



Advanced Metal Hydrides

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Project ID #STP 37 Ritter

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Objectives

- Show that an off-board process, referred to as the *physiochemical pathway*, promotes rehydrogenation of LiAlH_4 from Li_3AlH_6 , LiH and Al .
- Show that rehydrogenation can be carried out at relatively low pressures of around 3 bar.
- Show that the rehydrogenation kinetics are improved by adding a Ti catalyst and by mechanochemical treatment.



Project Timeline

12/05-1/06

Phase I

2/06-3/06

Phase II

4/06-7/06

Phase III

8/06-11/06

Phase IV

12/06-3/07

Phase V

4/07-7/07

Phase VI

- Present data on the effect of graphite and other carbon additives on the reversibility of Ti-doped NaAlH_4 . (complete)
- Present data on the effect of sonochemical doping as a pretreatment step prior to or as a replacement step for high energy ball milling of complex hydrides. (complete)
- Present data on the effect of high pressure and temperature high energy ball milling of complex hydrides. (complete)
- Present data on the reversibility of the Ti-doped LiAlH_4 when utilizing the new physiochemical pathway. (complete and on-going)
- Present data on the reversibility of the Ti-doped $\text{Mg}(\text{AlH}_4)_2$ when utilizing the new physiochemical pathway. (on-going)
- Present data on the potential reversibility of other metal-doped complex hydrides when utilizing the new physiochemical pathway (on-going)

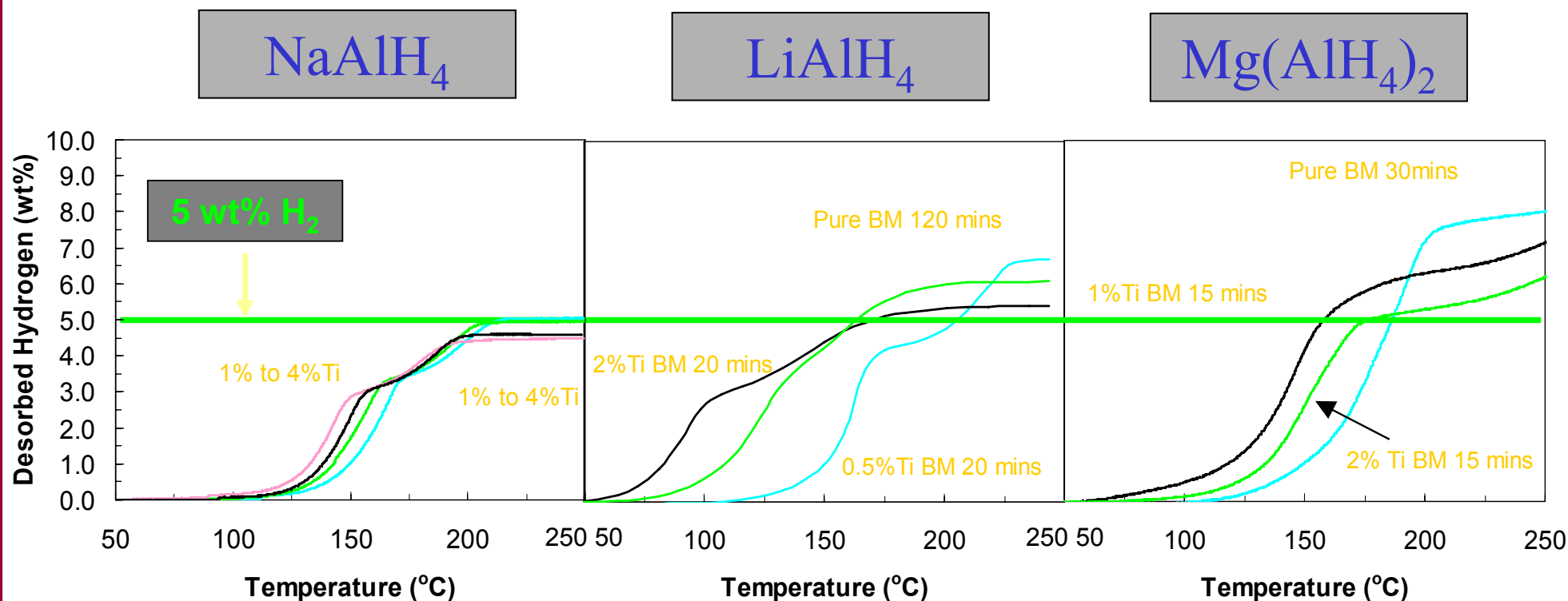


Approach

- prepare samples of NaAlH_4 , LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ doped with TiCl_3 using a conventional wet doping procedure prior to high energy ball milling
- prepare samples of LiAlH_4 doped with TiCl_3 according to the new physiochemical pathway
- cycle the prepared samples in a unique high pressure cycling facility to obtain qualitative discharge and charge kinetics
- discharge the prepared samples in a TGA to obtain quantitative kinetics and capacities under temperature programmed and constant temperature desorption modes
- characterize the prepared samples in terms of their dehydrogenation and hydrogenation kinetics, capacity and reversibility



