Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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Project ID # ST6

Overview

- Timeline
  - 11/30/02 Start
  - 12/31/06 End
  - 40% Complete
- Budget
  - $2.9 M Total Program
    - $2.1M DoE
    - $0.8M (27%) UTC/ALB
  - $0.43M DoE FY'04
  - $0.68M DoE FY'05

- Barriers
  - Gravimetric Density: 2 kWh/kg
  - Volumetric Density: 1.5 kWh/l
  - Charging rate: 1.5 kgH_2/min.
  - Discharging rate: 4 gH_2/sec.
  - Safety: Meets or exceeds applicable standards
  - Durability: 1000 cycles
- Partners
  - SRNL
  - Albemarle
  - IFE
  - QuesTek LLC

Objectives

Total Program Objectives

To develop **new complex hydride compounds that can:**

-Reversibly store $\geq$ 7.5 weight % capacity,

-Discharge H_2 at rates required for PEM fuel cell operation,

-Recharge for 1000 cycles with 100 % recovery.

First Year (2004) Objectives

-Implement and validate new atomic-thermodynamic predictive methods.

-Search out quaternary systems for high H capacity candidates formed from Na, Li, Ti, and/or Mg combined with Al and H, using multi-pronged approach:

Atomic-Thermodynamic Modeling

Solid State Processing (SSP)

Molten State Processing (MSP)

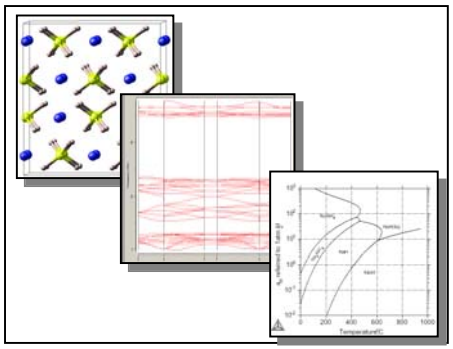
Solution Based Processing (SBP)

Approach
Virtual and Experimental Processing Methods

Discover reversible high H compounds, $Ak_xAe_yM^{+i}_z(AlH_4)_{(x+2y+iz)}$, formed between alkali (Ak) and alkaline earth (Ae) hydrides, metals (M), AlH_3, and H_2.

Atomic-Thermodynamic Modeling (UTRC)

- Survey broad compositional spaces
- Supplement thermodynamic data
- Generate descriptions of phase behavior



Solid State Processing, SSP (UTRC)

- Very rapid, low cost screening
- Limited conditions
- High cost for high volume production

Molten State Processing, MSP (SRNL)

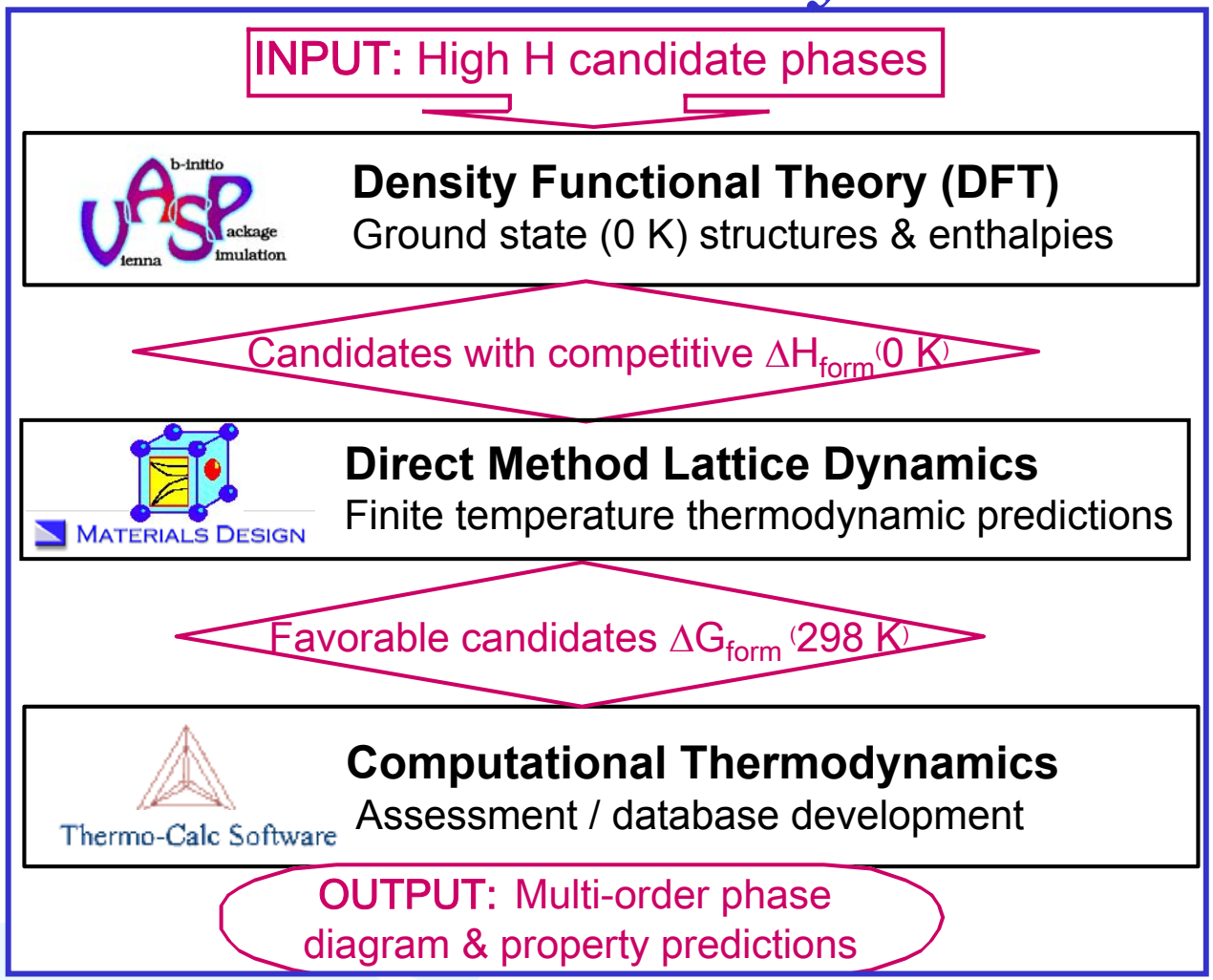
- Rapid screening
- Wide range of T & P
- Includes metastable phases
- Expensive equipment

Solution Based Processing, SBP (Albemarle)

- Excellent control
- High purity products
- Expensive processing
- Cost- effective high volume production

Unique aspect of approach: utilize a wide range of modeling and synthesis methods to search out and discover new high H_2 capacity systems.

Accomplishments: Established Atomic-Thermodynamic Flowpath



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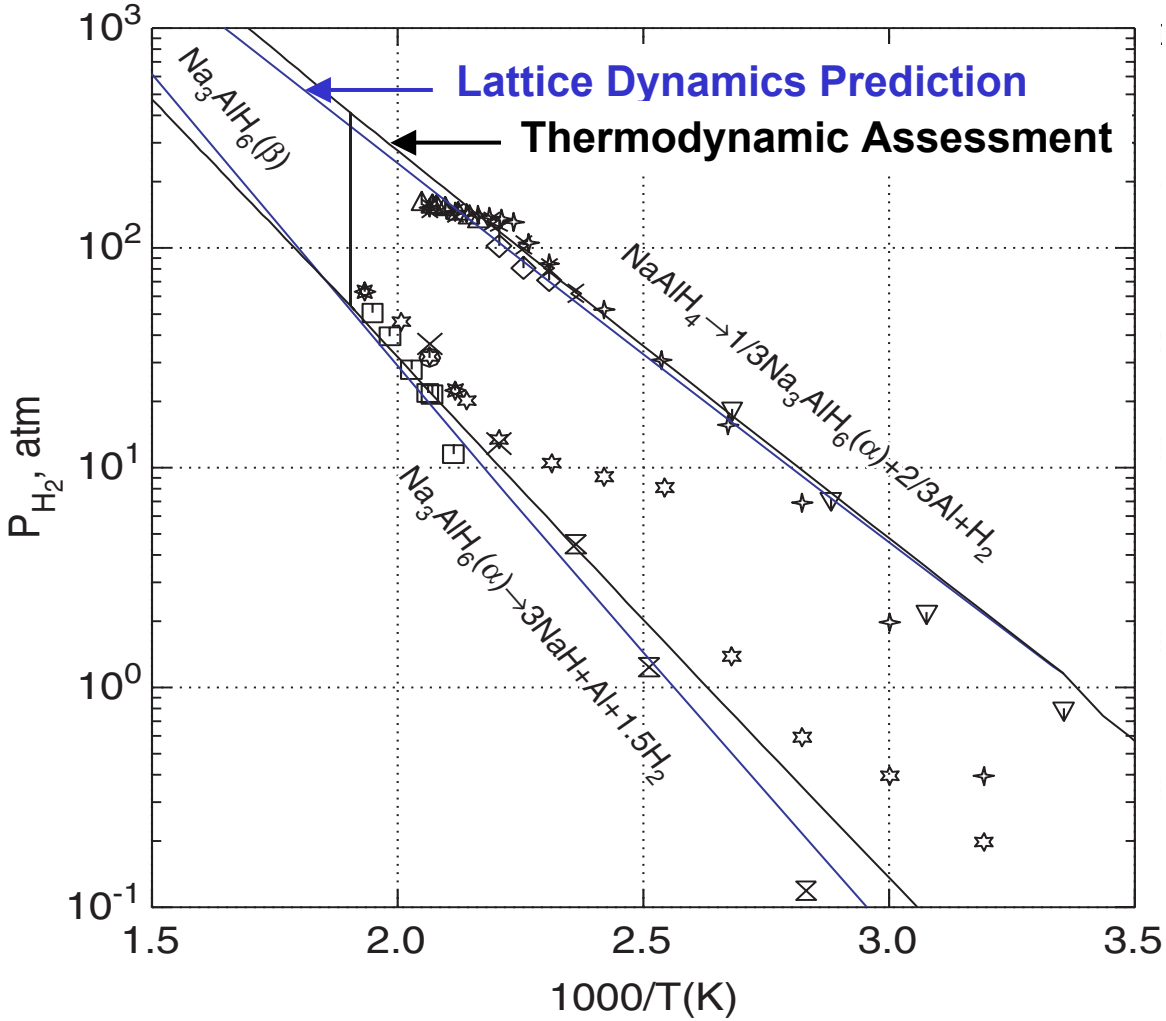
Coupled methodologies provide the capability to discover and evaluate high H capacity candidates' thermodynamic phase behavior, prior to experimentation.

