Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

Gregory J. Lewis
UOP LLC
May 17, 2006

Project ID # ST11

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: 5/1/2004
- End date: 4/30/2007
- % Complete: 67

Budget

- Total project funding
  - DOE: $2,000,000
  - UOP: $2,910,618
  - Ford: $ 75,000
- FY05 DOE: $604,423
- FY06 DOE: $525,032

Barriers

- Barriers addressed (DOE-2010)
  - Useable H_2 Density
    - 2.0 kWh/kg & 1.5 kWh/L
  - H_2 Delivery Temperature Range
    - -40 to 85˚C
  - Cycle Life
    - 1000 Cycles

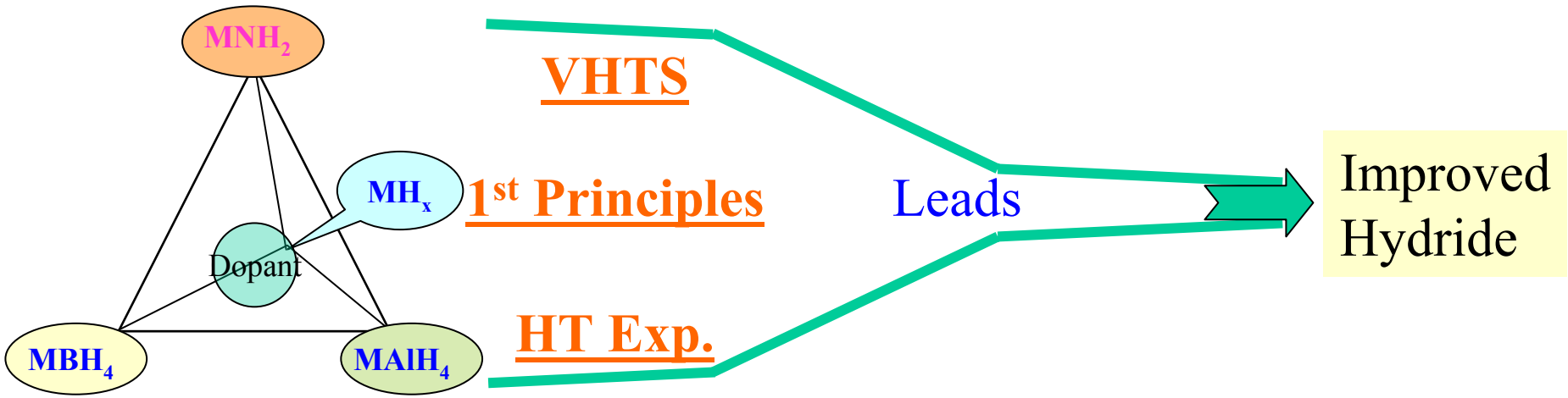
Partners

- Hawaii Hydrogen Carriers
- UCLA
- Ford
- Striatus

Objectives

■ **Overall**	■ **Discovery of a complex metal hydride through Molecular Modeling and Combinatorial Methods which will enable a hydrogen storage system that meets DOE 2010 goals** ■ **Deliverables:** • **Optimized material** • **Sample for independent testing at SWRI** • **Documentation**
■ **2004**	■ **Validation and Demonstration of VHTS (Molecular Modeling)** ■ **Validation and Demonstration of Medium Throughput Combinatorial Tools** ■ **Downselect from Na, Li, Mg/AlH_4**
■ **2005**	■ **Demonstration of High Throughput Combinatorial Tools** ■ **Identification of New Materials Approaching DOE Targets**

Approach



- **Modeling**
  - **Virtual High Throughput Screening, ~1000 compositions/month**
  - **DFT to predict new materials with favorable thermodynamics, refine leads**
- **Combi Synthesis & Screening**
  - **High Throughput (up to 48x)**
  - **Discrete, scalable sample preparation using ball-milling or solution-phase**
- **Follow up on Leads:**
  - **Characterization & modeling for increased understanding**
  - **Optimization, scale-up & multi-cycle testing**
- **Performance Validation:**
  - **Provide Sample to SWRI for independent testing**

High Throughput Capability: Testing

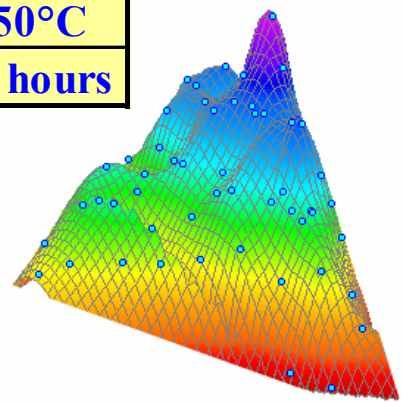
- **Capability:**
  - **Comparison of Medium Throughput (MT) and High Throughput (HT) systems:**

	MT Assay	HT Assay
No of Rx:	8	48
Max T:	220°C	350°C
Max P:	87 bar	120 bar
Desorption P:	Variable	~1 bar abs.

