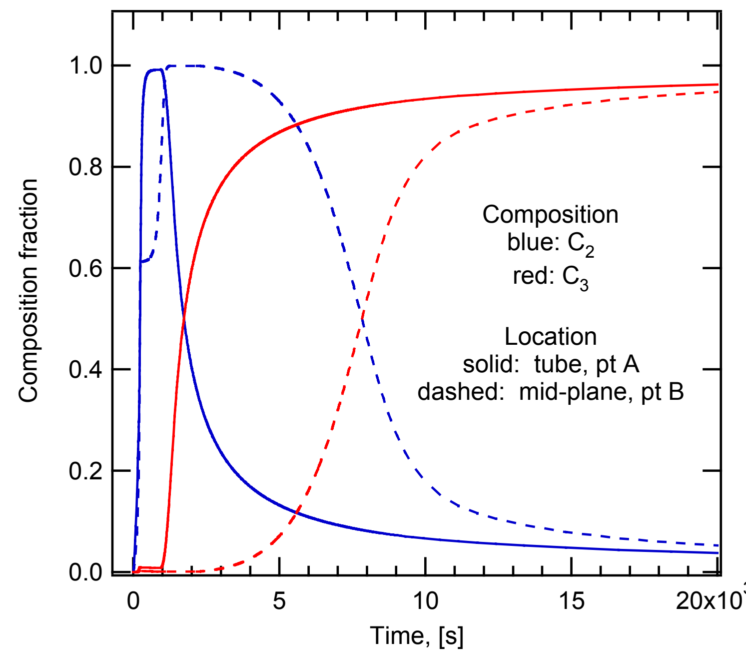


•Thermal contact resistance is significant for interference fit

System FEA Modeling
ABAQUS

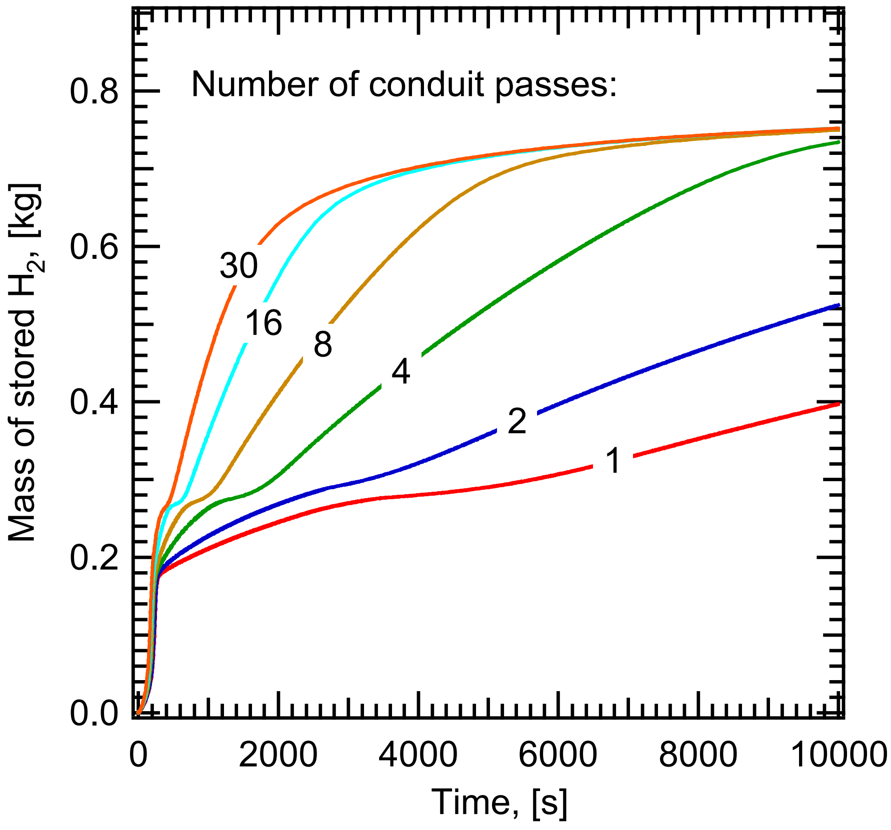
Vessel: 9” Dia. Vessel, 4 wt% Al foam, stainless steel tubing
Media: Albemarle $NaAlH_4$ + 2% Ti^{+3}
Starting state: Full discharged, 80°C
Charging state: 100 bar H_2 pressure, 120°C fluid flow



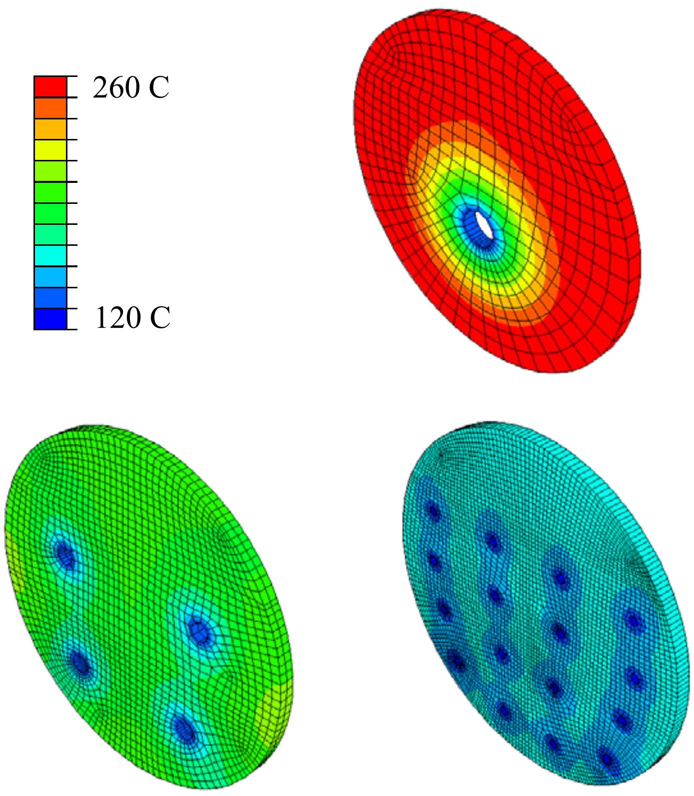


System Design Modeling

- ABAQUS subroutine calculates hydrogen mass via integration of C_i fields.
- Sensitivity study conducted for number of internal conduit passes during charging.



Temperature at t = 1400 s



Future Work
2003-04 Milestones

1. **Complete Safety Analysis**
2. **Perform 50g H_2 System Cyclic Evaluations**
3. **Assess/Complete Thermodynamic Modeling**
4. **Complete media cycling to assess durability.**
5. **Complete Prototype 1kg System Design & Fabrication**
6. **Complete Evaluation of 1kg System Prototype Capabilities to meet Go/NoGo criteria.**