Accomplishments:
Validation of First Principles (FP) Predictions



Experimental Data

Dymova 1974
- △ undoped $NaAlH_4$(liq)
- □ undoped Na_3AlH_6

Thomas 1999
- ◇ Ti-doped $NaAlH_4$
- ⧖ Ti-doped Na_3AlH_6

Gross 2002
- ▽ Ti-doped $NaAlH_4$

Bogdanovic 1997: PCI
- ∗ Ti-doped $NaAlH_4$
- × Na_3AlH_6 from Ti-doped NaA
- ⏲ Ti-doped Na_3AlH_6

Bogdanovic 2000: PCI
- ⨯ Ti-doped $NaAlH_4$
- ✵ Na_3AlH_6 from Ti-doped NaA

Bogdanovic 2000: dissociation
- ✧ Ti-doped $NaAlH_4$
- ✡ Ti-doped Na_3AlH_6

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QuesTek Innovations LLC

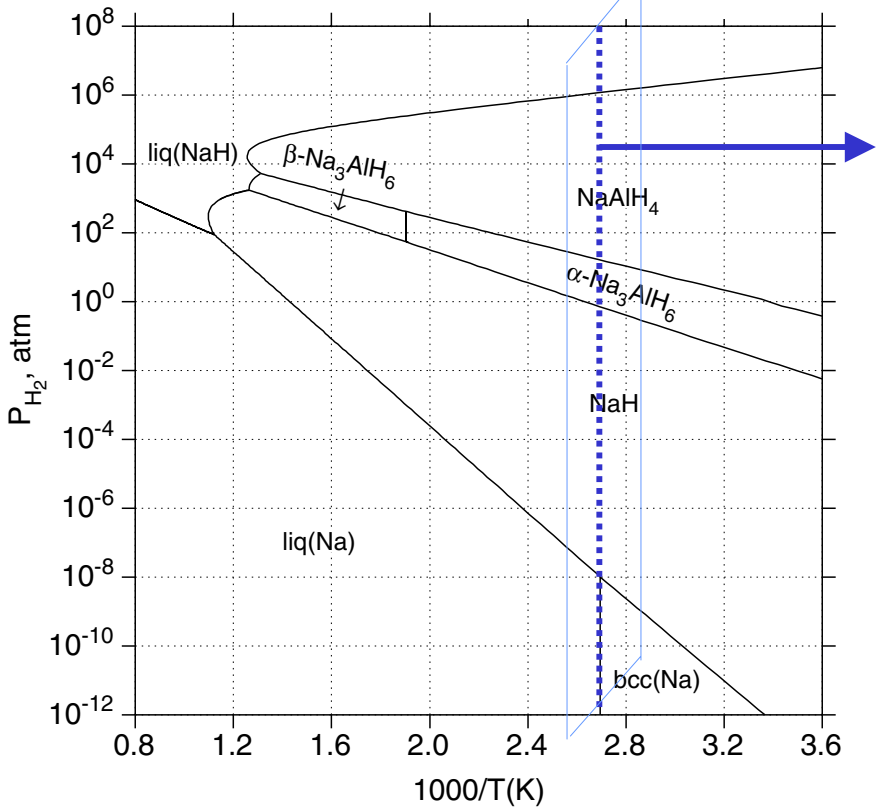
Materials Design

Thermo-Calc Software

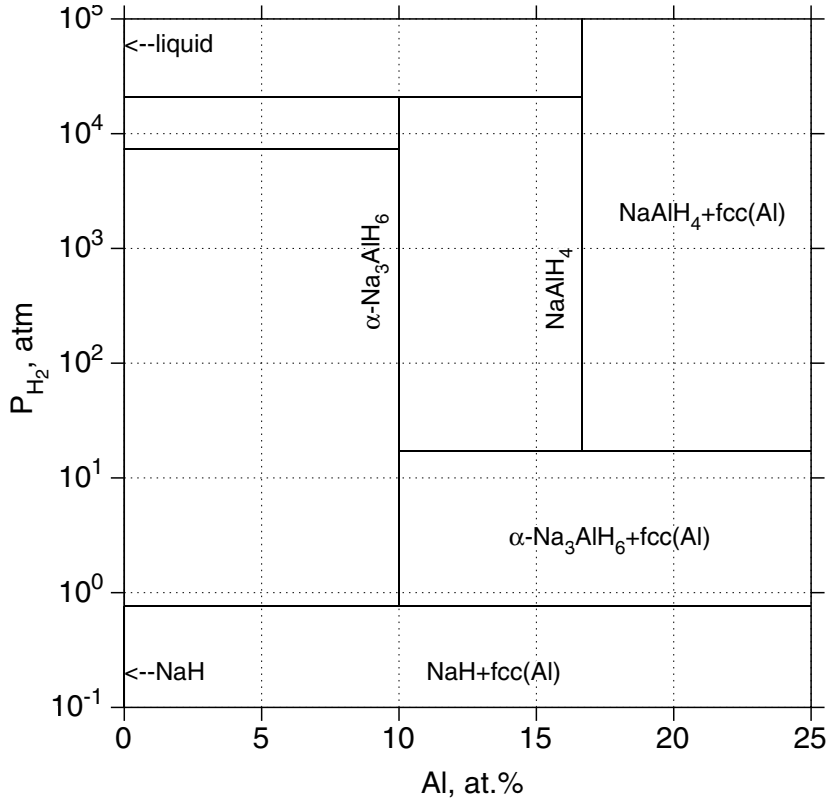
Validation with experiment: lattice dynamic predictions in excellent agreement with thermodynamic assessment of experimental Na alanate dissociation data.

Accomplishments:
Integrated Experimental & FP Predicted Data

Potential diagram 100°C



100°C Isothermal phase section



Predictions extend computational thermodynamics beyond experimental realm. Phase diagrams calculated from integrated assessment of experimental data and predictions used to evaluate candidate phase stability over a wide range of T & P.

QuesTek INNOVATIONS LLC | United Technologies | Thermo-Calc

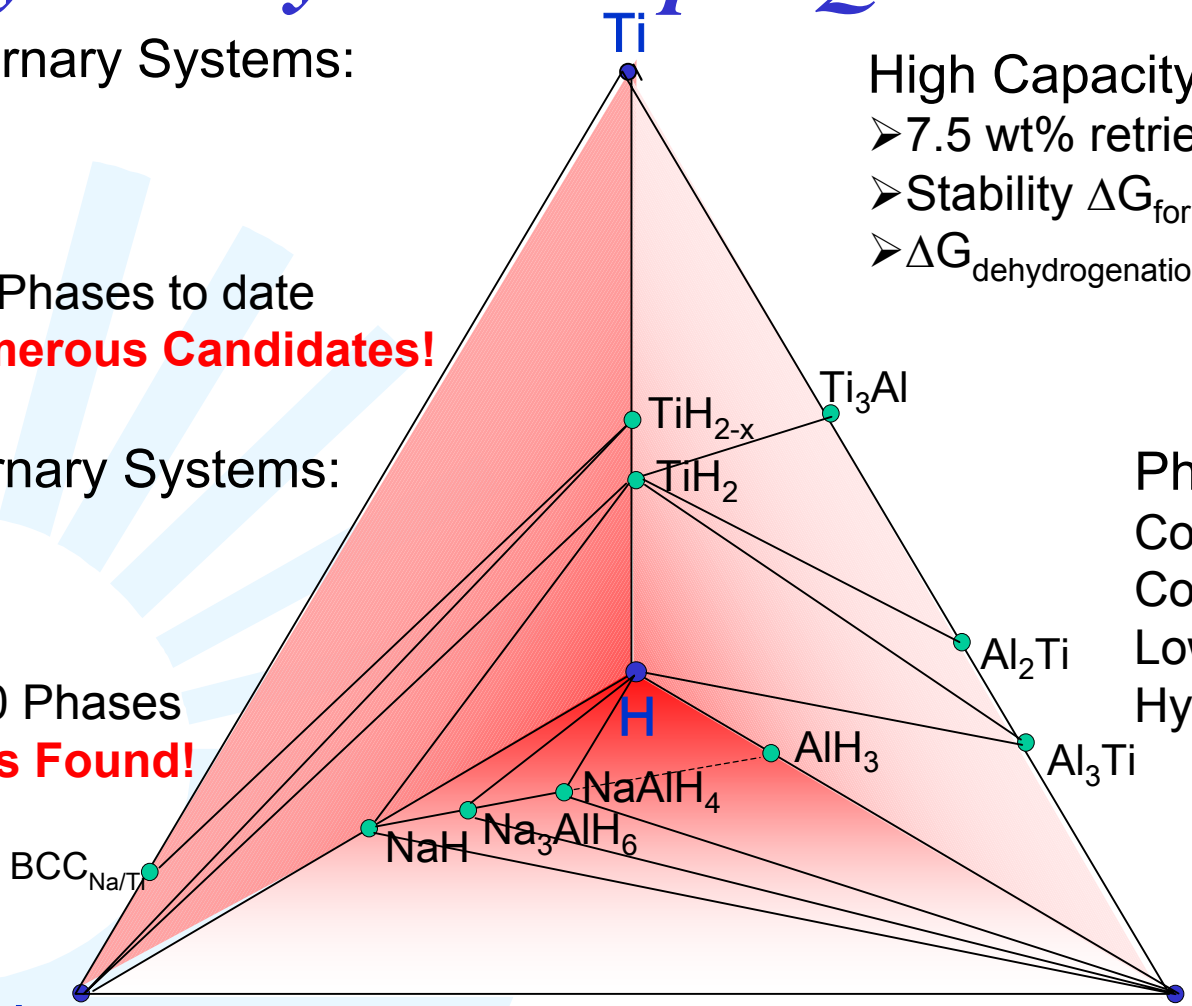
Accomplishments:
Virtually Surveyed Multiple Quaternary Spaces

Year II Quaternary Systems:
To Date:
Na-Mg-Al-H
Li-Mg-Al-H
Surveyed >40 Phases to date
Identified Numerous Candidates!