- **Test Protocol:**
  - **Perform multiple cycles of temperature programmed desorption + rehydriding:**

Std. Cond.	MT Assay	HT Assay
Desorption	To 220°C	Multiple T: 220-350°C
Rehydriding	125°C, 87 bar, 12 hours	125°C, 120 bar, 12 hours

  - **Second cycle represents reversible wt-%H**



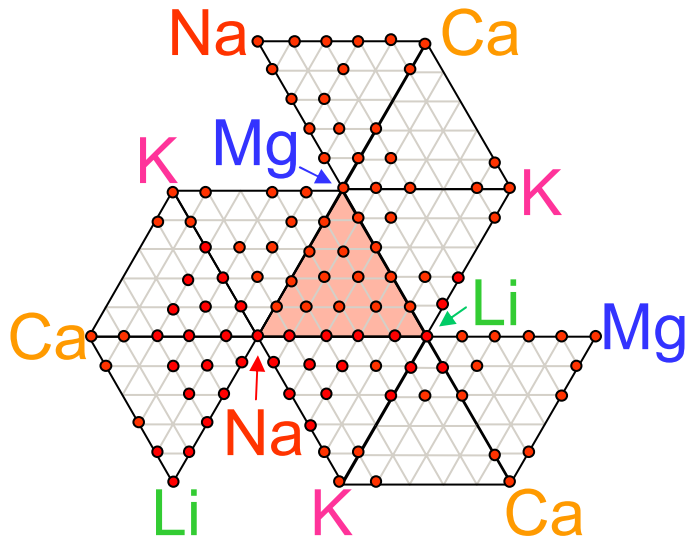
- **Status:**
  - **Both MT and HT Systems are operational**

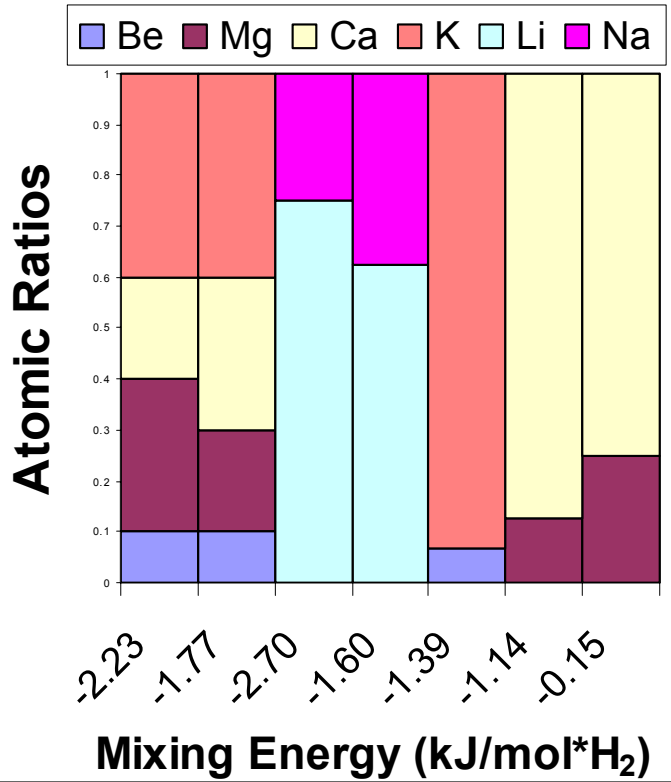
High Throughput Capability: Synthesis

- **Capability:**
  - **Automated solution and powder dispensing**
  - **MT Vacuum, filtration, sample washing and drying**
  - **Sample agitation, sample heating to 250°C**
  - **HT Milling (successful POP completed)**
- **Characterization:**
  - **HT XRD fully operational**
- **Status:**
  - **System undergoing shakedown at vendor**