Comparison of H₂ Desorption Capacities of Ti-Doped NaAlH₄, LiAlH₄ and Mg(AlH₄)₂

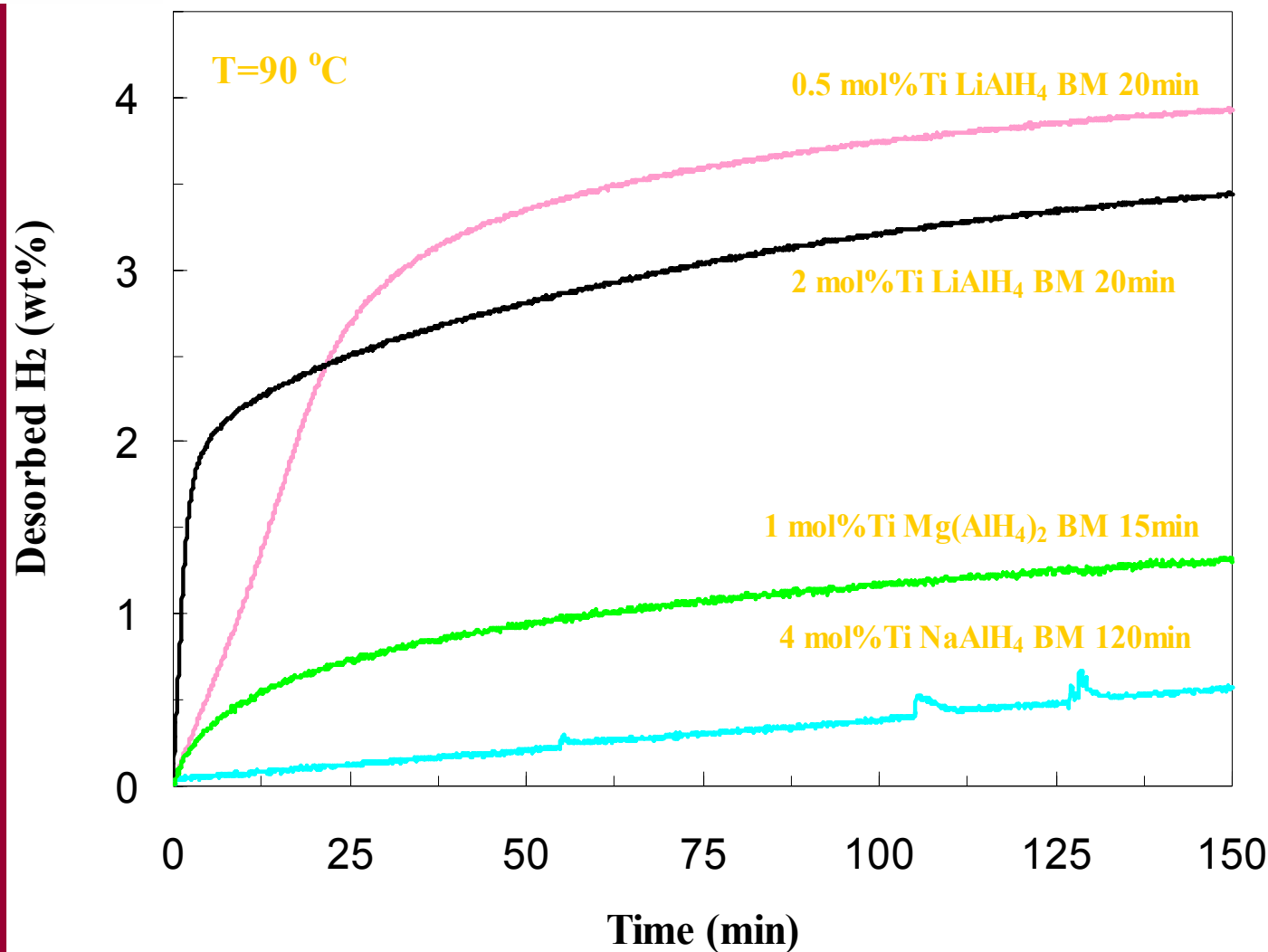


Note the higher capacities of Li and Mg alanates, and the lower dehydrogenation temperature of the Li alanate compared to Na alanate.

J. Wang, A. D. Ebner and J. A. Ritter, Adsorption 11 (2005) 811.



Ti-Doped NaAlH_4 , LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ at 90 °C



Significant release of H_2 from LiAlH_4 BM for 20 min.

Small amount of Ti needed for dramatic effect on H_2 release from LiAlH_4 .

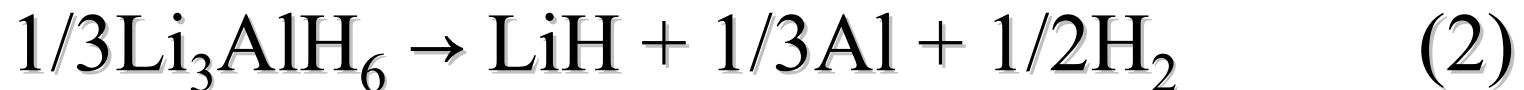
Ti-doped LiAlH_4 exhibits about 20 times higher H_2 production rates than Na and Mg alanates.

J. Wang, A. D. Ebner and J. A. Ritter, Adsorption 11 (2005) 811.



Ti-Doped LiAlH_4

- With fast dehydrogenation kinetics at reasonable temperatures, LiAlH_4 releases up to 7.9 wt% H_2 according to the following reactions:



- The reversible storage of hydrogen in LiAlH_4 has not been conclusively demonstrated.
- Although partial reversibility of Rxn. 2 has been claimed by Chen et al (2001), results by Wang et al (2005) have shown no reversibility of either reactions under similar conditions.

Chen, J.; Kuriyama, N.; Xu, Q.; Takeshita, H. T.; Sakai, T. J. Phys. Chem. B 105 (2001) 11214.

J. Wang, A. D. Ebner and J. A. Ritter, Adsorption 11 (2005) 811.



Thermodynamics of $\text{LiH} \leftrightarrow \text{Li}_3\text{AlH}_6 \leftrightarrow \text{LiAlH}_4$ Reactions

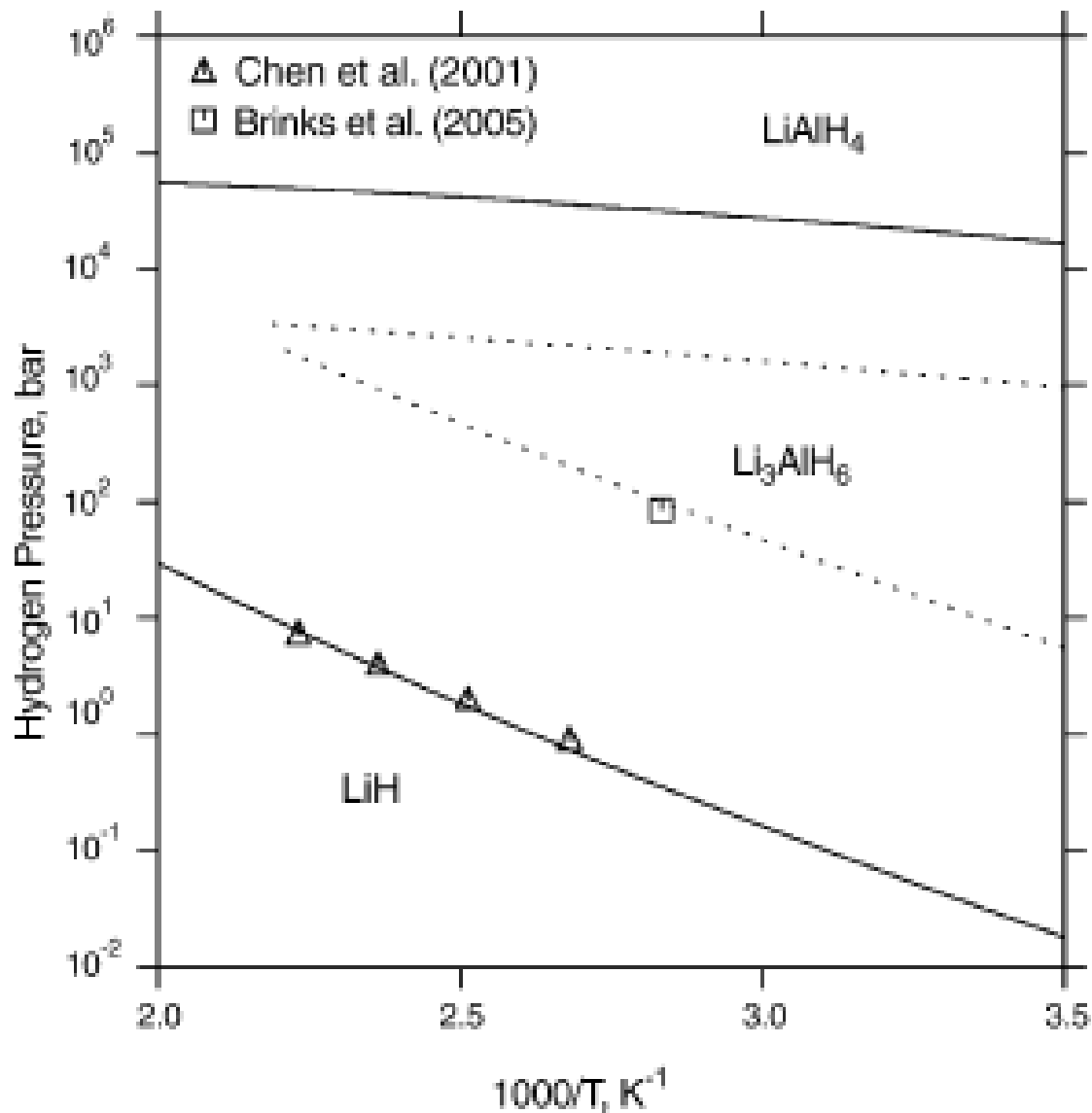
LiAlH ₄ Formation Reactions	ΔH_r^* (kJ/mol)	ΔG_r^* (kJ/mol)
$\text{LiH} + \text{Al} + 3/2\text{H}_2 \rightarrow \text{LiAlH}_4$	-21.97	34.27
$\text{Li}_3\text{AlH}_6 + \text{Al} + 1/2\text{H}_2 \rightarrow \text{LiAlH}_4$	-3.46	27.68