Year I Quaternary Systems:
Na-Ti-Al-H
Li -Ti-Al-H
Na-Li-Al-H
Surveyed >170 Phases
No Candidates Found!

High Capacity Media Criteria:
- 7.5 wt% retrievable H capacity
- Stability $\Delta G_{formation} << O$
- $\Delta G_{dehydrogenation} \rightarrow O$

Phases Simulated:
Complex hydrides
Competing phases
Lower order phases
Hypothetical End-Members



Aerial View of Na-Ti-Al-H Quaternary Pyramid

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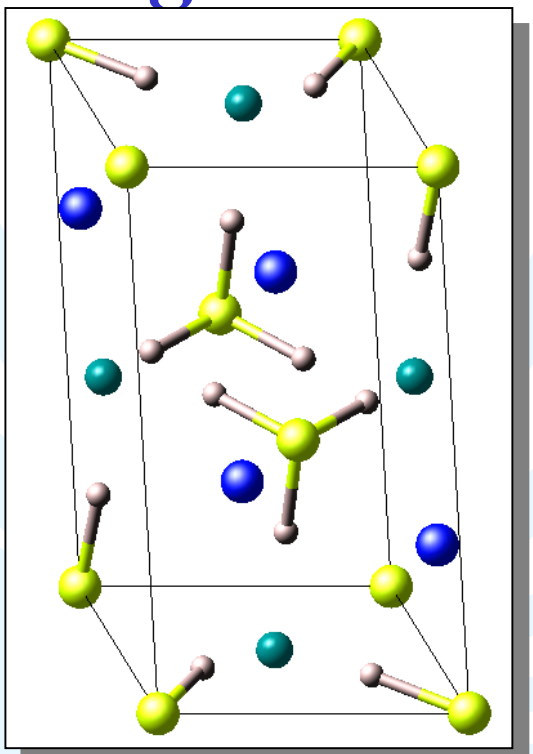
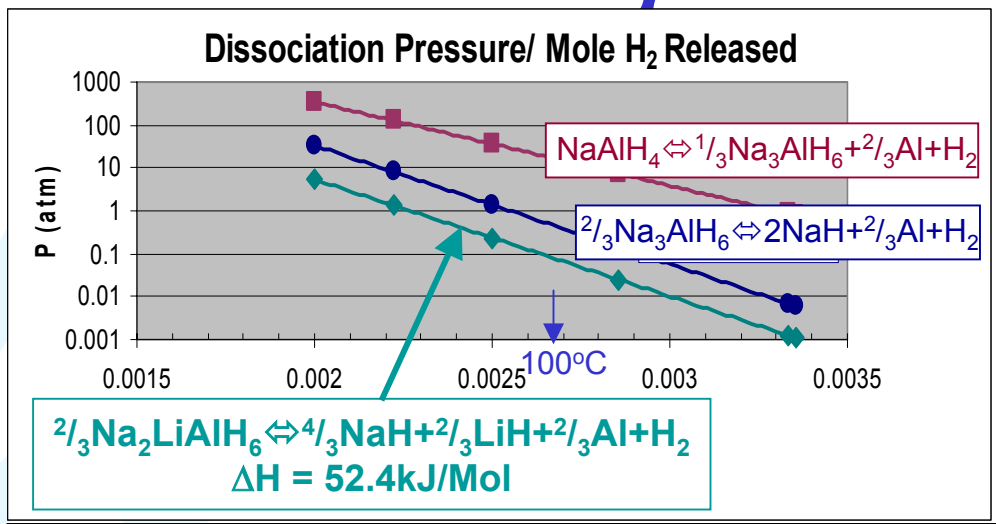
FP atomic-thermodynamic methodologies used to accelerate survey of broad compositional phase spaces, reducing and focusing experimental effort.

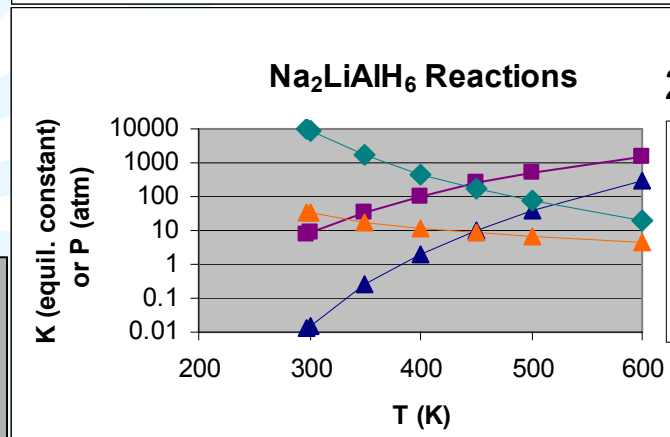
Accomplishments: Integrated Predictions and Experiments



Na_2LiAlH_6 $P2_1/c$
Stable Low T Structure
ID from Collaboration



Predicted and experimental *(Fossdal et. al, J. Alloys Compd., in press.)* dissociation P are in excellent agreement.



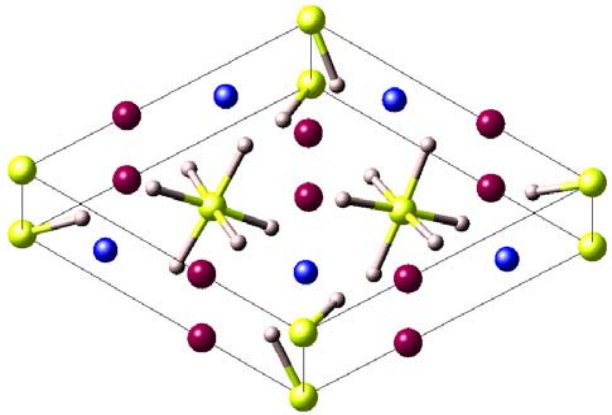
First two reactions correspond to a 2-step 5.2 w/o H_2 reversible system.

- $^4/_3NaAlH_4 + {}^2/_3LiH \Leftrightarrow {}^2/_3Na_2LiAlH_6 + {}^2/_3Al + H_2$
- $^2/_3Na_2LiAlH_6 \Leftrightarrow {}^4/_3NaH + {}^2/_3LiH + {}^2/_3Al + H_2$
- $^2/_3LiAlH_4 + {}^4/_3NaH \Leftrightarrow {}^2/_3Na_2LiAlH_6$
- $^2/_9Li_3AlH_6 + {}^4/_9Na_3AlH_6 \Leftrightarrow {}^2/_3Na_2LiAlH_6$

1st, 3rd & 4th reactions for synthesis.

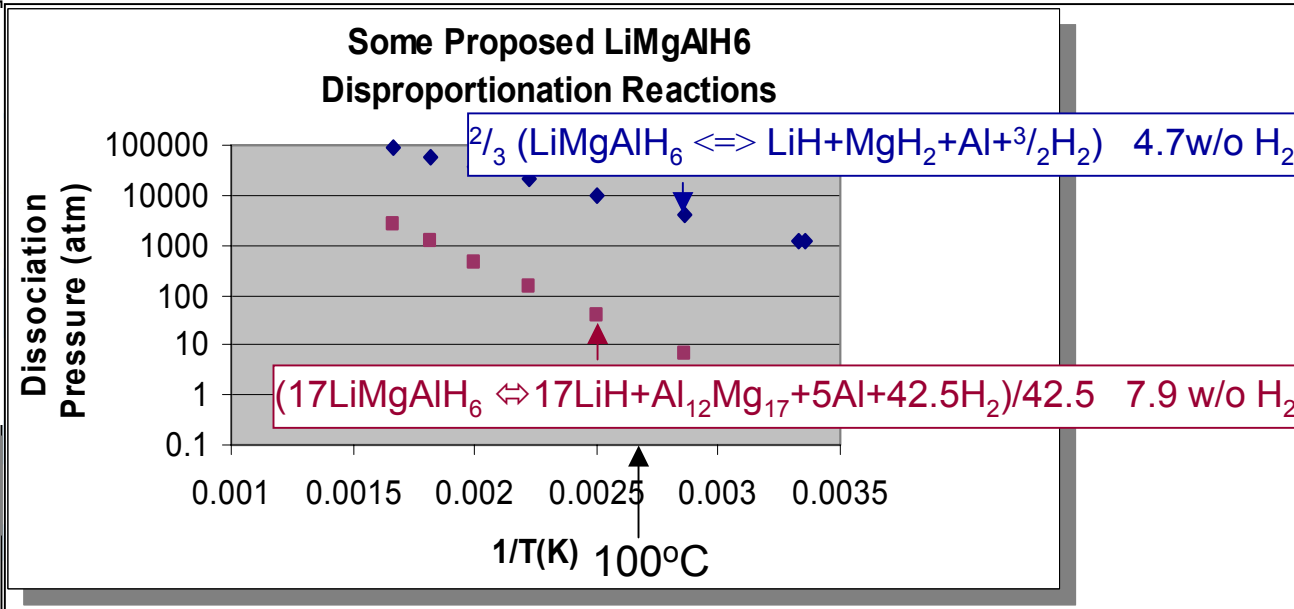
Successfully employed FP predictions to evaluate Na_2LiAlH_6 structure and phase behavior. Explained observed synthesis and disproportionation reactions.