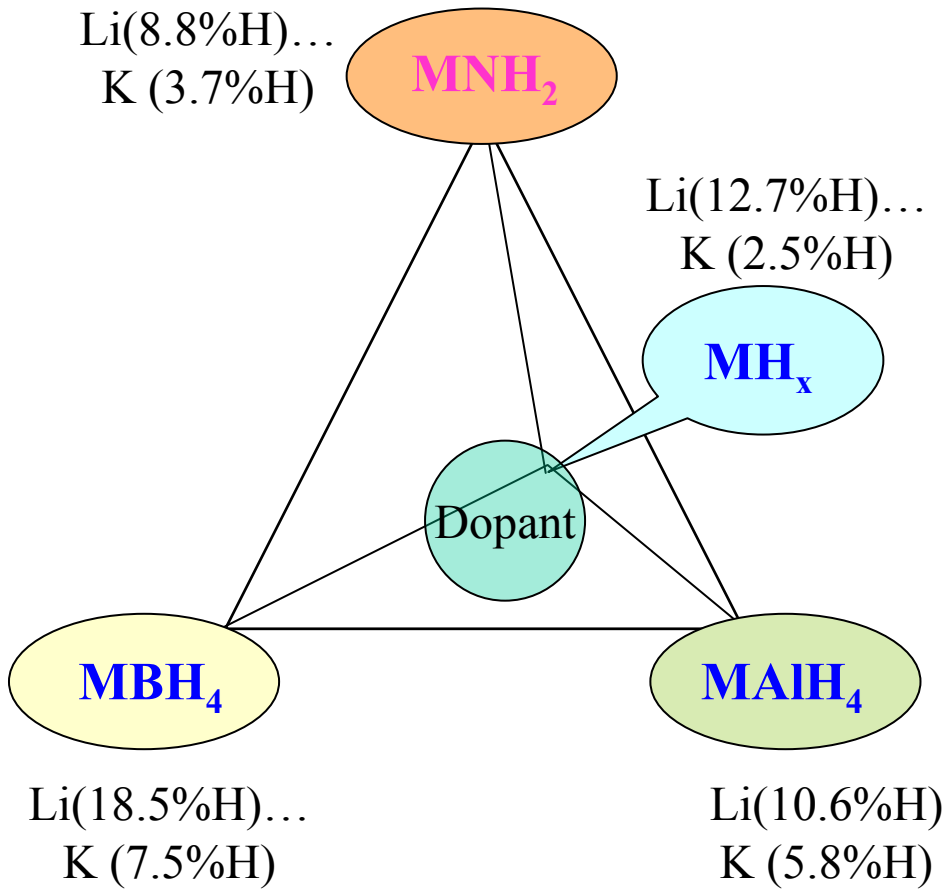
New Results for Mixed Alanates

- **Experimental Results:**
  - **Multiple ternary alkali/alkaline earth alanate phase diagrams searched starting from dehydrided side**
  - **No stable mixtures found under our conditions.**
- **Virtual High Throughput Screening:**
  - **Mixtures of Li + Na + K + Be + Mg + Ca Alanates**
  - **981 mixed phases scanned in less than a month.**
  - **Only seven new phases were found with negative heats of mixing.**
  - **None of these phases are stable w.r.t decomposition at R.T.**
  - **Simple model based on packing of AlH_4 groups explains lack of stable mixtures.**
- **Conclusion:**
  - **No alanate mixtures likely to meet DOE targets**
- **Status:**
  - **No more alanate-only work planned.**
  - **Medium Throughput techniques, VHTS validated**
  - **VHTS method is currently being extended to mixtures containing borohydrides, amides and transition metals.**





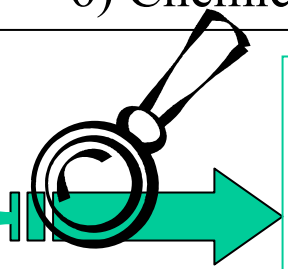
Expansion of Phase-Space Beyond Alanates



M = alkali, alkaline earth, other cations

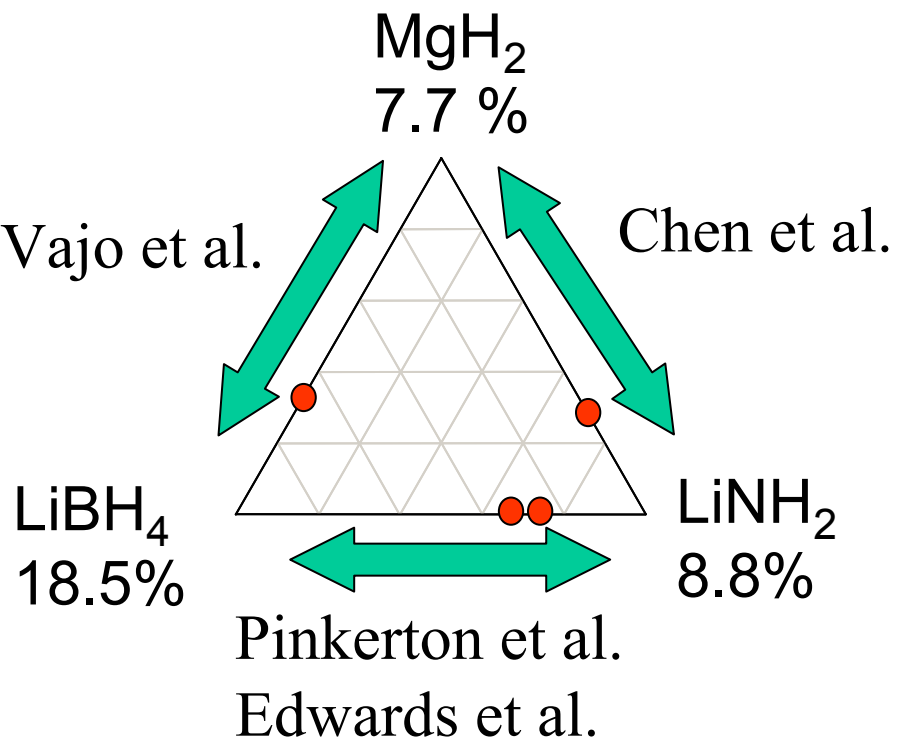
Focus on regions of greatest interest:

1) High wt% H
2) Favorable thermodynamics
3) Encouraging experimental results
4) Availability of crystal structures
5) Availability of reagents
6) Chemical insight/analogy



Combinatorial Experimentation & Molecular Modeling

First Down-Select: $LiNH_2 – MgH_2 – LiBH_4$ Phase Diagram



Partial success in literature along edges:

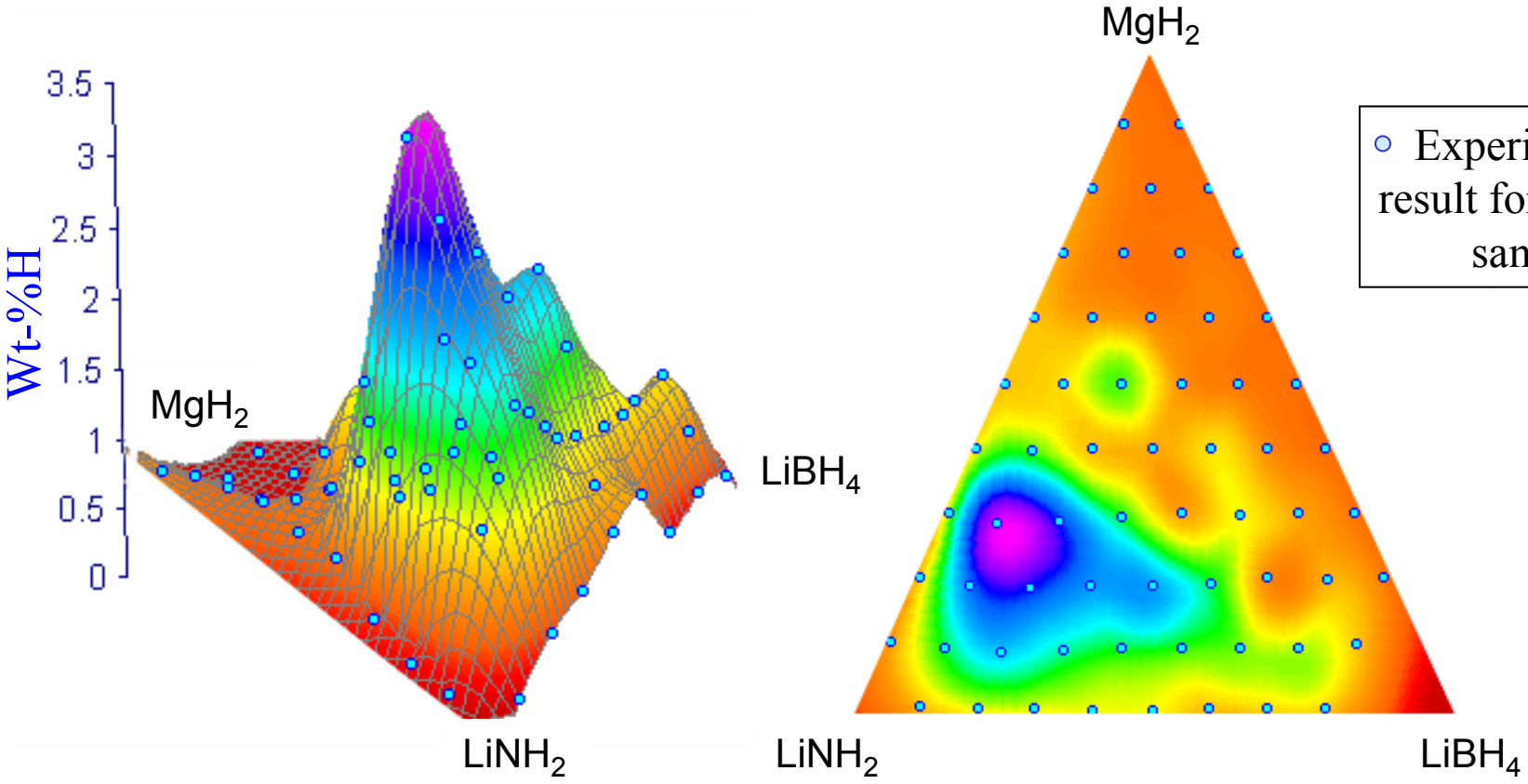
Vajo: 8 – 10 wt.% H_2
MgH_2 + 2 $LiBH_4$
Reversible 300-450°C

Chen: 5.9 wt. % H_2
MgH_2 + 2 $LiNH_2$
Reversible >200°C (?)

