



Development of Complex Metal Hydride Hydrogen Storage Materials

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Objectives

- Study the effect of different metal dopants and co-dopants on dehydrogenation (discharge or desorption) of NaAlH_4
- Study the effect of different carbon materials as a co-dopant with Ti and Al powder on dehydrogenation (discharge or desorption) and hydrogenation (charge or adsorption) of NaAlH_4
- Study the effectiveness of a new sonochemical pretreatment method for improving the dehydrogenation and hydrogenation kinetics of NaAlH_4
- Study the reversibility of LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ when doped with Ti under conditions similar to those that are effective with Ti-doped NaAlH_4



Project Timeline

6/04-8/04

8/04-11/05

10/04-12/05

6/05-5/05

3/05-8/05

7/05-11/05

Phase I

Phase II

Phase III

Phase IV

Phase V

Phase VI

- ❖ Phase I: Complete analysis of the effect of co-dopants on the performance of the NaAlH_4 system (status: completed)
- ❖ Phase II: Complete analysis on the reversibility of the Ti-doped LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ systems (status: on-going)
- ❖ Phase III: Complete Raman and molecular modeling analyses on the Ti-doped NaAlH_4 system (status: nearly complete)
- ❖ Phase IV: Complete analysis on the Ti-doped NaAlH_4 system with carbon additive (status: nearly complete)
- ❖ Phase V: Complete analysis on the effect of high temperature and pressure ball milling of complex hydrides (status: initiated)
- ❖ Phase VI: Complete analysis on long-term cycling and scale-up of promising complex hydrides (status: not initiated)

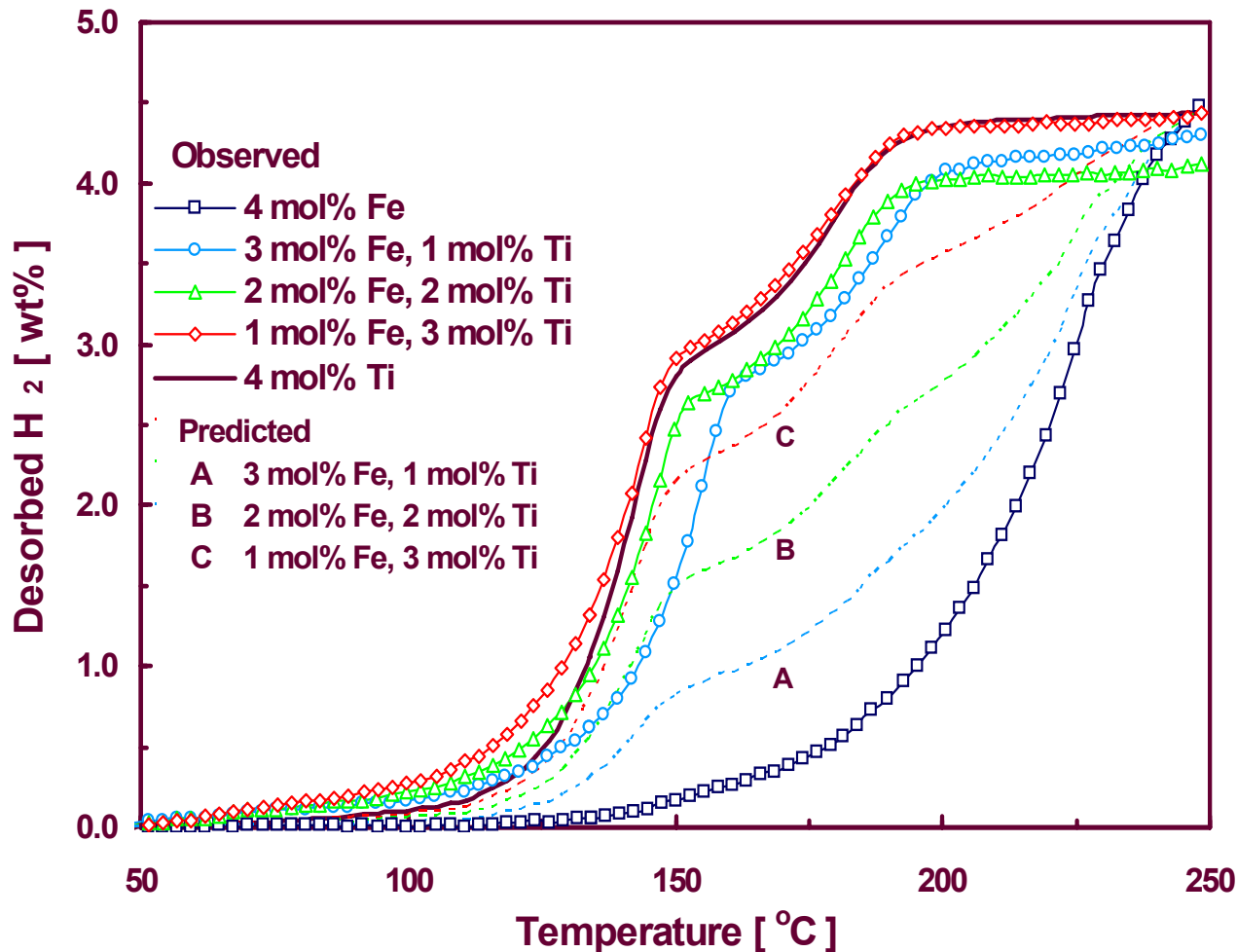


Approach

- prepare samples of NaAlH_4 , LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ using a conventional wet or new sonochemical doping procedure prior to high energy ball milling
 - ❖ samples possibly doped with Ti, Zr, Fe, Al powder and or various forms of carbon
- 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