$$\Delta G = \Delta H - T\Delta S \longrightarrow \text{Entropic limitation!}$$

The $\text{LiH} \rightarrow \text{LiAlH}_4$ and $\text{Li}_3\text{AlH}_6 \rightarrow \text{LiAlH}_4$ reactions will not occur at standard conditions without a change in the thermodynamic properties of the LiAlH_4 .



Thermodynamics of $\text{LiH} \leftrightarrow \text{Li}_3\text{AlH}_6 \leftrightarrow \text{LiAlH}_4$ Reactions



$\text{Li}_3\text{AlH}_6 \rightarrow \text{LiAlH}_4$
might occur when the
 H_2 pressure is around
1000 bar!

Therefore, $\text{LiH} \rightarrow \text{LiAlH}_4$
and $\text{Li}_3\text{AlH}_6 \rightarrow \text{LiAlH}_4$ are
thermodynamically not
possible under practical
temperatures and
pressures.*

The thermodynamics
must be altered.

* J. Jang, J. Shim, Y. W. Cho and B. Lee *J. Alloys Compounds*, in-press on-line (2006).

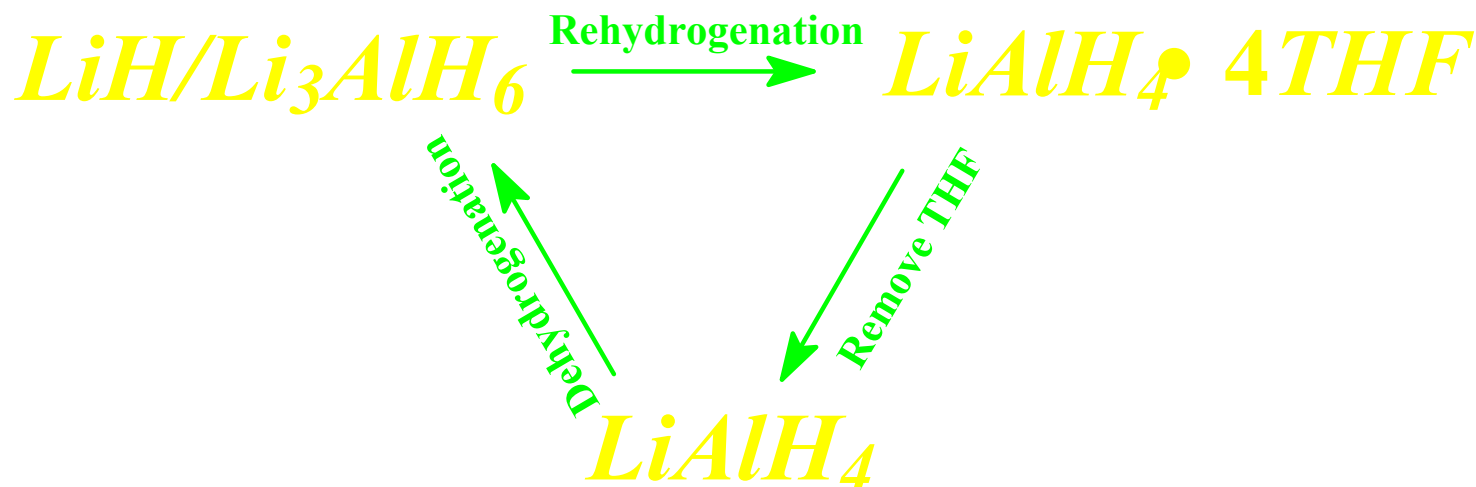


How to alter the thermodynamics?

Thermodynamics of $\text{LiH} \leftrightarrow \text{Li}_3\text{AlH}_6 \leftrightarrow \text{LiAlH}_4$

Reactions in THF

Surmised that LiAlH_4 may be regenerated from LiH and Li_3AlH_6 by forming a $\text{LiAlH}_4 \cdot 4\text{THF}$ adduct with subsequent removal of THF.



H. Clasen, *Angew. Chem.* 73 (1961) 322.

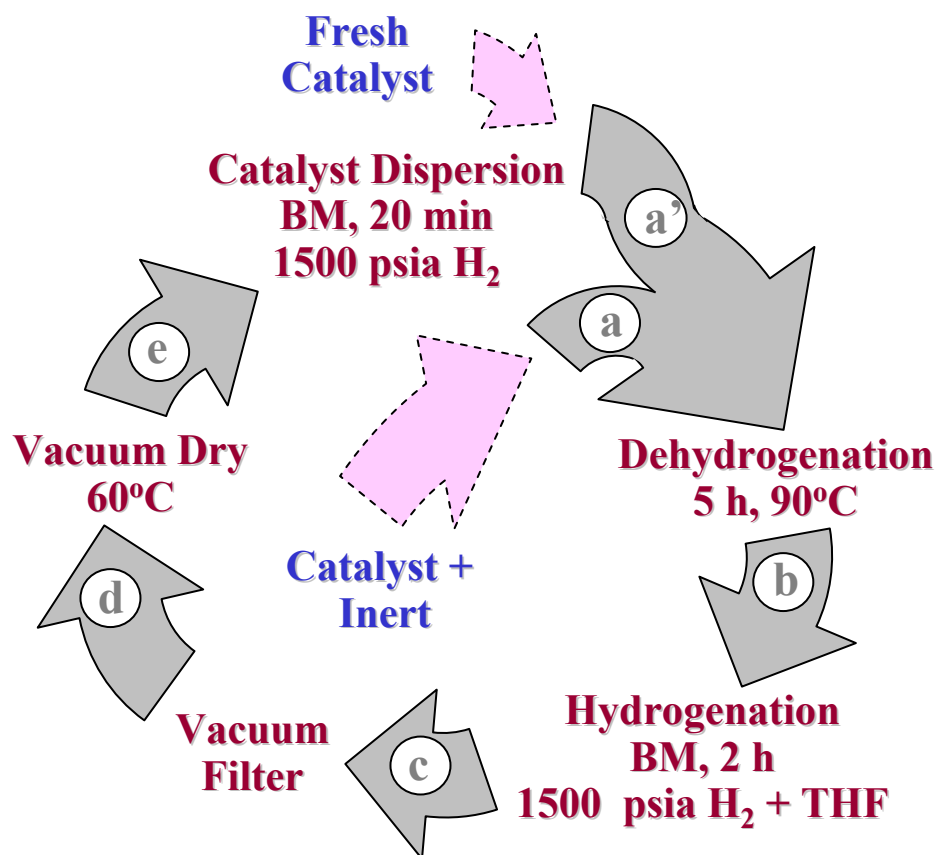
The ΔH associated with the formation of the $\text{LiAlH}_4 \cdot 4\text{THF}$ adduct is -30 to -40 kJ/mol.* With $\Delta G = \Delta H - T\Delta S$, the $\text{LiH} \rightarrow \text{LiAlH}_4$ and $\text{Li}_3\text{AlH}_6 \rightarrow \text{LiAlH}_4$ reactions should occur if the $\text{LiAlH}_4 \cdot 4\text{THF}$ adduct forms when these reactions are carried out in THF.