Pinkerton: > 10 wt. % H_2
2 $LiNH_2$ + $LiBH_4$
Irreversible
Edwards/Pinkerton: $Li_4BH_4(NH_2)_3$

Using High Throughput experimentation UOP has covered the full phase diagram

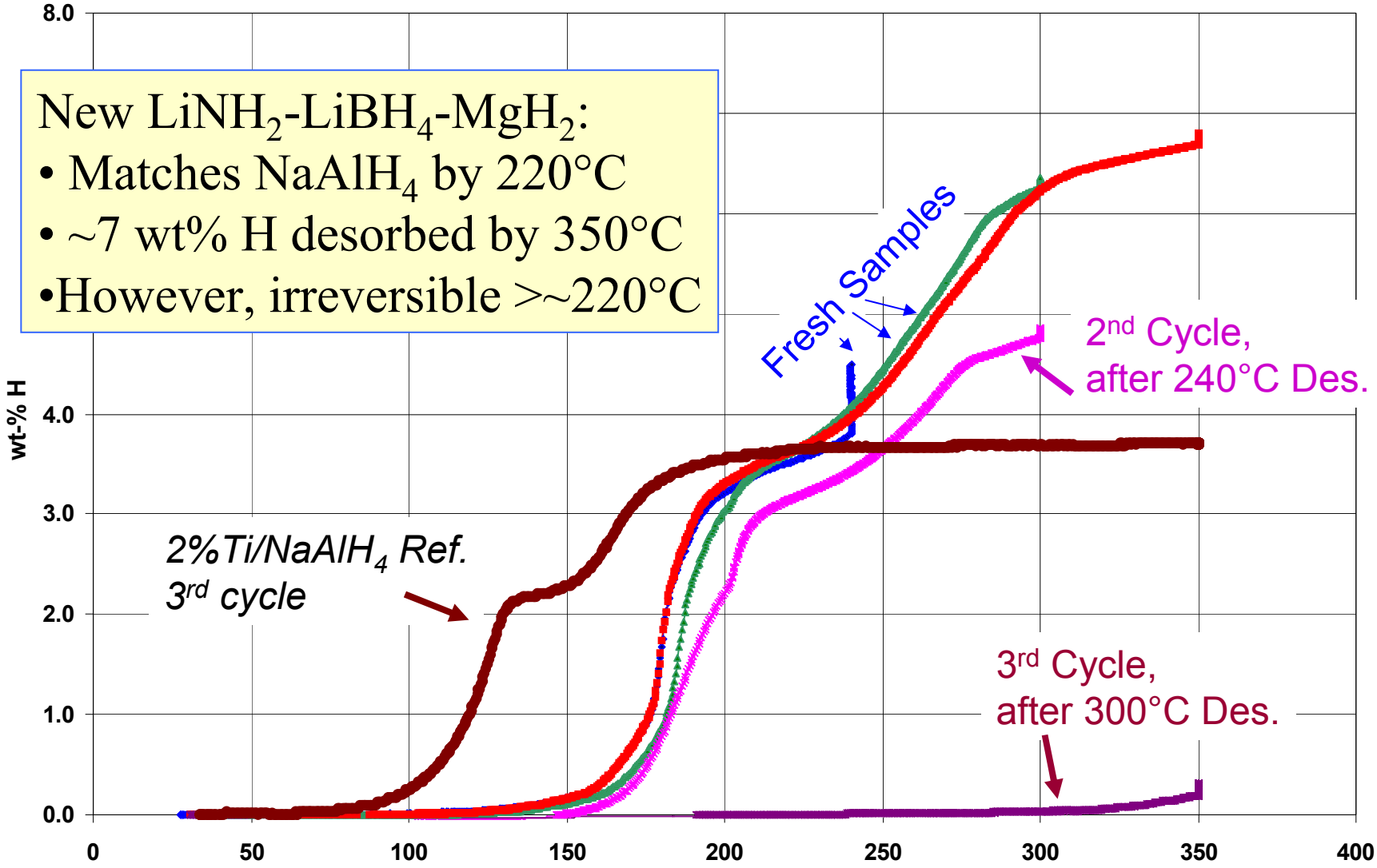
$LiNH_2 + MgH_2 + LiBH_4$: Experimental MT Results Reversible %H (Des#2 to 220°C)