TPD: Synergistic Effects of Co-Dopants, Ti and Fe, on the Dehydrogenation of NaAlH_4

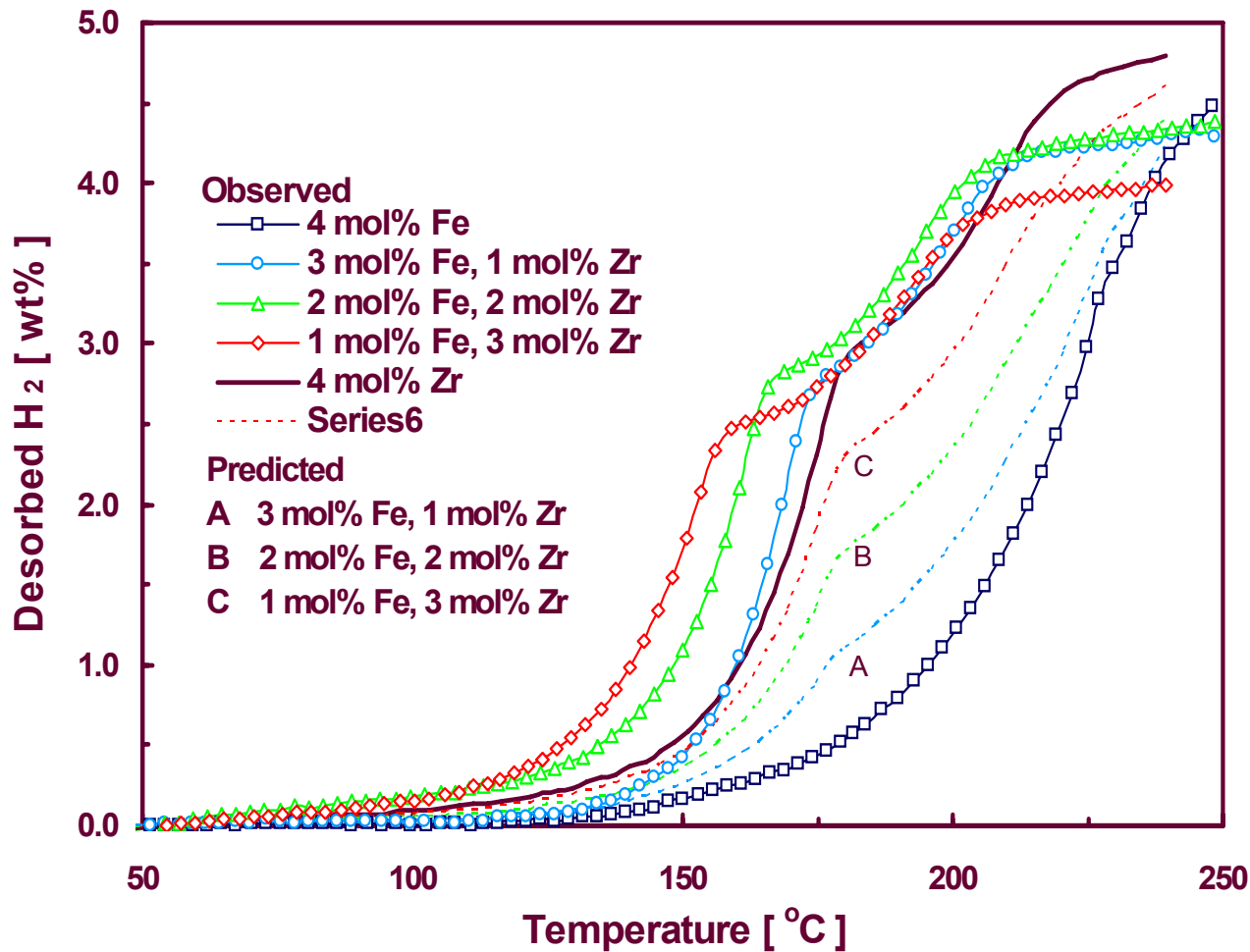


- Predicted TPD is expected behavior of a simple physical mixture, i.e., linear combination, of the two metal dopants.
- Observed TPD is the actual synergistic behavior of the two metal dopants.
- Observed synergism, in some cases, is **much better** than 4 mol% Ti alone!
- Thought to be due to the “metal-metal bond polarity” concept borrowed from bi-metallic catalysis concepts.

J. Wang, A. D. Ebner, R. Zidan, and J. A. Ritter, *J. Alloys and Compounds*, **391**, 245-255 (2005).



TPD: Synergistic Effects of Co-Dopants, Zr and Fe, on the Dehydrogenation of NaAlH_4