* E. C. Ashby, R. R. Dobbs, and H. P. Hopkins *J. Am. Chem. Soc.* 95 (1973) 2823.



Five-Step Physiochemical Pathway

One Dehydrogenation/Hydrogenation Cycle
with Ti-Doped LiAlH_4

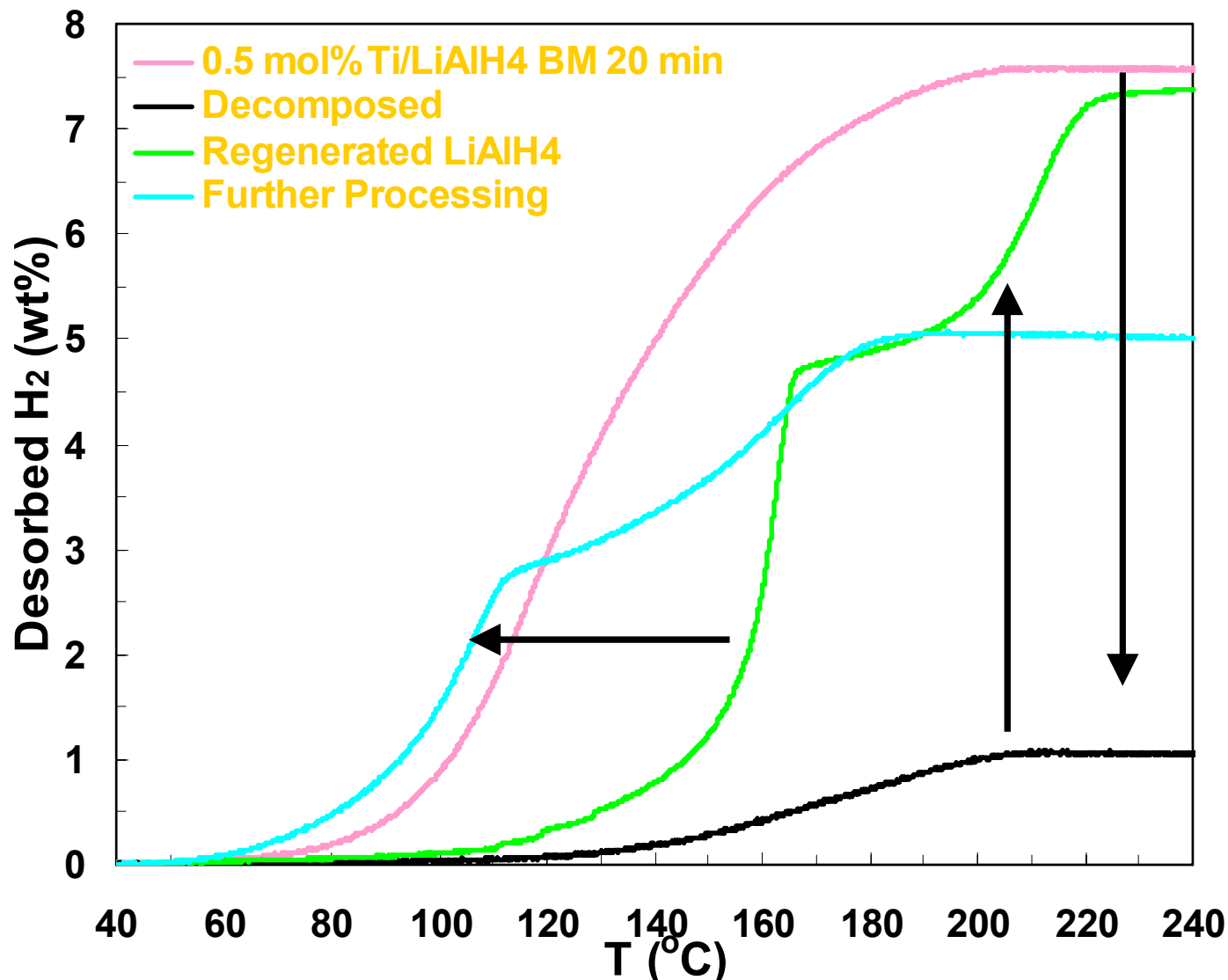


Ti-doped LiAlH_4 can be fully regenerated at reasonable conditions through this novel physiochemical pathway.

Since the THF can be readily recovered, only thermal and mechanical energy are required to regenerate the alanate.