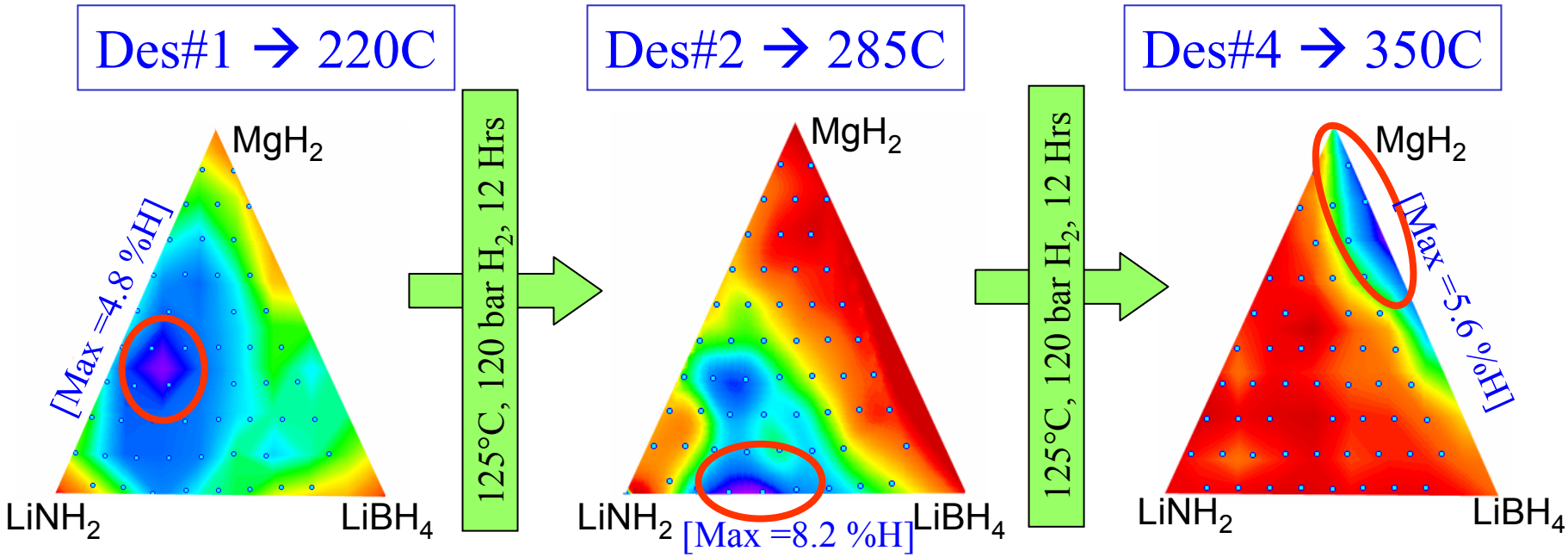
Optimum Reversible wt%H for ***Ternary*** System, Optimum at Very Low $LiBH_4$

5 $LiNH_2$ + 2.2 MgH_2 + 1 $LiBH_4$: Comparison with 2%Ti/$NaAlH_4$; Deactivation @ High-T

New $LiNH_2$-$LiBH_4$-MgH_2:
- Matches $NaAlH_4$ by 220°C
- ~7 wt% H desorbed by 350°C
- However, irreversible >~220°C



HT-Assay Results Show Chemistry Shifts As Desorption Temperature Increases



- 220°C: ***Ternary*** optimum, reversible
- 285°C: ***Ternary*** becomes irreversible
- 285°C: ***Binary*** optimum (irreversible)
- 350°C: Optimum moves to MgH_2 (reversible)

○ Experimental result for discrete sample

$LiNH_2$ - MgH_2 - $LiBH_4$ New Material

Major Phases present by HT-XRD

$$5\ LiNH_2 : 2.2\ MgH_2 : LiBH_4$$

↓ *Milling/ 350 rpm*

$$MgH_2 + Li_2NH/LiNH_2 + Li_4BH_4(NH_2)_3$$

↓ *Dehydride/240°C*

$$Li_2Mg(NH)_2 + Li_2NH + Li_4BH_4(NH_2)_3 + (Li_3BN_2)$$

H_2/1250 psig/125°C/12 hr ⇅ *Dehydride/240°C*

$$Mg(NH_2)_2 + Li_4BH_4(NH_2)_3$$

Comparison of $LiNH_2$ – MgH_2 – $LiBH_4$ Material to Literature

Points on Phase Diagram Edge

Hydride 200°C - Desorb 220°C – Hydride 200°C – Desorb 220°C

Composition	Source	Cycle 1	Cycle 2
2 $LiNH_2$: MgH_2	Chen et al.	0.5%	0.5%
2 $LiBH_4$: MgH_2	Vajo et al.	0.0%	0.0%
2 $LiNH_2$: $LiBH_4$	Pinkerton et al.	0.2%	0.2%
0.6 $LiNH_2$: 0.3 MgH_2 : 0.1 $LiBH_4$	This work	3.8%	3.4%
5 $LiNH_2$: 2.2 MgH_2 : $LiBH_4$	This work	3.4%	3.3%

Experimental Follow-Up & Additional Work

- **Follow-Up on $LiNH_2 + MgH_2 + LiBH_4$ New Material:**
  - **Improve understanding:**
    - **Characterization to ID active phase, irreversible reaction**
    - **Analyze desorbed H_2 for impurities (TPD/MS)**
  - **Validation:**
    - **PCT measurements to confirm results (H_2C)**
  - **Performance Improvement:**
    - **Evaluate dopants for new material to lower Des-Temp.**
      - Ti has been tested: no improvement
- **Other New Material searches (On-Going):**
  - **Extend screening to other phase diagrams in phase space**
  - **New mixed metal borohydrides (H_2C)**
    - **New compound formation observed, need to assess reversible H_2 capacity**