Accomplishments: Identification of High Capacity Candidates



$LiMgAlH_6$ Candidate

Many mixed alkali/alkaline earth alanate candidates predicted to have ΔH_{form} (0 K) >-8 kJ/mol*atom



Numerous possible disproportionation products are currently being evaluated. Actual reversible H_2 content dependent upon identification of most favorable dehydrogenation end products.

Combined predictive methodologies are effective in identifying and evaluating new candidate hydrides, yielding recommendations for experimental evaluation.

Accomplishments

New High H Capacity Material Search Strategy

A method of predicting destabilized alanate compounds with *in-situ* rechargeability can be described thermodynamically as:

$$M^1(AlH_4)_y + M^2H_x \Leftrightarrow M^1M^2H_i + Al + {}^{(4y+x-i)}/_2H_2$$

where:

$$\Delta G \sim 0 \sim G_f{}^o{}_{M1M2Hi} + G_f{}^o{}_{Al} + RT\ln(P_{H2}) - G_f{}^o{}_{M1(AlH4)y} - G_f{}^o{}_{M2Hx}$$

at $70<T<120^oC$ & $1<P<100$ bar and M^1 & M^2 are metal ions.

Systematic Approach:

-Comprehensively search databases to select candidates from known phases.

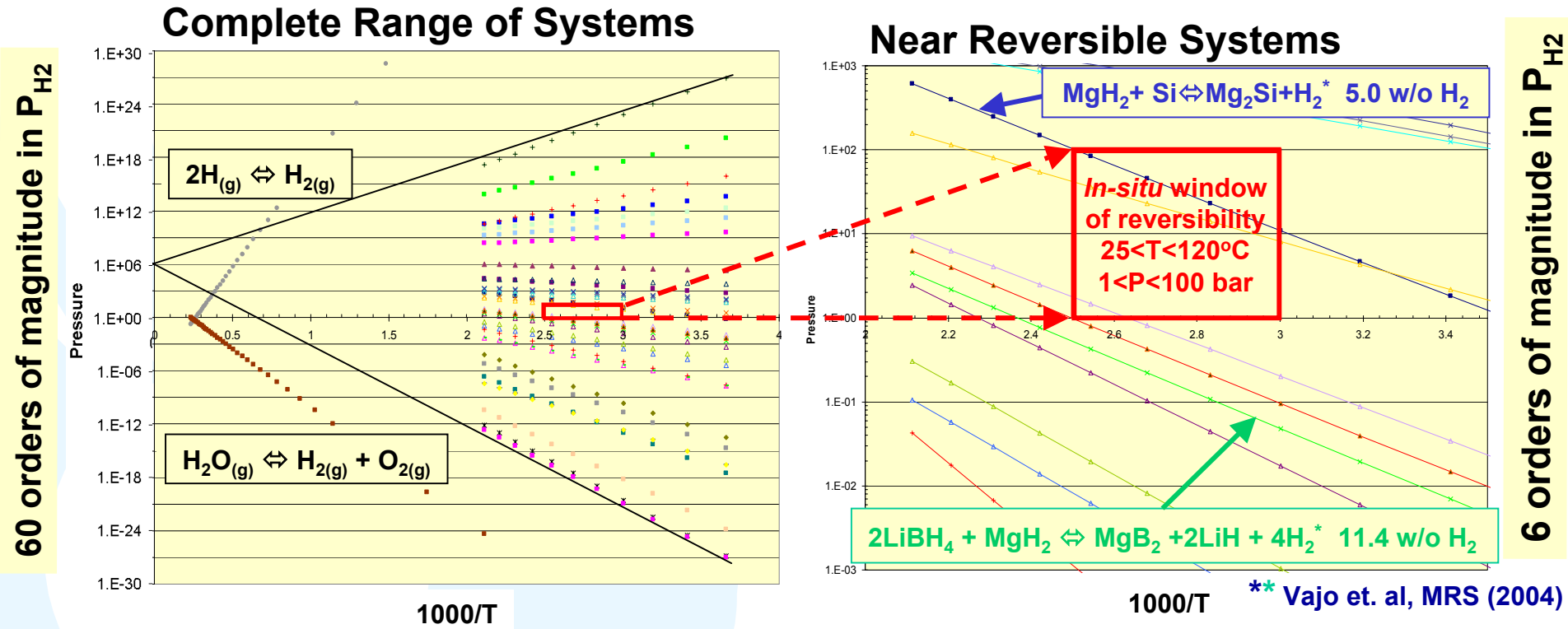
-Identify candidate phase chemical reactions, prioritize according to H_2 storage capacity.

-Where thermodynamic data is unavailable, predict thermochemical properties.

-Conduct thermodynamic assessments combining both experimental and predicted data to evaluate *in-situ* reversibility for hydrogen storage.

New modeling tools used to select candidates for focused synthetic evaluation.

Accomplishments
New Hydrogen Storage Opportunities



- All in-situ rechargeable systems have $\Delta H_f \approx$ 40 kJ/mole H_2.
- $\Delta H_f \approx 0$ kJ/mole H_2 reactions can only be achieved at ~10^6 bar.
- This results from ΔS_f for MH_x approximately constant.

Thermodynamic assessments of *in-situ* reversible hydrogen storage reactions.

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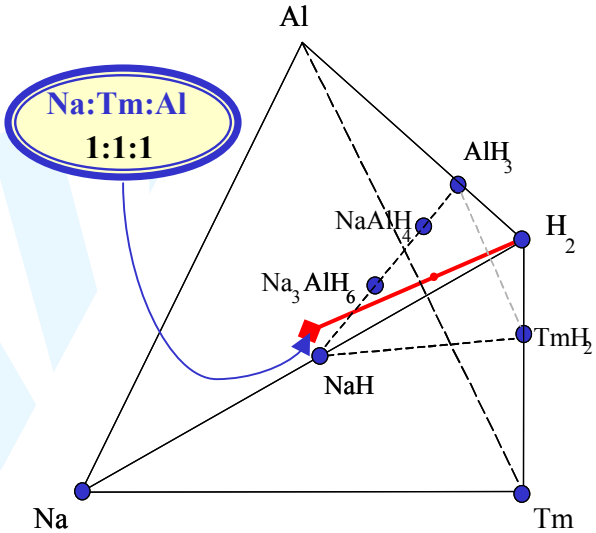
Accomplishments
Solid State Processing (SSP) System Surveys

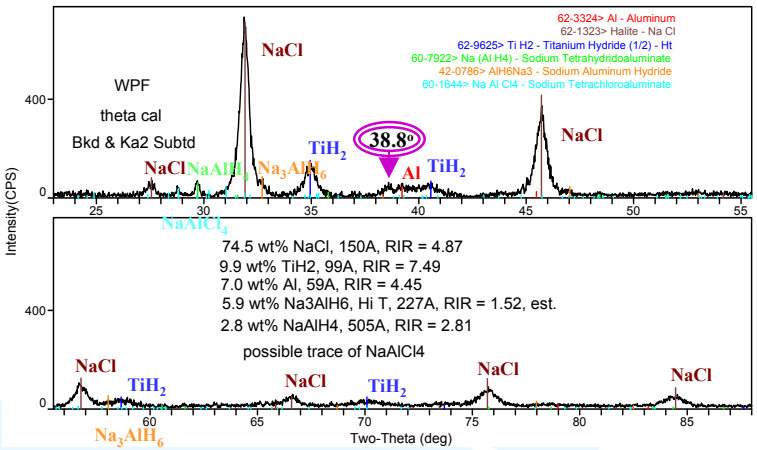


Am/Ae/Tm

Na:Ti:Al
Na:Li:Al
Na:Mg:Al
Na:Ti:Li:Al
Na:Ti:Mg:Al
Na:Li:Mg:Al
Li:Mg:Al

Processing

- Hand Mix ⇨ XRD
- SPEX Mill 3 hr. ⇨ XRD
- 200barH_2/60°C/20 hr ⇨ XRD
- 200barH_2/80°C/20 hr ⇨ XRD
- 200barH_2/100°C/20 hr ⇨ XRD
- 200barH_2/120°C/20 hr ⇨ XRD



Analysis

Semi-quantitative analysis using:
MDI Corp. Jade 7.0
utilizing data bases:
ICDD/PDF-2 Release 2002
ICSD Release 2004/2.

High throughput SSP screening of 7 quaternary/quinary systems completed.