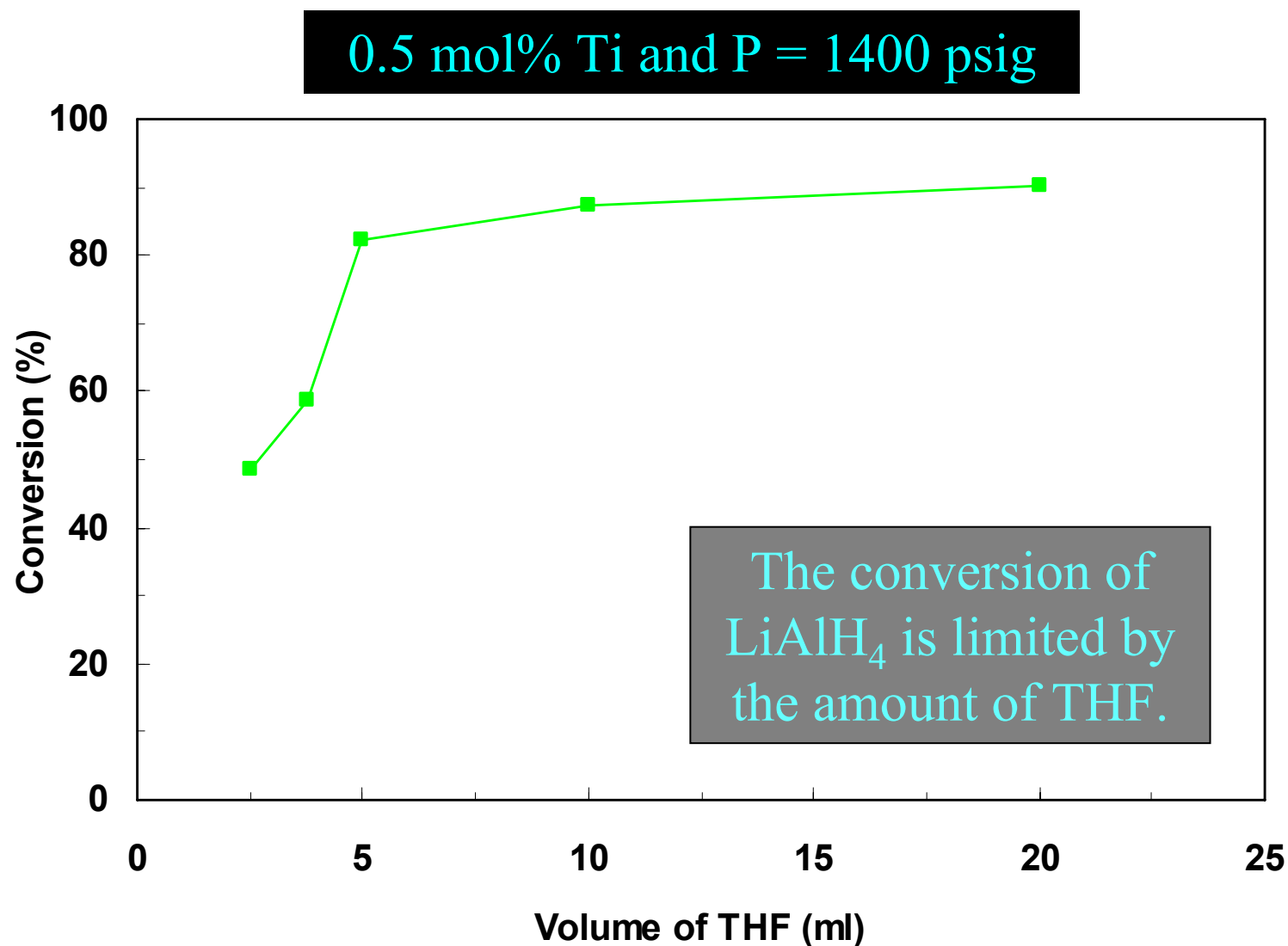
TPD: Different Stages Through One Typical Cycle of Ti-Doped LiAlH_4



Li alanate can be fully regenerated at reasonable conditions through a proprietary physiochemical route; however, it requires off-board reprocessing.



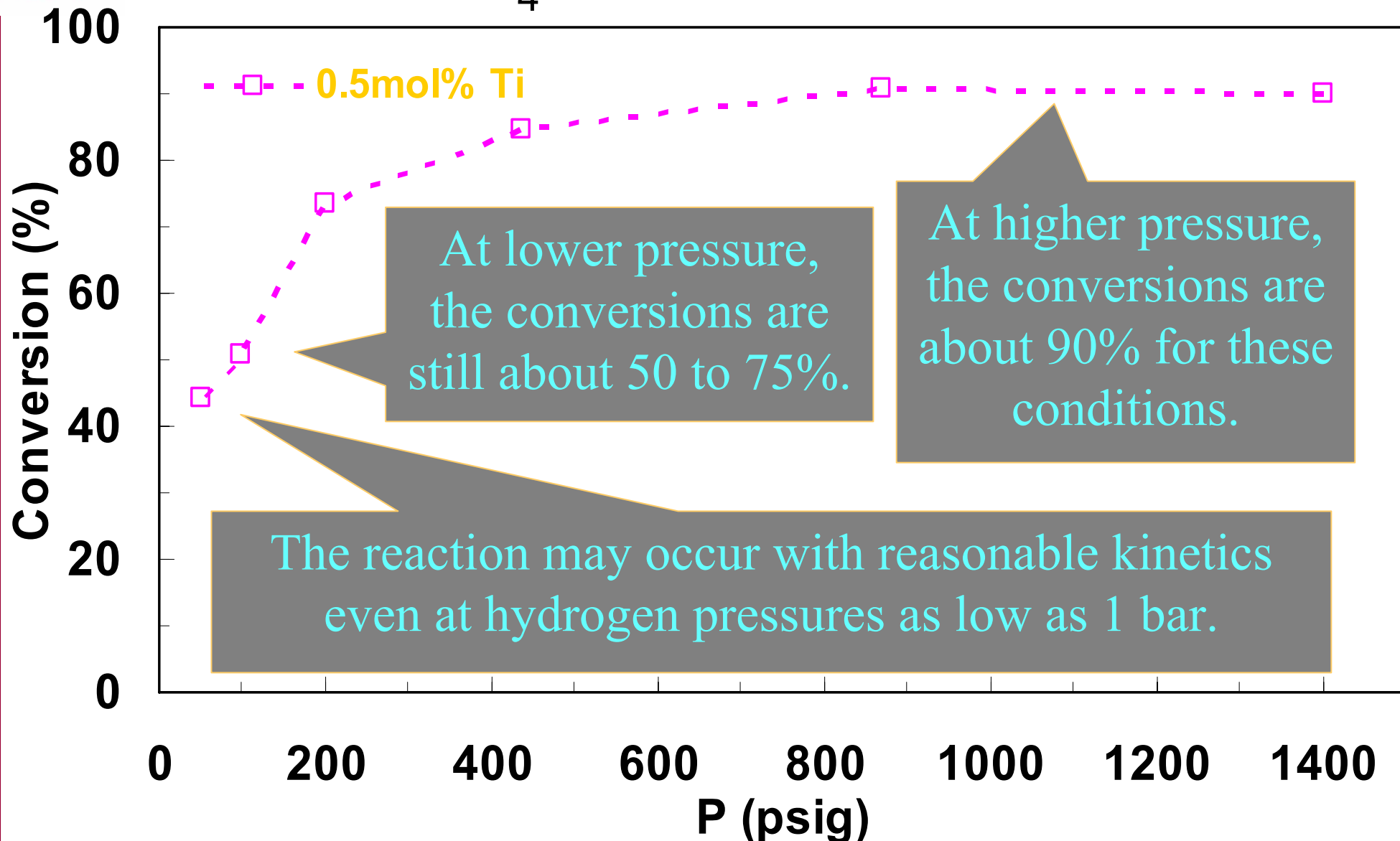
Effect of Volume of THF on the Rehydrogenation of LiAlH_4 in Terms of Conversion



J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, Provisional Patent Application, filed May 18, (2005).