First-Principles Modeling

- **First-Principles can steer us *away* from certain regions:**
  - **Mixtures of alanates and borohydrides**
    - **$LiAlH_4$-XBH_4, with X=Li, Na, K: no stable compounds found**
- **First-Principles can guide us *toward* promising reaction:**
  - **Predicted novel materials/reactions with targeted thermodynamics**
    - **7-15 wt.%H (*material-only, theoretical)***
    - **~120 g/L volumetric H_2 densities (*material-only, theoretical)***
    - **30-40 kJ/mol-H_2, including vibrational contributions**

For more information, see Vidvuds Ozolins' POSTER.

Some Examples of Reactions:

REACTION	ΔH (kJ/mol-H_2)			ΔS at 298 K [J/(K mol-H_2)]	H_2 Wt. %	H_2 Density (g H_2/L)
	Static	With ZPE	T=300 K			
MATERIAL #1	57	35	41	111	10	125
MATERIAL#2, REACTION #1	51	31	38	117	15	120
MATERIAL#2, REACTION #2	52	31	37	115	13	120
MATERIAL#2, REACTION #3	53	31	38	114	12	120

Future Work

FY06

- **Experimental Capability:**
  - **Bring HT-Synthesis capability on line**

FY06 + FY07

- **Continue Work In Three Focus Areas:**
  - **#1: Follow-up on $LiNH_2 – MgH_2 – LiBH_4$ (understanding, improvement)**
  - **#2: New mixed metal borohydrides (currently in synthesis stage)**
  - **#3: Systems with 20-50 kJ/mol*H_2 and >7 wt-%H predicted by modeling**
- **Explore Other Parts of Expanded Phase Space:**
  - **First-Principles Modeling, VHTS, & Experiment**
- **Follow-Up On Leads:**
  - **Improve Performance:**
    - **Optimize compositions**
    - **Evaluate dopants, synthesis variables, process variables**
  - **Improve Understanding:**
    - **Identify active phase, reaction chemistry, side-reactions**
    - **Analyze desorbed H_2 for impurities (TPD/MS)**
    - **Validation, kinetics, EQ, cycle measurements using PCT @ H_2C**

FY07

- **Provide sample for independent testing at SWRI**
- **Obtain additional properties for system design (Coordinate with DOE)**
  - **Volumetric capacity, heat of reaction, thermal properties, etc.**

Summary

- **High Throughput Synthesis & Testing (*):**
  - **High Throughput Test system operational (results shown here)**
  - **High Throughput Synthesis equipment in shakedown at vendor**
- **Modeling:**
  - **VHTS demonstrated for ~1000 six-component alanate mixtures**
  - **VHTS being adapted to expanded phase space**
  - **First-Principle modeling has predicted multiple reactions with favorable thermodynamics**
- **Alanates:**
  - **Completed evaluation of mixed alanates**
- **Expanded Phase Space:**
  - **Discovered New Material in $LiBH_4$ -MgH_2 – $LiNH_2$ phase diagram(**)**
    - **Lower-Temperature desorption compared to related binary literature systems**
    - **Follow-up to improve understanding, performance on-going**
  - **Exploration of other phase diagrams in phase space on-going**

Year Two Go/No-Go's:

- **(*): *Demonstration of High Throughput Combinatorial Tools***
- **(**): *Identification of New Materials Approaching DOE Targets***

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY05 materials****	**FY06 materials****
Material			2%Ti/NaAlH4	0.6LiNH2+0.3MgH2+0.1 LiBH4
Specific Energy	kWh/kg (wt. % H2)	2 (6 wt.%)	1.5 (4.4 wt%)	1.1 (3.4 wt-%)
Volumetric Energy (Capacity)	kWh/L	1.5	1.1	0.5
Desorption Temperature			Max rate at 133, 198°C	Max rate at 181°C
Plateau Pressure			(not measured)	(not measured)
Addl. information			Second-cycle desorption from 35°C /1 bar to 235°C/16 bar, un-optimized powder density of 0.724 kg/L.	Second-cycle desorption from 35°C /1 bar to 220°C/13 bar; un-optimized powder density of 0.452 kg/L..