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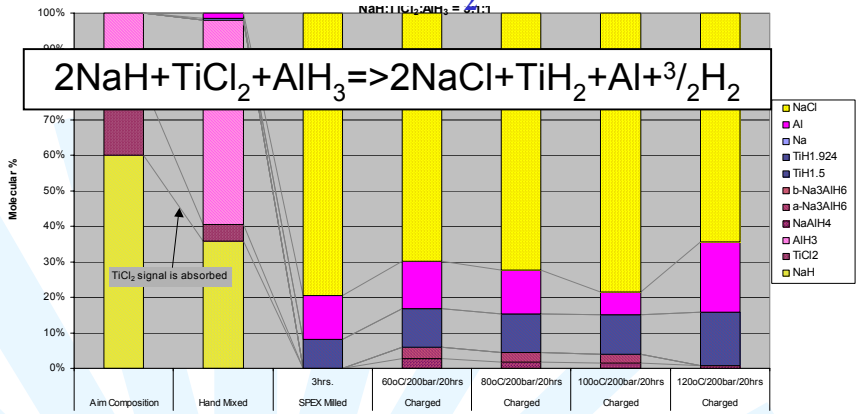
Accomplishments

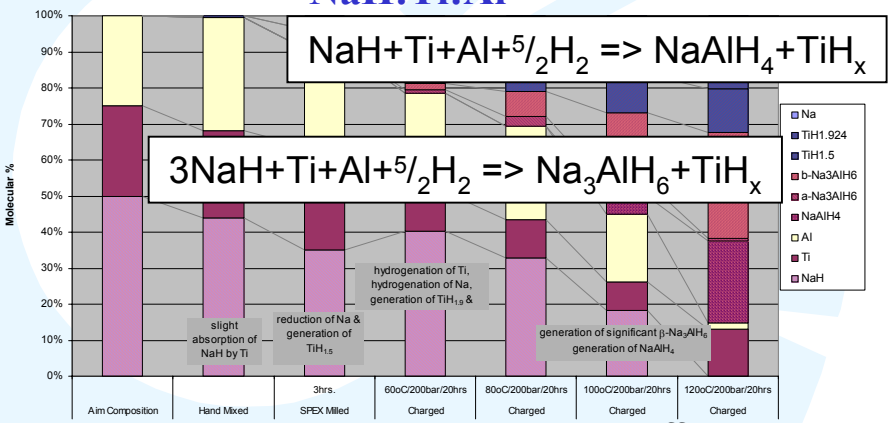
Development of SSP $NaH:TiH_2:AlH_3$ Method

$NaH:TiCl_2:Al$



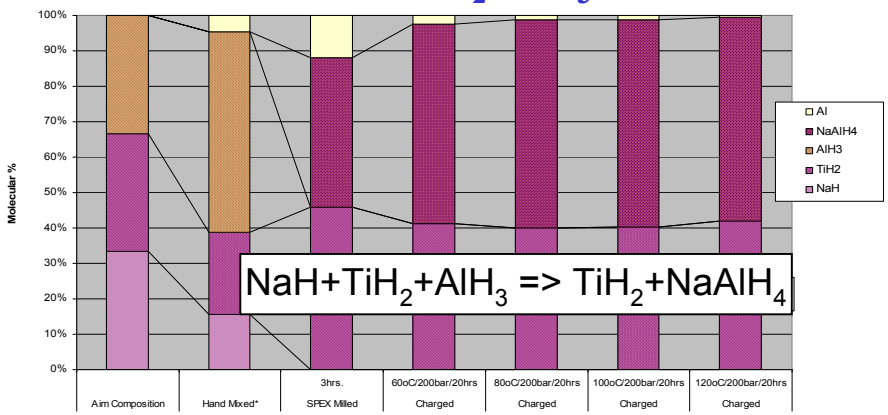
Cations introduced via chloride additions led to far too much MCl_x to be effective.

$NaH:Ti:Al$



Primary metal additions were only an effective method of synthesizing Na_xAlH_y at temperatures > 100°C.

$NaH:TiH_2:AlH_3$



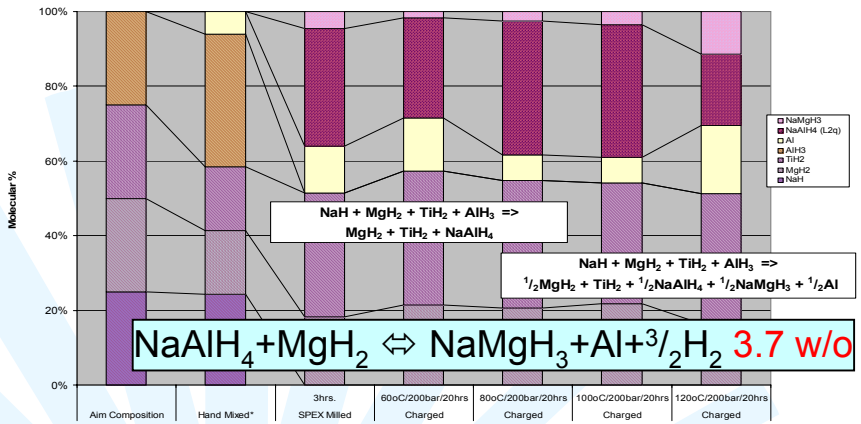
The most effective method was to add cations as hydride species. This method readily produced $NaAlH_4$ upon SPEX milling.

No previously unidentified phases found in the Na-Li-Ti-Al-H systems.

Accomplishments

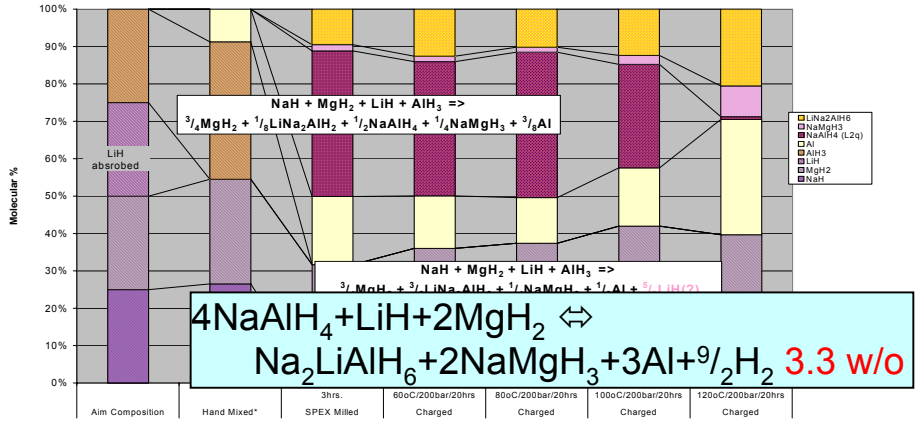
SSP NaH-LiH:MgH_2:TiH_2:AlH_3 System Survey

NaH:MgH_2:TiH_2:AlH_3



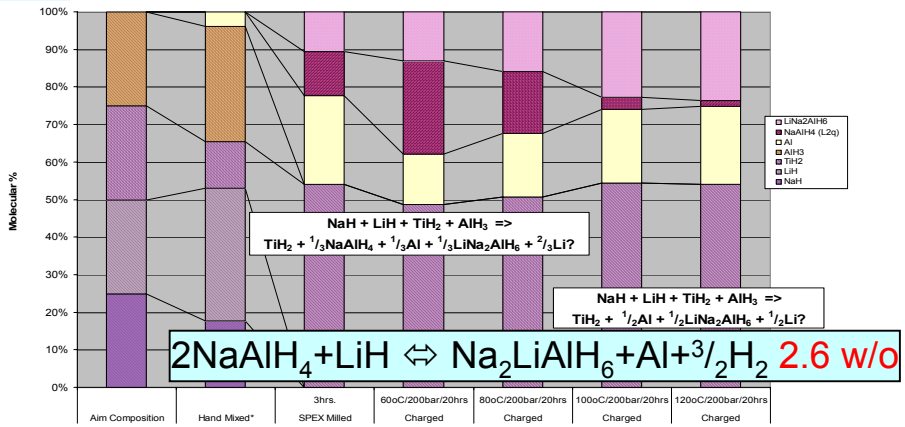
$NaAlH_4 + MgH_2 \Leftrightarrow NaMgH_3 + Al + {}^3/_2H_2$ 3.7 w/o

NaH:MgH_2:LiH:AlH_3



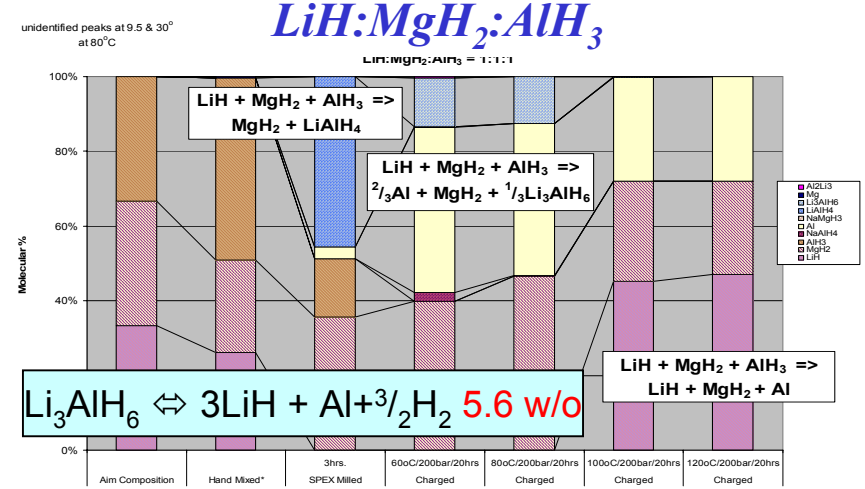
$4NaAlH_4 + LiH + 2MgH_2 \Leftrightarrow Na_2LiAlH_6 + 2NaMgH_3 + 3Al + {}^9/_2H_2$ 3.3 w/o

NaH:TiH_2:LiH:AlH_3



$2NaAlH_4 + LiH \Leftrightarrow Na_2LiAlH_6 + Al + {}^3/_2H_2$ 2.6 w/o

LiH:MgH_2:AlH_3



$Li_3AlH_6 \Leftrightarrow 3LiH + Al + {}^3/_2H_2$ 5.6 w/o

Numerous mixed compound systems identified having H_2 capacities ranging from 2.6-5.6 w/o, and which are rechargeable ≤ 200 bar at T<120°C.

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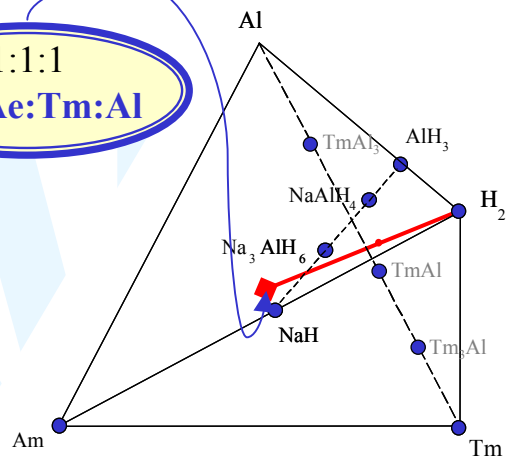
Accomplishments
SSP 2005 Approach Going Forward

1:1:1
Am/Ae:Tm:Al



Mg_2NiH_4
Mg_2CoH_5
Mg_2FeH_6

?