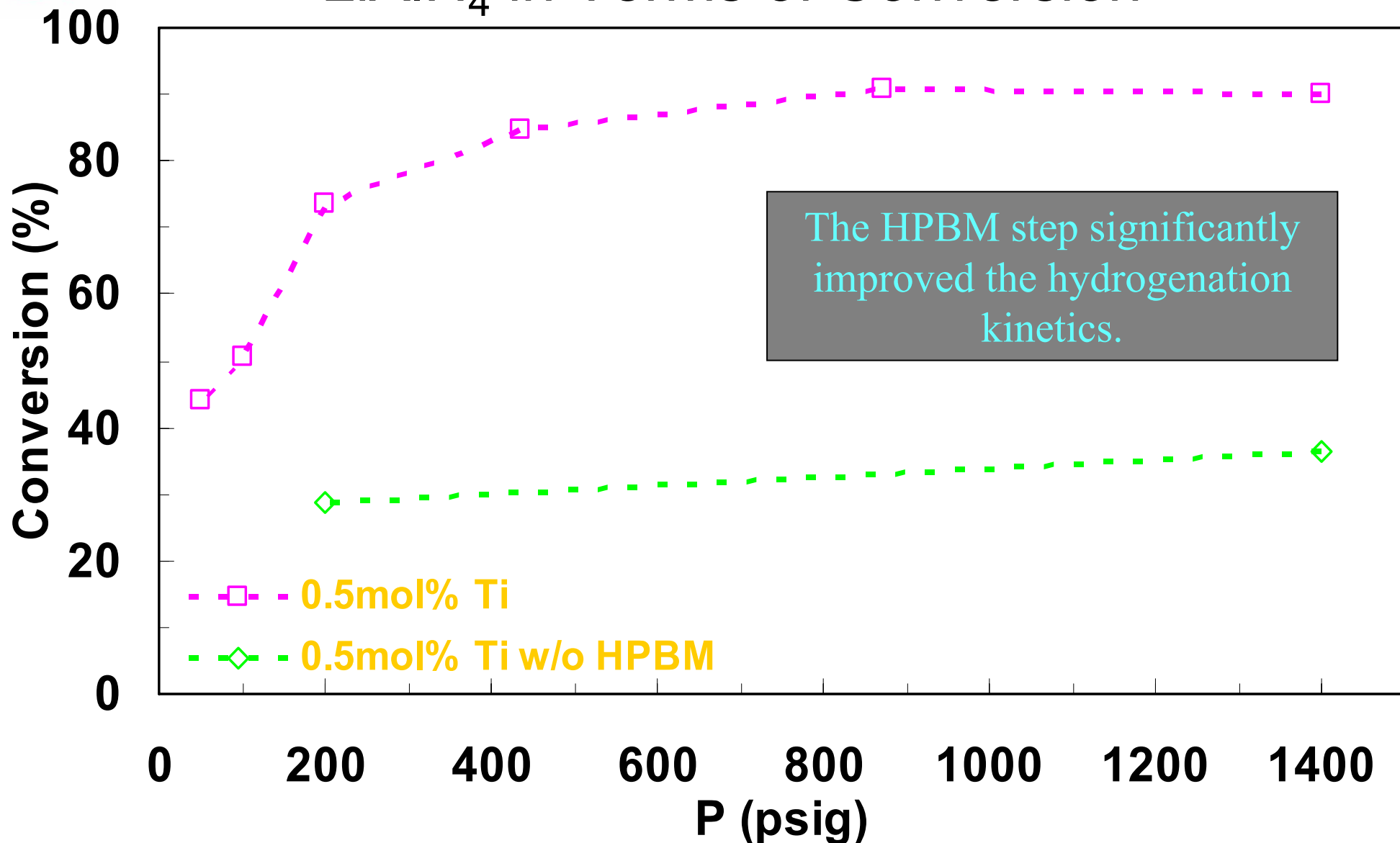
Effect of H_2 Pressure on the Rehydrogenation of LiAlH_4 in Terms of Conversion



J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, Provisional Patent Application, filed May 18, (2005).

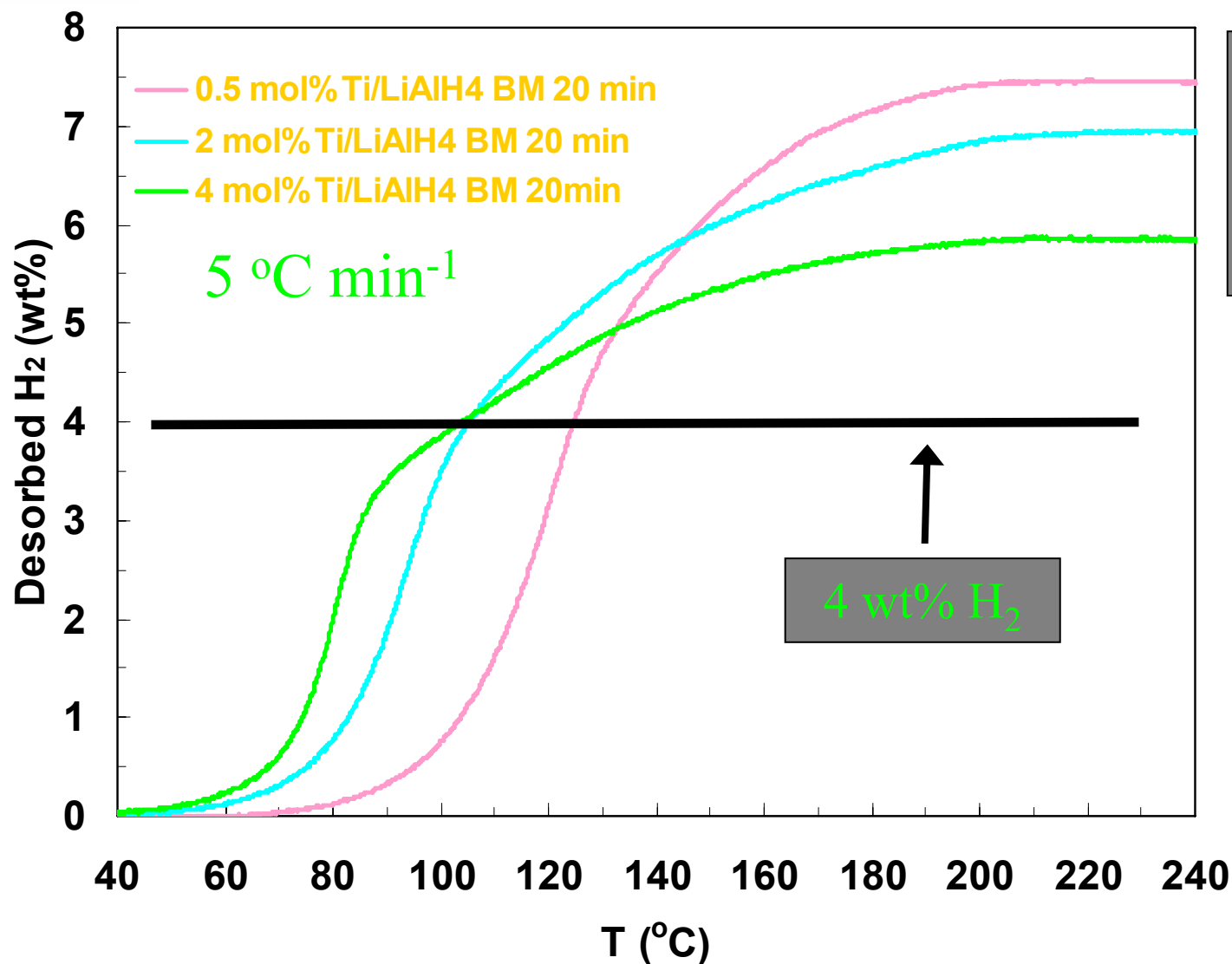


Effect of HPBM on the Rehydrogenation of LiAlH_4 in Terms of Conversion





TPD: Effect of Ti Catalyst Concentration on the Dehydrogenation Kinetics of LiAlH_4