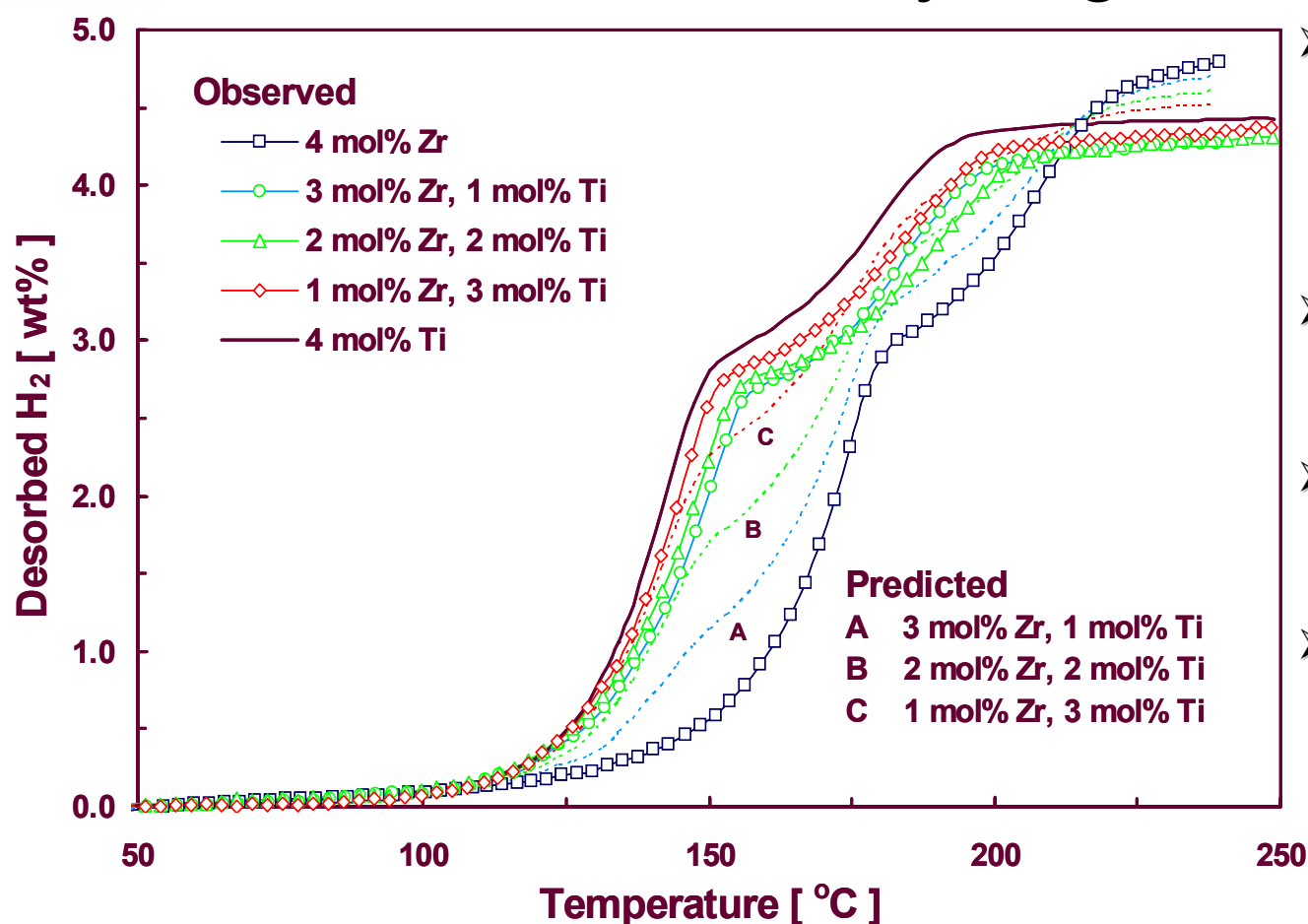


- Predicted TPD is expected behavior of a simple physical mixture, i.e., linear combination, of the two metal dopants.
- Observed TPD is the actual synergistic behavior of the two metal dopants.
- Observed synergism, in most cases, is **much better** than 4 mol% Zr alone!
- Consistent with the “metal-metal bond polarity” concept, in that **Zr and Fe** are from **opposite sides** of the periodic table.

J. Wang, A. D. Ebner, R. Zidan, and J. A. Ritter, *J. Alloys and Compounds*, **391**, 245-255 (2005).



TPD: Synergistic Effects of Co-Dopants, Ti and Zr, on the Dehydrogenation of NaAlH_4