$Li_2Mg(NiH_4)_2$
$Na_2Mg(CoH_5)_2$
$LiNaMg(FeH_6)_2$

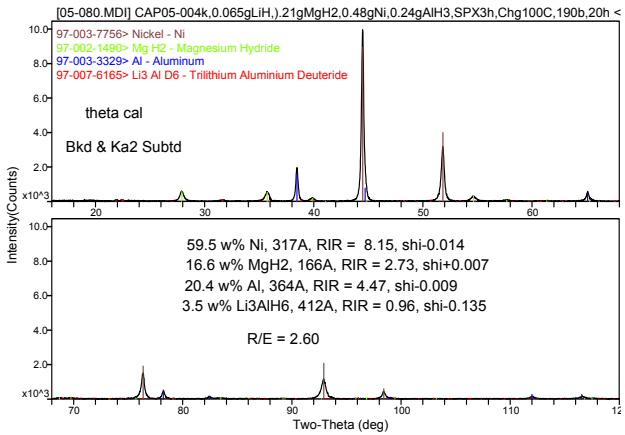
Ak/Ae/Tm

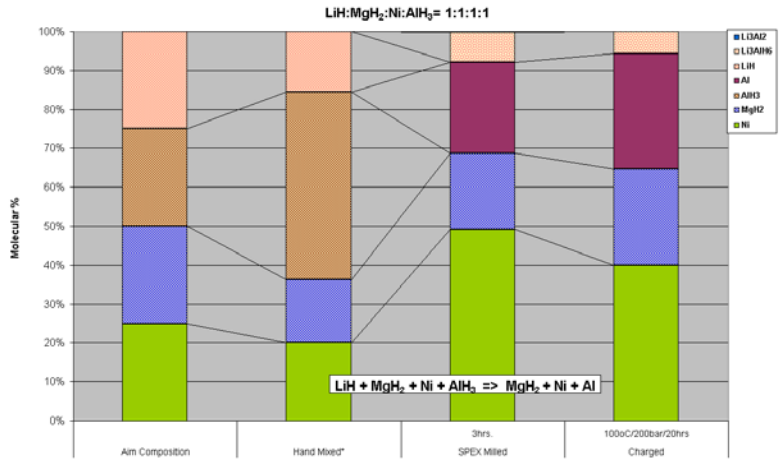
Li:Ni:Al
Na:Ni:Al
Mg:Ni:Al
Li:Mg:Ni:Al
Na:Mg:Ni:Al
Li:Co:Al

Na:Co:Al
Mg:Co:Al
Na:Mg:Co:Al
Li:Fe:Al
Na:Fe:Al
Mg:Fe:Al

CY '04:
Hand Mix, Ball Mill
60, 80, 100 & 120°C
/200bar/20 hrs

CY '05:
Hand Mix, Ball Mill
100°C/200bar/20 hrs





- Moving on to transition metal substituted systems.
- Maximize compositional ranges covered by using fewer thermal treatments.

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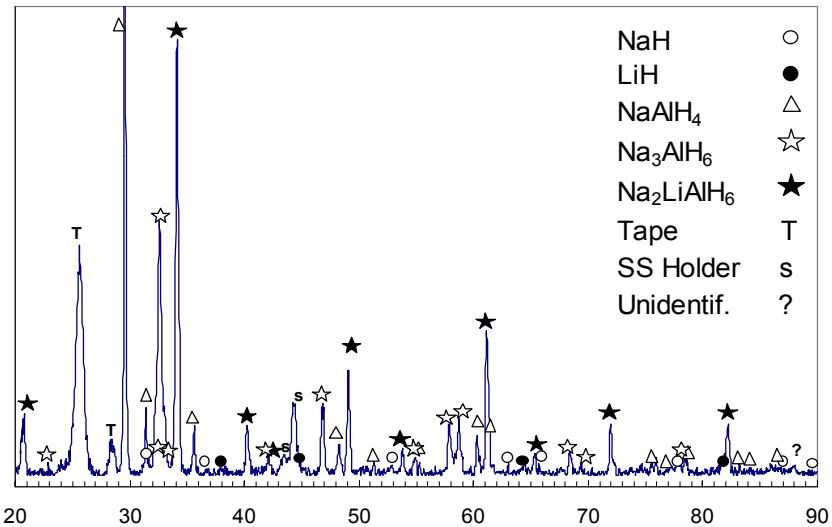
Accomplishments
Molten State Processing (MSP) Proof of Concept

$NaH + LiH + NaAlH_4 \Rightarrow Na_2LiAlH_6$



Processing Conditions

190°C, 200 bar, 15 min. dwell time, agitated

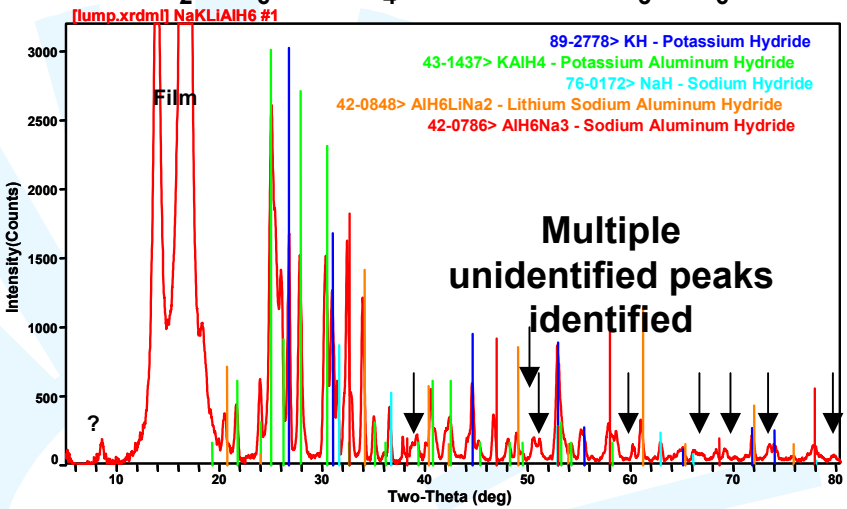
Range of Processing Conditions

RT-600°C
200 bar
8 hr dwell time
Quiescent or agitated
1 liter ~600g capacity

Demonstrated MSP advantages: Solvent- and anion-free processing produces high yields of clean complex hydrides. One liter pressure vessel scaleable to meet system demonstration requirements.

Accomplishments
MSP Compositional System Surveys

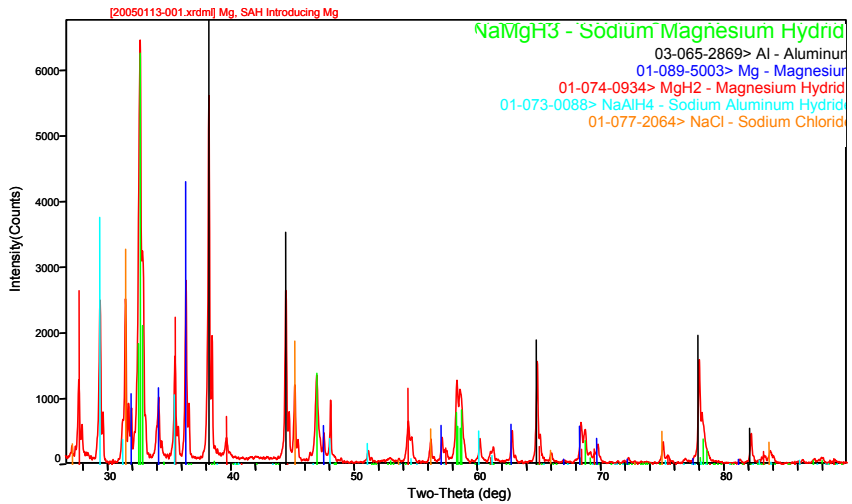
$NaAlH_4+LiH+KH=>$
$LiNa_2AlH_6+KAlH_4+NaH+KH+Na_3AlH_6+$?



Processing Conditions

190°C, 200 bar, 15 min. dwell time, agitated

$NaAlH_4+MgH_2=> Al+NaMgH_3+Mg$



Processing Conditions

190°C, 200 bar, 15 min. dwell time, agitated

Four quaternary/quinary composition systems investigated to date:

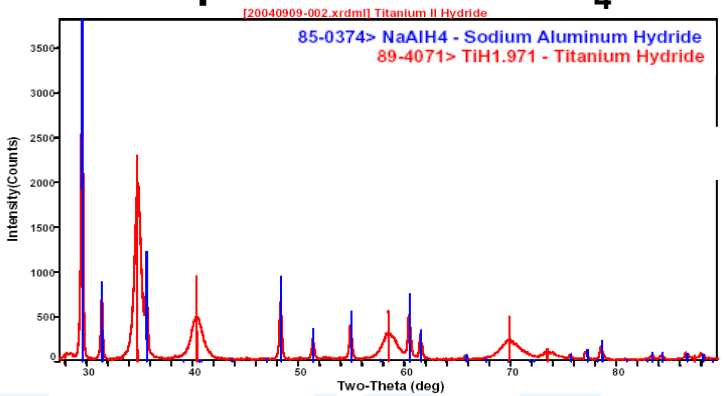
Na-Li-Al-H
Na-Ti-Al-H
Na-K-Li-Al-H
Na-Mg-Al-H

Multiple unidentified peaks observed in Na:Li:K:Al:H system provided evidence for formation of new compounds.