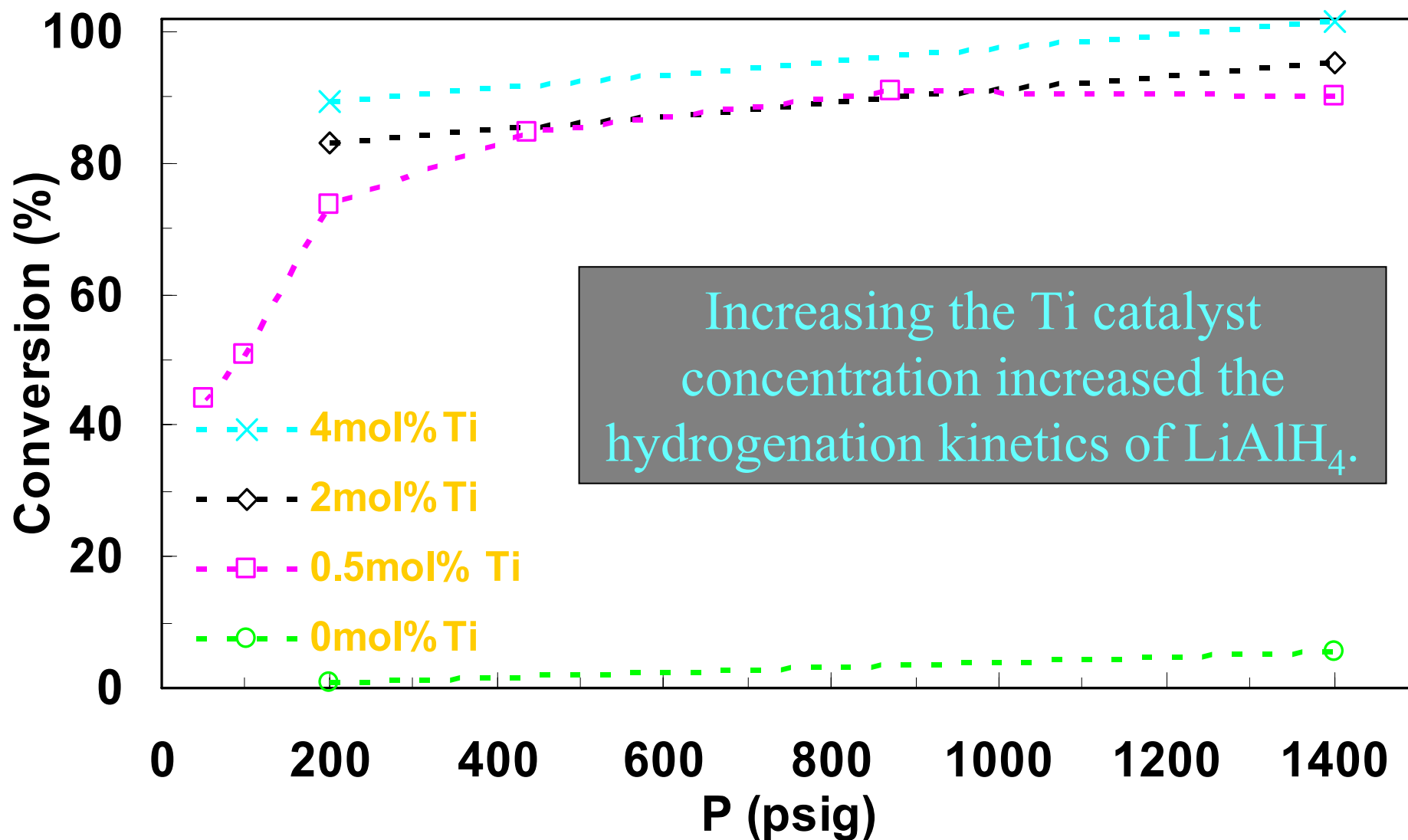


Ti-doped Li alanate is stable under this ball milling condition.

The dehydrogenation kinetics of Ti-doped Li alanate increases by increasing Ti amount, with trade-off with H_2 capacity.



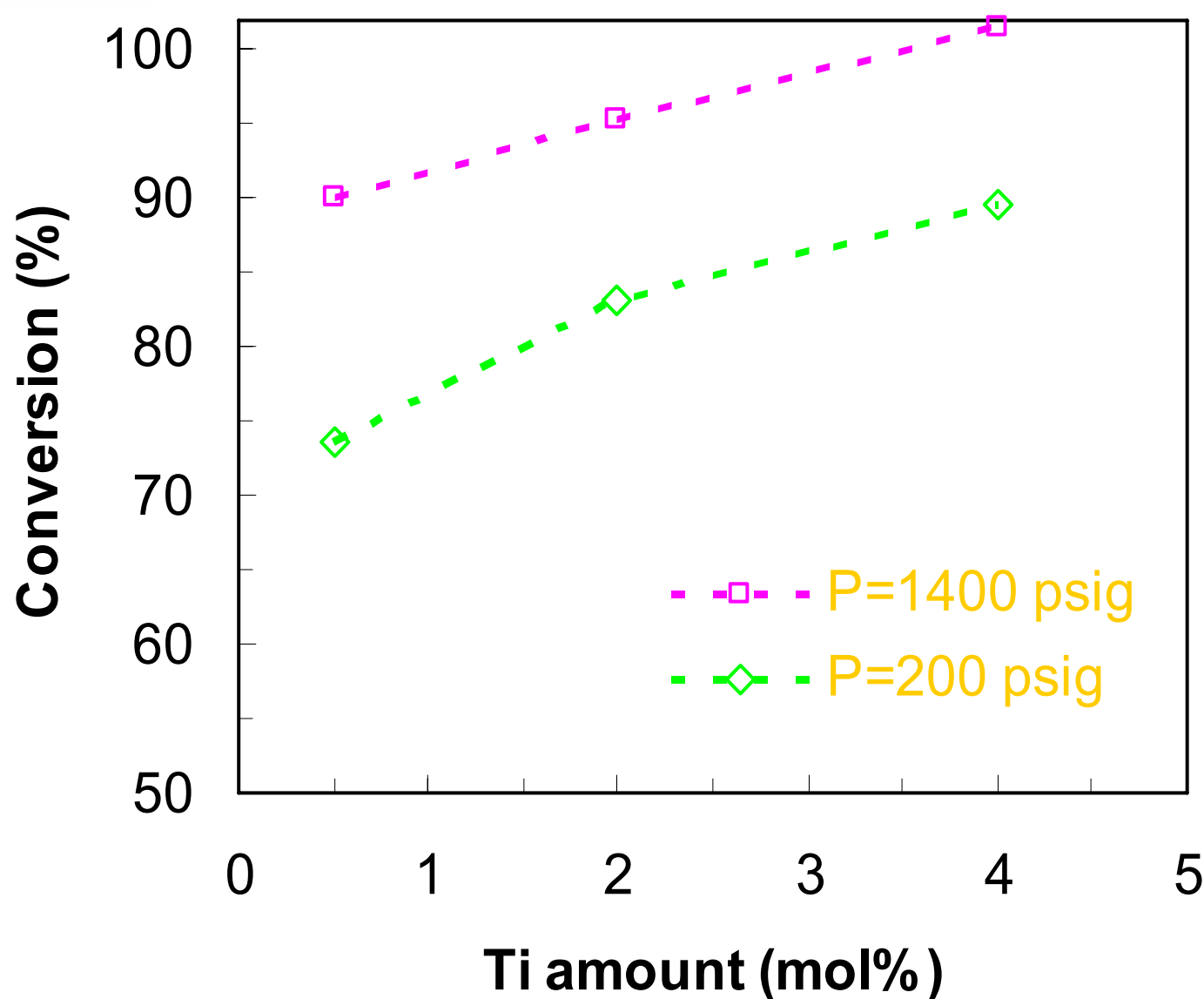
Effect of Ti Catalyst Concentration on the Rehydrogenation of LiAlH_4 in Terms of Conversion



J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, Provisional Patent Application, filed May 18, (2005).