The Team

DOE Project Manager

UOP
Dave Lesch – Project Manager
Adriaan Sachtler – Team Leader, Testing
John Low – Modeling
Greg Lewis – Synthesis
Syed Faheem – Synthesis
Lisa Knight – Combi Synthesis
Paul Dosek – Combi Testing
Doug Galloway – Characterization
Leon Halloran – Characterization

Ford
Chris Wolverton
Modeling

UCLA
Vidvuds Ozolins
Modeling

H_2C
Craig Jensen
Char/Testing

Striatus
Laurel Harmon
Informatics

Backup Slides – Not for Presentation

Program Changes
(Reviewed with DOE, FreedomCAR Tech Team)

- **Deliverables:**
  - **Removed scale-up and system design deliverables.**
  - **In stead, screening for new materials will continue to end of program.**

- **Scope of Work – Phase Space:**
  - **Alanates not promising → phase space expanded**

Responses to 2005 Reviewers' Comments

- **Re - future plan not being clear enough, and project being limited to alanates:**
  - **We have obtained agreement to substantially expanded the phase space, as shown in this presentation.**
- **How do the PIs view the heat of formation effect? How about the packing properties? Or in general, system effects?**
  - **(a) In order to lower the heat rejected during refueling, a lower Delta-H is clearly desirable. However, for very low Delta-H a cryogenic system will be required – unless the Delta-S can be changed substantially. We are working closely with Ford and its hydrogen vehicle teams to assess the heat management issues to keep our discovery effort focused on practical materials. In our modeling, Delta-H is screened from 20-50 kJ/mol. Experimentally, cooling capability can be added if modeling or characterization indicate that our measurements are missing low-T H_2.**
  - **(b) With the HT-Assay we are now routinely tracking powder densities. We are also starting to measure H_2 purities for selected samples. Other properties will be determined for promising materials as we get closer to targets.**
- **…Can we now assume that we can rely on the modeling to guide us to the systems we should study? -- If so, in principle we should be able to save lots of measurement time and resources by relying on the modeling supported by a few judiciously planned experiments?**
  - **The shift to a new class of materials requires substantial model development effort, including validation. Experimental follow-up to model predictions often requires difficult material syntheses. Therefore, in reality, it takes time to get to the point where modeling precedes experimentation. However, we have demonstrated this approach in the completion of the alanate work.**

Publications and Presentations

- **3/18/2004: Freedom CAR Tech Team Review**
- **5/26/2004: HFCIT Annual Program Review**
- **1/20/2005: Freedom CAR Tech Team Review**
- **5/24/2005: HFCIT Annual Program Review**
- **J.W. Adriaan Sachtler, Gregory J. Lewis, John J. Low, David A. Lesch, Paul M. Dosek, Syed A. Faheem, Yune D.T. Le, Craig M. Jensen, Vidvuds Ozolins, Blanka Magyari-Kope, and C. Wolverton, "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods," poster at the IPHE International Hydrogen Storage Technology Conference, Lucca, June 19 - 22, 2005.**
- **C. Wolverton, "Hydrogen Storage and Nanoscale Modeling at Ford Motor Company", Materials Science Colloquium, Cornell, Sep 05.**
- **C. Wolverton, "What can we learn from first-principles calculations of materials?", Materials Science Colloquium, MIT, Oct. 05.**
- **Gregory J. Lewis, J. W. Adriaan Sachtler, John J. Low, David A. Lesch, Syed A. Faheem, Paul M. Dosek, Lisa M. Knight, and Craig M. Jensen, "High Throughput Screening of Complex Metal Hydrides for Hydrogen Storage," Fall Materials Research Society Meeting, Symposium A5.5, Boston, Nov. 30, 2006**
- **C. Wolverton, "Advances in the Rational Design of Catalysts and Sorbents", Invited Talk, IFP workshop on First-Principles Studies of Catalyst Supports and Hydrogen Storage Materials, Lyon, France, Dec. 05.**
- **1/12/2006: Freedom CAR/Tech Team Review**
- **C. Wolverton, "Hydrogen Storage Activities at Ford Motor Company", Invited Seminar, PNNL, Jan. 06.**
- **C. Wolverton, "Nanoscale Modeling at Ford Motor Company", Materials Science Colloquium, Northwestern, Feb. 06.**
- **C. Wolverton, "Atomistic Modeling at Ford Motor Company", Invited Talk, American Physical Society Meeting, Mar. 06.**

Critical Assumptions and Issues

- **A hydride meeting DOE targets can be found.**
  - **A hydride enabling DOE system targets may not be possible.**
    - **Using Combinatorial High Throughput experimentation coupled with modeling, we are in a strong position to search the pertinent phase quickly and help make this assessment, identifying the desired compound if it exists.**
- **Volatile impurities with Boride, Amide systems**
  - **Loss of ammonia, diborane or other volatile species would adversely affect fuel cell and may limit life of storage material.**
    - **Additives to the hydride may stabilize volatile species**
    - **Guard bed may be used to protect fuel cell**
    - **Additives to H_2 to restore lost components may be considered.**
- **DOE Funding**
  - **Reduced DOE funding will adversely affect progress.**
    - **Restore funding to original budget amount / extend project.**

Acknowledgement

- **Acknowledgement is made to the US Department of Energy for sponsorship under contract number DE-FC36-04G014013.**