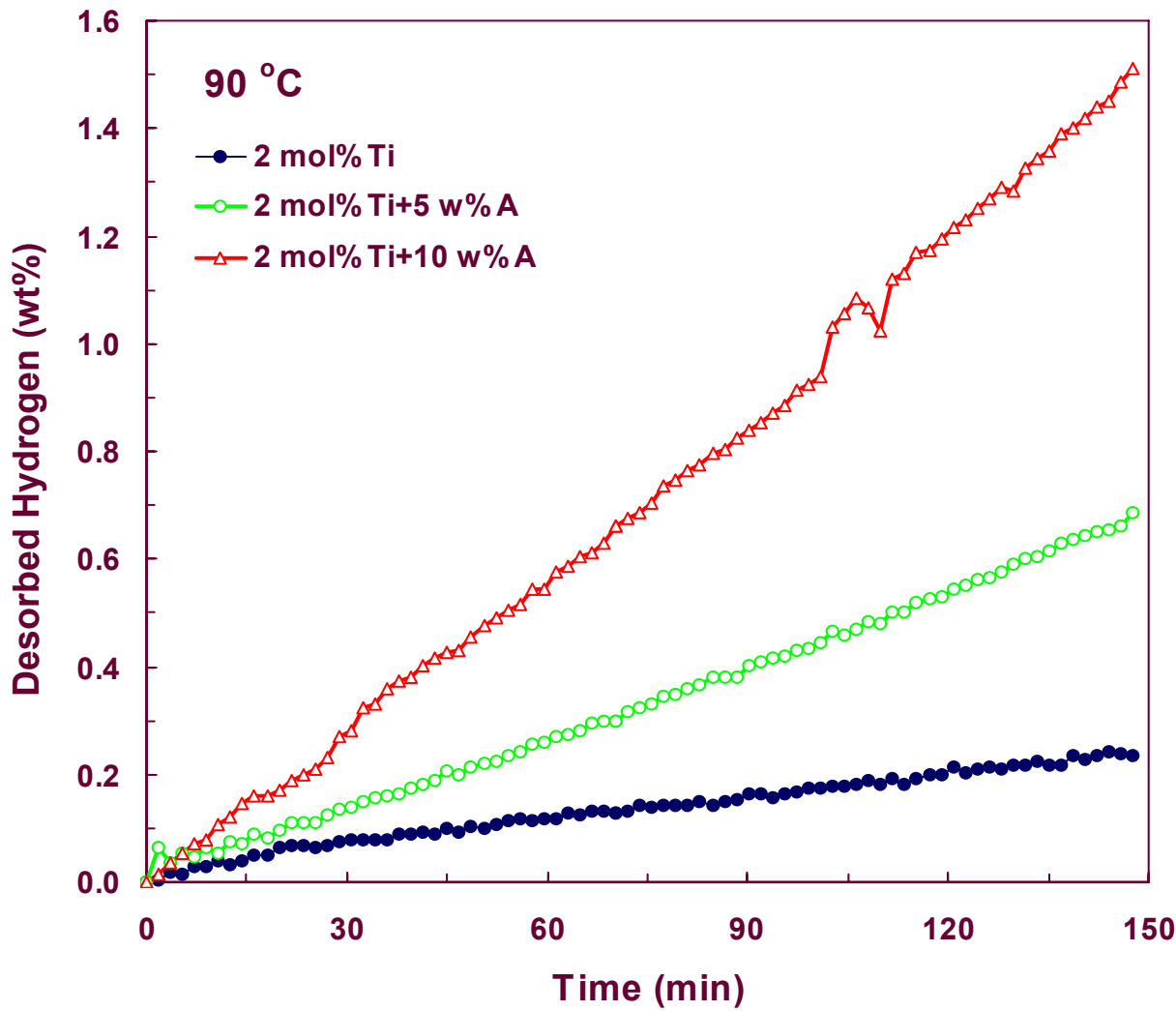


- Predicted TPD is expected behavior of a simple physical mixture, i.e., linear combination, of the two metal dopants.
- Observed TPD is the actual synergistic behavior of the two metal dopants.
- Observed synergism, in all cases, is **never** better than 4 mol% Ti alone!
- Consistent with the “metal-metal bond polarity” concept, in that **Ti and Zr** are from **same left** side of the periodic table.

Is there a combination of early and late transition metals that could instill superior performance compared to a single metal dopant like Ti? This supposition is being explored.



CTD: Effect of Graphite (A) Concentration on Dehydrogenation of 2% Ti-NaAlH₄



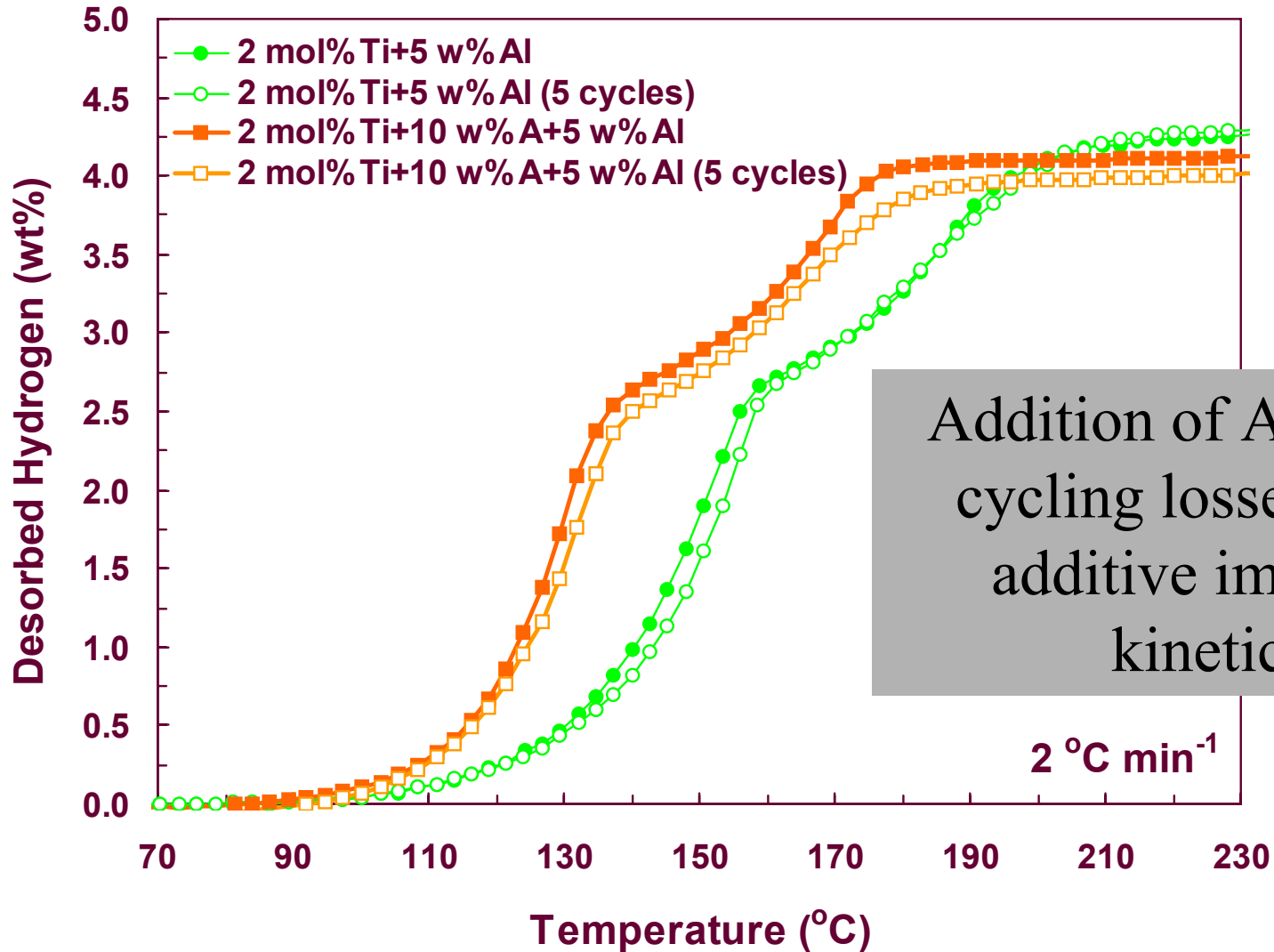
At 90°C, 10 wt% additive produces six fold increase in kinetics!