Effect of Ti Catalyst Concentration on the Rehydrogenation of LiAlH_4 in Terms of Conversion



The conversion increased almost linearly from 73 to 90% at low pressure and from 90 to 100% at high pressure, when the Ti catalyst concentration was increased from 0.5 to 4 mol%.



Conclusions

- The Ti-doped LiAlH_4 produced by a novel physiochemical pathway exhibited a hydrogen storage capacity of around 4 wt% in the 100 °C range, making it perhaps one of the best performing hydrogen storage materials known.
- The Ti-doped LiAlH_4 was also easily rehydrogenated through the physiochemical route at essentially ambient temperature and pressures of 3–60 bar.
- The formation of a $\text{LiAlH}_4 \bullet 4\text{THF}$ adduct in THF was found to play the essential role in fostering rehydrogenation.
- The unique feature of this off-board, physiochemical route is that it enables regeneration of a complex hydride material that to date has resisted regeneration through more conventional on-board routes that are being pursued with, for example, NaAlH_4 .
- This physiochemical pathway, or variations thereof, may also be amenable to fostering the reversibility of other higher capacity complex hydrides, like other alanates and possibly even boronates.



Publications and Presentations

Publications

1. J. Wang, A. D. Ebner and J. A. Ritter, "On the Reversibility of Hydrogen Storage in Novel Complex Hydrides," *Adsorption*, 11, 811-816 (2005).
2. J. Wang, A. D. Ebner, R. Zidan, and J. A. Ritter, "Synergistic Effects of Co-Dopants on the Dehydrogenation Kinetics of Sodium Aluminum Hydride," *J. Alloys and Compounds*, **391**, 245-255 (2005).
3. J. Wang, A. D. Ebner, R. Zidan, and J. A. Ritter, "Effect of Graphite on the Dehydrogenation and Hydrogenation Kinetics of Ti-Doped Sodium Aluminum Hydride," *J. Alloys and Compounds*, 395, 252-262 (2005).
4. T. Prozorov, J. Wang, A. D. Ebner and J. A. Ritter, "Sonochemical Doping of Ti-Catalyzed Sodium Aluminum Hydride," *J. Alloys and Compounds*, in press on-line (2006).
5. J. Wang, A. D. Ebner and J. A. Ritter, "Physiochemical Pathway for Cyclic Dehydrogenation and Rehydrogenation of LiAlH_4 ," *J. American Chemical Soc.*, in press on line (2006).
6. T. Wang, J. Wang, A. D. Ebner and J. A. Ritter, "Reversible Hydrogen Storage Properties of NaAlH_4 Doped with Scandium," *Chemical Communications*, submitted (2006).
7. J. Wang, A. D. Ebner, and J. A. Ritter, "Kinetic Behavior of Ti-Doped Sodium Aluminum Hydride when Co-Catalyzed with Carbon Nanostructures," *Nano Letters*, submitted (2006).

Presentations

1. J. Wang, T. Prozorov, T. Wang, A. D. Ebner and J. A. Ritter, "Hydrogen Storage in Complex Hydrides: Reversible Reaction that Mimics Adsorption Behavior," AIChE 2005 Annual Meeting, Cincinnati, OH, November 2005.
2. J. Wang, T. Wang, A. D. Ebner and J. A. Ritter, "Physiochemical Pathway to reversible Hydrogen in Complex Hydrides," TMS 2006: 125th Annual Meeting and Exhibition, San Antonio, TX, March, 2006, invited.

Patent Applications

1. R. Zidan, J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, "Hydrogen Storage Material and Process Using Graphite Additive With Metal Doped Complex Hydrides," Patent Application, US Patent Application 2005/0032641A1 (2005).
2. J. Ritter, A. D. Ebner, C. H. Holland and T. Prozorov, "Method for Improving the Performance of Metal-Doped Complex Hydrides," Provisional Patent Application, filed February 28 (2005).
3. J. Ritter, A. D. Ebner, J. Wang and C. H. Holland, "Physiochemical Pathway to Reversible Hydrogen Storage in Complex Hydrides," Provisional Patent Application, filed June 23 (2005).



Collaborations

Current

- Ragaiy Zidan: SRNL (melt processing and scale-up)
- Chris Williams: USC (Raman spectroscopy studies)
- Vitali Rasolov: USC (*ab initio* studies)
- Alex Angerhofer: UF (EPR studies)

Future

- potential to interact with or become part of the Metal Hydride Center of Excellence at SNL



Future Research Directions

FY06 – FY07

- continue to explore the new physiochemical pathway that fosters reversibility in LiAlH_4 and other metal-doped complex hydrides
- continue to explore bimetallic and metal-carbon catalyzed complex hydrides
- continue to synthesize and study the reversibility of other metal doped complex hydrides
- continue to characterize metal doped complex hydrides using temperature programmed desorption, constant temperature desorption and constant temperature cycling curves



Technical Barriers and Targets

Hydrogen Storage

DOE Targets:

2007 – 1.5 kWh/kg (4.5 wt %), 1.2 kWh/L, \$6/kWh

2010 – 2 kWh/kg (6 wt %), 1.5 kWh/L, \$4/kWh

2015 – 3 kWh/kg (9 wt %), 2.7 kWh/L, \$2/kWh

Technical Barriers:

- high system weight, high volume
- high cost of storage
- durability of at least 1500 cycles
- lower than expected energy efficiency
- long refueling time
- lack of availability of codes and standards
- no life cycle and efficiency analyses



Project Safety

- The most significant hydrogen hazards associated with this project are:
 - High reactivity of solid chemical hydrides when exposed to humidified air
 - Toxicity: Avoid ingestion or contact with eyes and mucous membranes
- The approach to deal with this hazard is:
 - Handle hydrides in an inert atmosphere within a glove box
 - Use small quantities for laboratory experiments
 - Blanket reactor with inert gas



2006-2007 Budget

- Total Funding (18 mo Period Beginning 11/05)
 - \$194,875 + \$43,000
- Personnel
 - PI: 2.0 academic and 0.5 summer months
 - Research Professor: 1.0 calendar months
 - Two PhD Students plus Tuition: 36 calendar months
- Travel
- Materials and Supplies