Accomplishments
MSP Produced Highly Active $NaAlH_4$

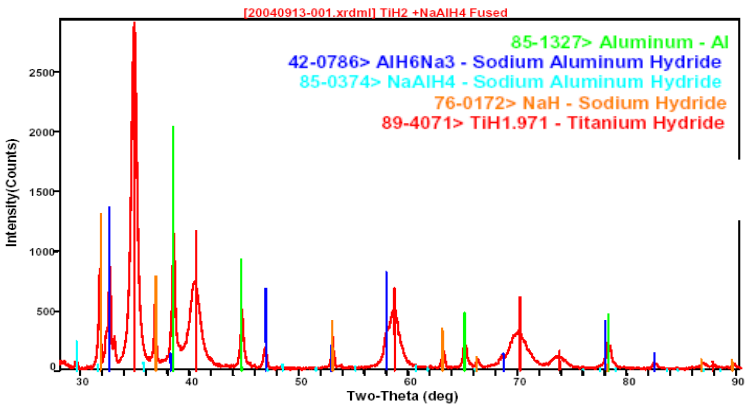
Before Fusion

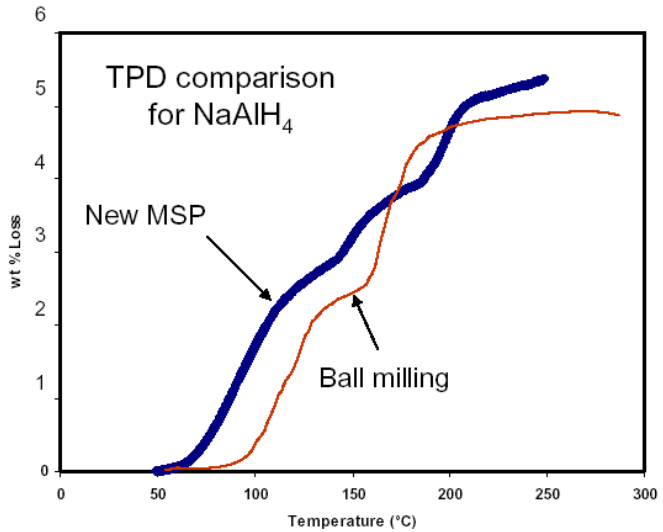
Solid-state processed $NaAlH_4$ + 4%TiH_2



After Fusion

At 200 bar. 190°C.15 min.





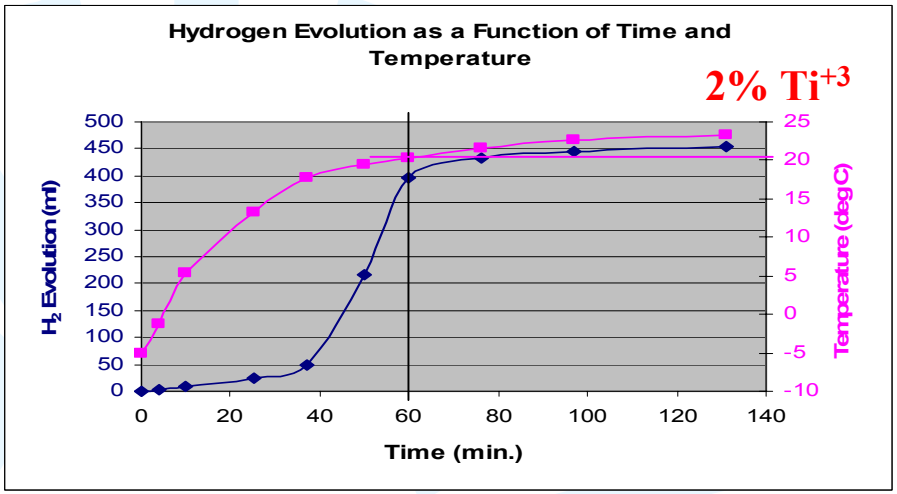
TPD discharge experiments showed MSP hydrides to be more active than conventionally ball milled hydrides. This material is being kinetically examined for possible use in CCHSS#2.

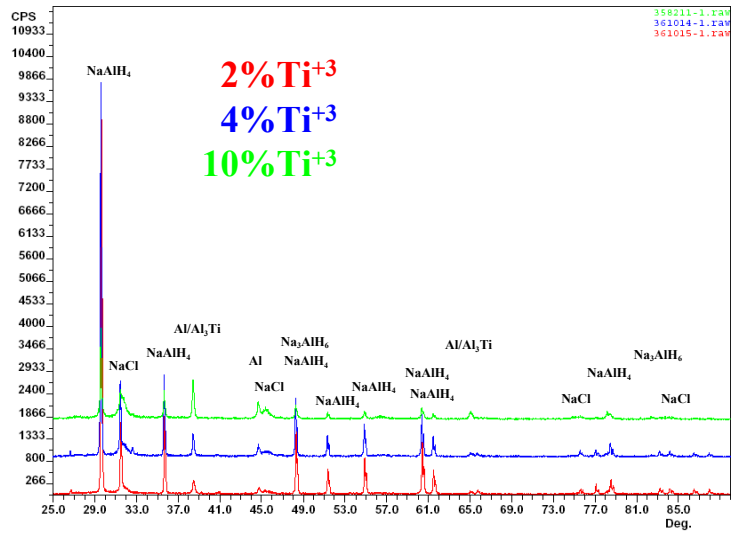
Accomplishments

Solution Based Processing (SBP) Ti/Na Alanates

$TiCl_4(THF)_2 + Al(i\text{-}Bu)_3 \rightarrow TiCl_3(THF)_3$

$NaAlH_4 + xTiCl_3(THF)_3 \rightarrow NaTi_xAl_{1-x}H_4 + ...$





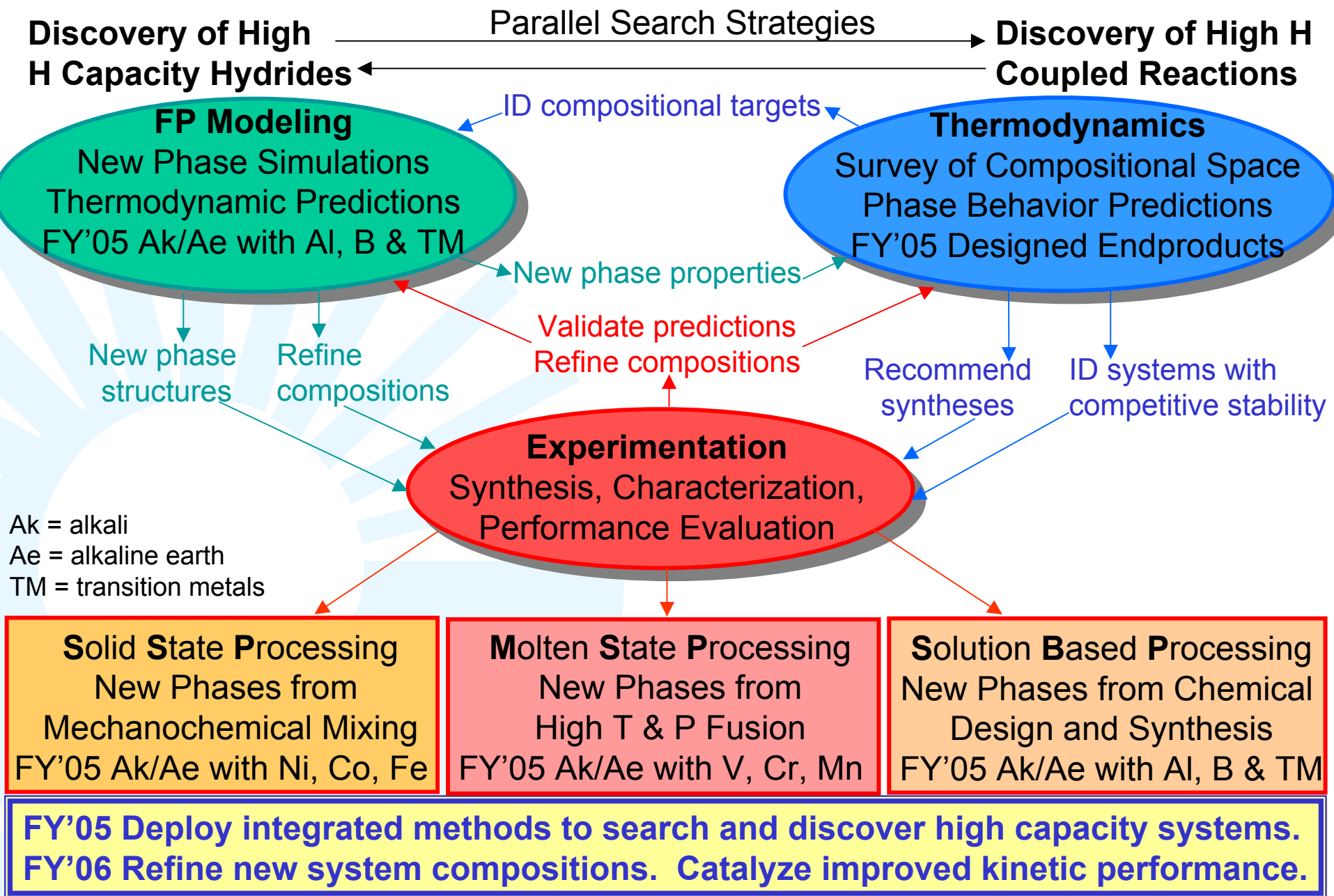
- Complete solution doping reaction at 25°C.
- Disproportionation to Al_3Ti.
- New ordered phases observed in related systems.

Demonstrated SBP synthesis route to homogeneous Ti^{+3} doped alanates. This material is being kinetically examined for possible use in CCHSS#2.

$NaTi_xAl_{1-x}H_4 \rightarrow xAl_3Ti + 6xH_2 + (1\text{-}3x)NaAlH_4$

Mole ratio Ti:Al	2:100	4:100	10:100	33:100
Mole ratio H_2:Ti	7.7	6.7	6.4	5.7

Future Work



FY'05 Deploy integrated methods to search and discover high capacity systems.
FY'06 Refine new system compositions. Catalyze improved kinetic performance.