Best dehydrogenation kinetics observed so far for this widely studied complex hydride!

R. Zidan, J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, US Patent 2005/0032641A1



TPD: Effect of Cycling on Dehydrogenation of 2% Ti-NaAlH₄ with 10 wt% Graphite (A) and 5 wt% Al



Addition of Al reduces cycling losses, while additive improves kinetics!

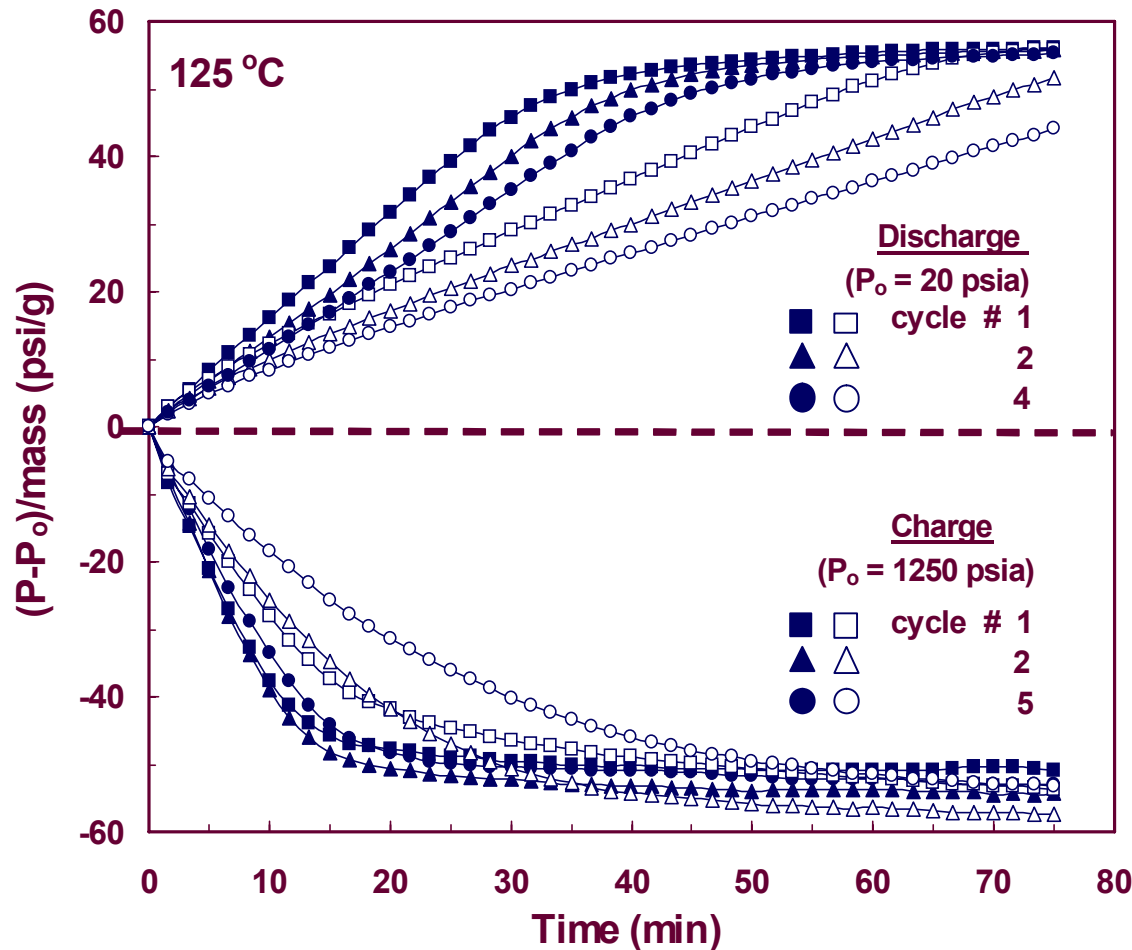


Influence of Graphite on Hydrogenation and Dehydrogenation Rates During Cycling

Doped and Ball Milled Samples of NaAlH_4

Empty symbols: 2.0 mol% Ti and 5 wt% Al

Filled symbols: 2 mol% Ti, 10 wt% Graphite and 5 wt% Al



Influence of graphite on both dehydrogenation and hydrogenation (charge) kinetics is clearly observed. Upon co-doping with graphite, the time for charging is markedly decreased by a factor of four, from about 60 min to about 15 min.

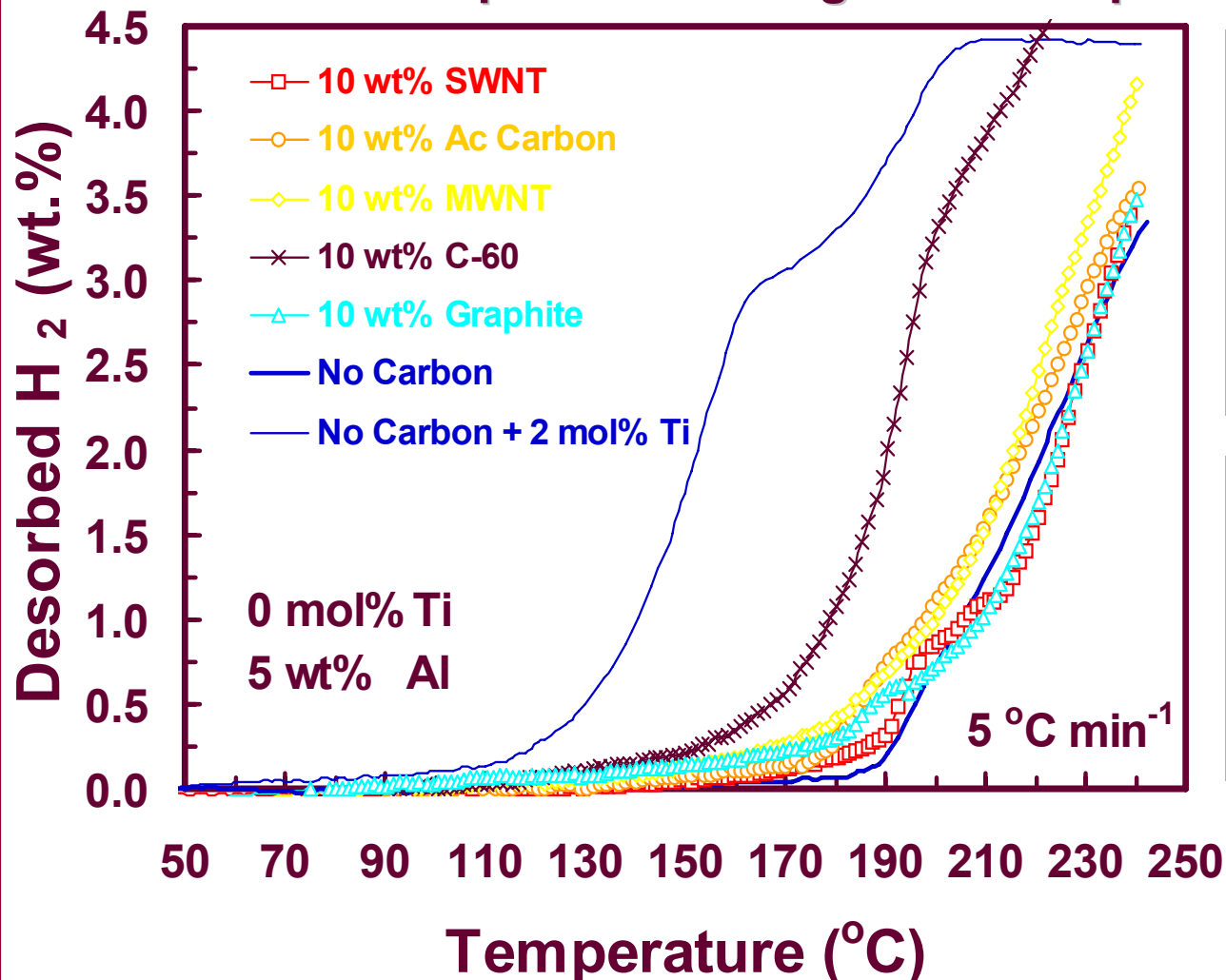
These results may represent the best charge kinetics to date for a sample of NaAlH_4 doped with as little as 2 mol% Ti.



TPD: Influence of Different Carbon Materials on Dehydrogenation Rates of **undoped and uncycled** NaAlH₄