Responses to Previous Year Reviewers' Comments

- **Comment**

  "Consider broadening to include non-alanate materials?"

  By adding other complexing elements such as B, Ga … vastly increases the scope of investigation, thus limiting empirical investigations into all possible combinations. Additions of these elements will be investigated atomistically and empirically where modeling indicates high hydrogen capacity materials are stable.

- **Comment**

  "DOE should consider how this project relates to or coordinates with the Sandia Metal Hydride Center of Excellence?"

  UTRC has always maintained a high degree of communication with SNL and many of its CoE partners through DoE sponsored meetings, IEA meetings, and laboratory visits. This communication will continue.

- **Comment**
  - "Need validation that the modeling is predicting properties correctly."
  - "Need to insure that the modeling efforts are not independent of experiment."

  As shown in the progress to date, modeling and empirical results have shown very good agreement. We have a very high confidence level in modeling predictions when phonon approach is incorporated. The modeling & empirical efforts are designed to be interdependent with each other, and are closely coordinated with monthly meetings used to exchange data, ideas, and concepts.

Backup Slides

Publications

O. M. Løvvik, S. M. Opalka, H. W. Brinks, and B. C. Hauback, "Crystal structure and thermodynamic stability of the lithium alanates $LiAlH_4$ and Li_3AlH_6," Phys. Rev. B 69 134117-134125 (2004).

H.W. Brinks, B.C. Hauback, C.M. Jensen, and R. Zidan, "Synthesis and crystal structure of Na_2LiAlD_6," J. Alloys Compd. 392(1-2) 27-30 (2005).

O. M. Lovvik and S. M. Opalka, "First-principles calculations of Ti-enhanced NaAlH4," Phys. Rev. B 71 054103-1-10 (2005).

O. M. Lovvik, O. Swang, and S. M. Opalka, "Modeling alkali alanates for hydrogen storage by density-functional band-structure calculations" submitted 4/05 J. Mater. Res.

C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from First Principles Calculations to Thermodynamic Modeling," submitted 4/05 Phys. Rev. B. Two related papers on the Na-Al-H and Na-Ti-Al-H system currently in preparation.

Presentations

O. M. Løvvik and S. M. Opalka, "First-principles calculations of Ti-enhanced NaAlH4." International Symposium of Metal Hydrogen Systems (MH2004), Cracow, Poland, September 10, 2004.

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

R. Zidan, "Hydrogen Storage R&D Key Issues for the Hydrogen Economy," and "Solid-State Hydrogen Storage Systems," Hydrogen Economy Workshop, Invited Speaker as Representative for the Department of Energy, Cairo, Egypt, January 31 – February 2, 2005.

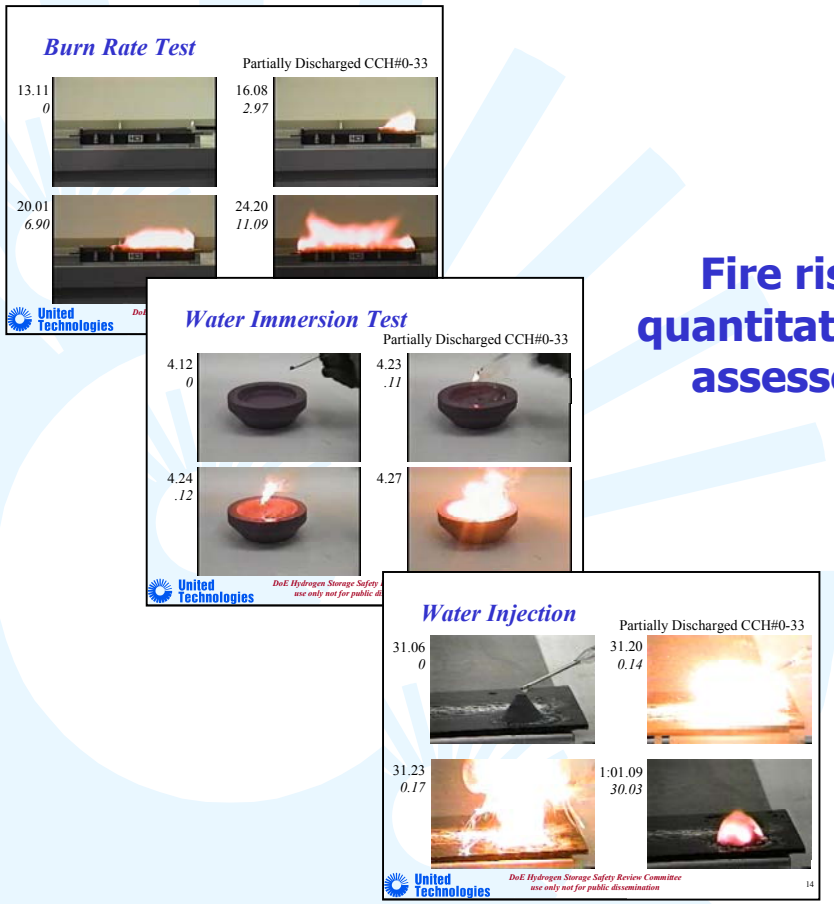
C. Qiu, S. M. Opalka, D. L. Anton, and G. B. Olson, "Thermodynamic Modeling of Sodium Alanates," Materials Science & Technology 2005, to be held in Pittsburgh, PA, on September 25-28, 2005.

S. M. Opalka, O. M. Lovvik, H. W. Brinks, B. C. Hauback, and D. L. Anton, "Combined Experimental-Theoretical Investigations of the Na-Li-Al-H System," Materials Science & Technology 2005, to be held in Pittsburgh, PA, on September 25-28, 2005.

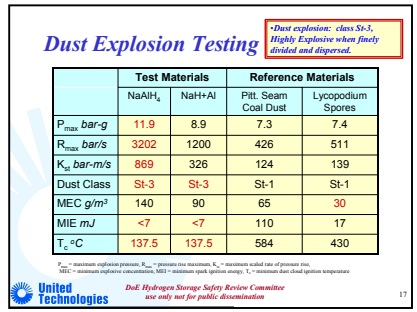
Multiple collaborations foster H_2 storage research progress and communication.

Safety

Risk Identification



Explosion risks quantitatively assessed



Fire risk quantitatively assessed

Appendix V- UTRC Risk Assessment Form

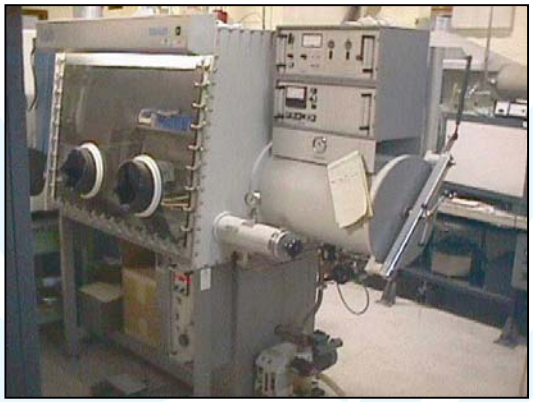
Date	Room Number	Participants
5/4/04	S145H	Tom Ververis, Xia Tang, Ron Brown, Jodi Vecchiarelli

No	Process, Task or Step	Potential hazard	Controls in Place	Likelihood Occurrence	Potential Impact	Risk Rank	Controls Required To reduce risk further/Name/Date
1	Mixing Powder Media Preparation	Fire, Explosion	All work is done in glovebox filled with Nitrogen Containers inside glove box sealed Gloves inspected every day Nitrogen pressure checked every day Moisture and O2 sensor in glovebox Positive pressure maintained in glove box	2	3	6 Med	
2	Hydrogen Storage Running Test	Failure of High Pressure Systems Fire, Explosion	Restricted use Risk assessments Local rules and procedures Pressure rated components Pressure relief valves Automatic controllers; Redundant valves Detailed Procedures; Employee training Critical valve Maintenance Remote gas line shutoff and purge if loss of power or ventilation All test stands in hoods All equipment leak tested (H2 sniffer) Flash arrestor Moisture filters	2	3	6 Med	Lower Pressure
3	Hydrogen Storage, Running Test	High Temp. Oil Bath, Burns, Oil spill	Warning sign "Hot Oil" Secondary containment Redesigned Jack stand gard in place Located in hood.	2	2	4 Low	
4	Vacuum System (Hydrogen),Running Test	Explosion	Special Hydrogen Vac. Pumps Sparkless	2	3	6 Med	
5	Working in glovebox	Ergonomic pain	Limited time in glovebox to 45 minutes max. Set up to avoid awkward reaching	2	2	4 Low	
6	Lifting, transporting samples	Ergonomics	Training, procedures Weight kept to < 30 pounds	2	2	4 Low	

Comprehensive risk assessment performed on all major operations quantitatively describing both impact and probability of occurrence.

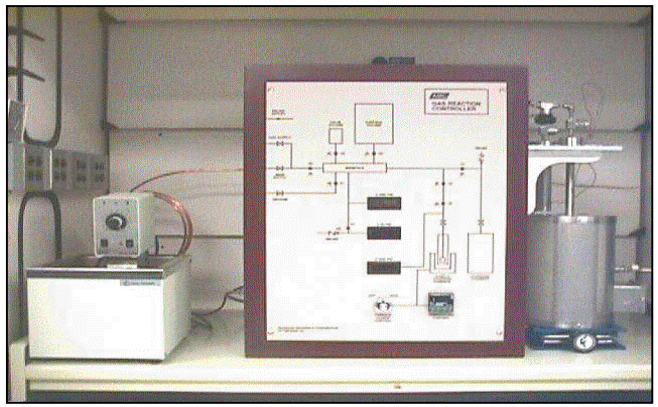
Safety

Risk Mitigation



Material handled under inert gas

Incoming material stored in fire cabinet



Materials tested in commercial equipment installed in a glove box

Media stored under inert gas

All risks reduced to low impact or negligible probability.