All samples doped with 5 wt% Al

All samples containing carbon doped with 10 wt%



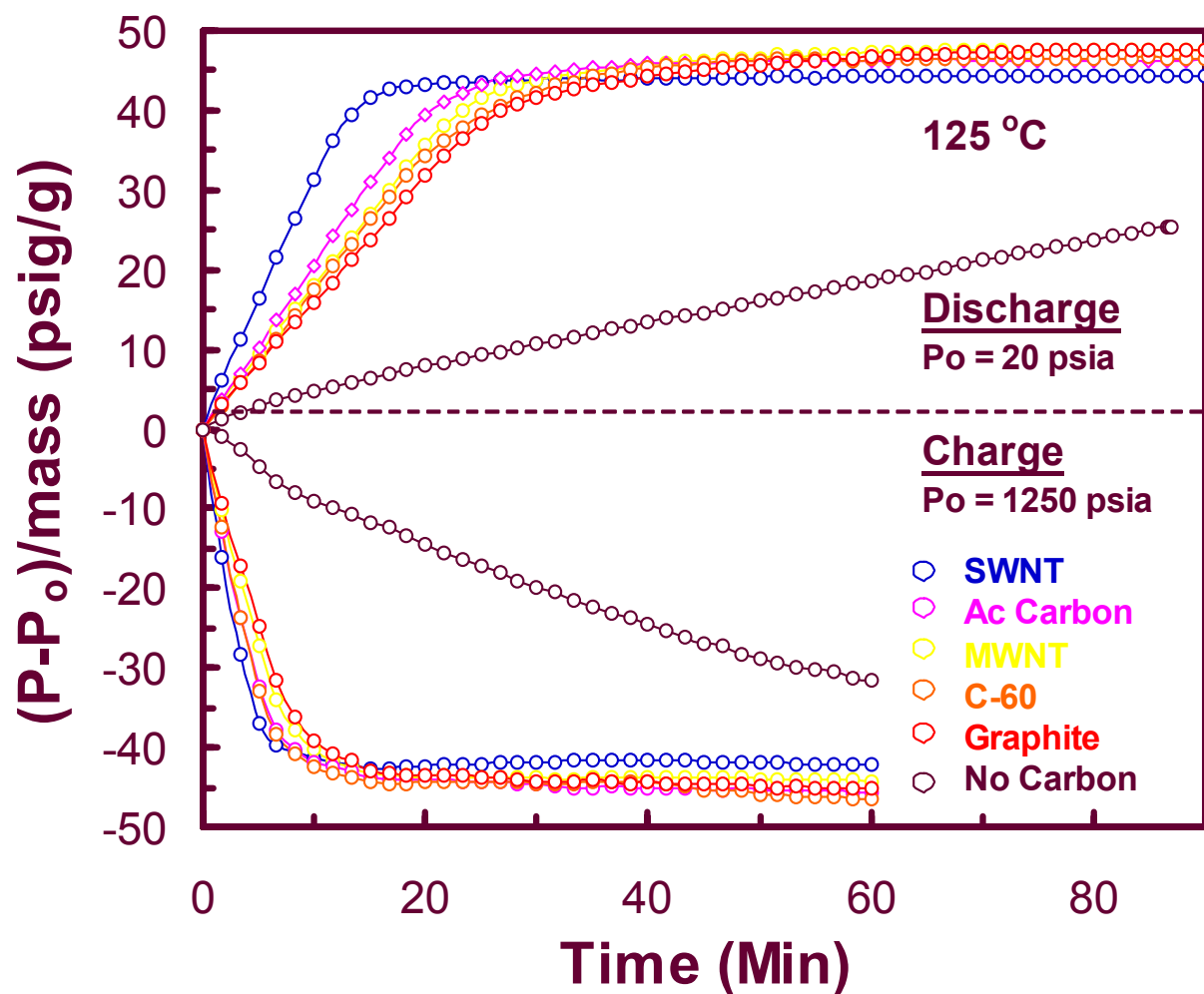
Samples doped only with carbon display very little effect, no matter the type of carbon, except for C-60 (most likely a metal impurity).

Carbon alone is not an effective catalyst for complex hydrides contrary to that suggested in the literature!



Influence of Different Carbon Materials on Dehydrogenation and Hydrogenation Rates of Carbon-Doped and Cycled NaAlH_4

All samples doped with 2 mol% Ti and 5 wt% Al and cycled 5 times
All samples containing carbon doped with 10 wt%



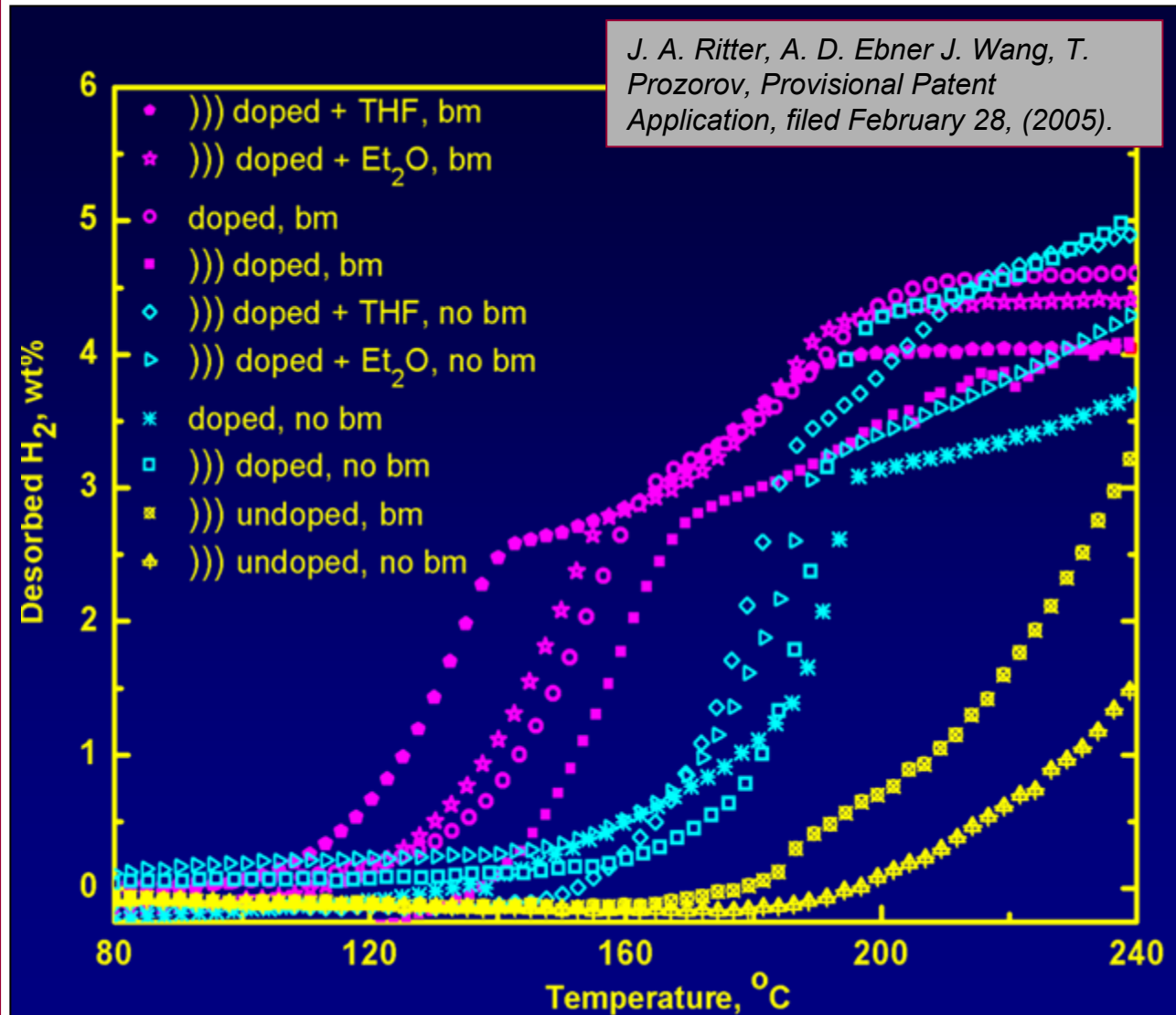
Samples doped with Ti and carbon consistently showed faster dehydrogenation and rehydrogenation rates over just Ti-doped samples.

Samples doped with SWNTs and graphite showed the strongest and weakest effects, respectively.

At $T = 125$ °C and $P = 1,250$ psia charging of Ti and carbon doped materials occurs within 10 min!



TPD: Effect of Sonochemical Pre-Treatment (PT) on the dehydrogenation of doped (2 mol% Ti) and undoped, and ball milled and unball milled samples of NaAlH_4



- The effect of the sonochemical PT is shown in terms of TPD runs at $5^{\circ}\text{C}/\text{min}$.
- In general, samples that have undergone sonochemical PT consistently exhibit lower decomposition temperatures.
- Best case observed for sonochemically doped sample of NaAlH_4 with 2 mol% Ti in decalin with THF as a co-solvent.

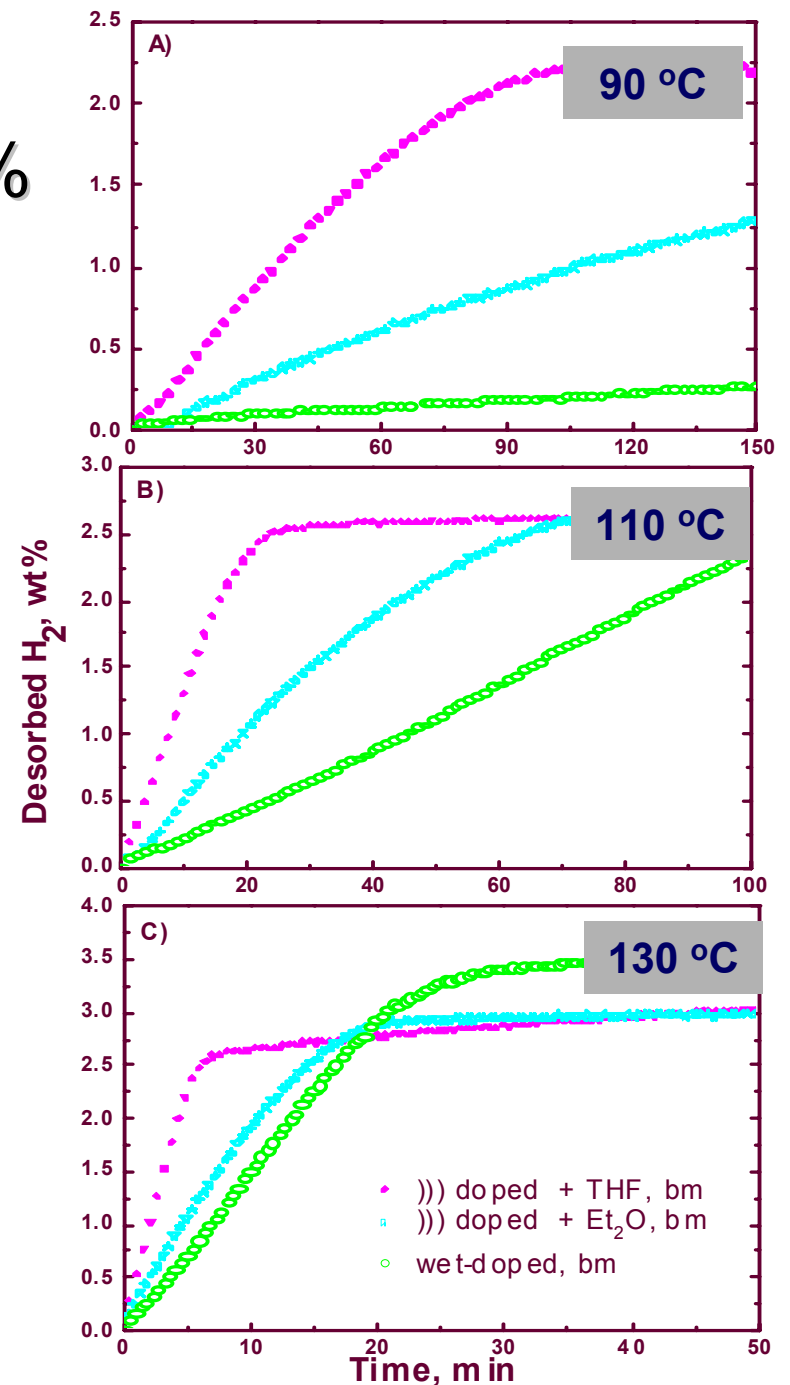


CTD: Effect of Sonochemical Pre-Treatment (PT) on 2 mol% Ti-Doped NaAlH_4

During constant temperature desorption the dehydrogenation kinetics of sonochemically doped and ball milled samples of NaAlH_4 increased by factors of 9.0, 5.1 and 3.1 respectively at 90, 110 and 130 °C over those exhibited by conventionally wet doped and ball milled samples.

J. A. Ritter, A. D. Ebner, J. Wang, T. Prozorov, Provisional Patent Application, filed February 28, (2005).

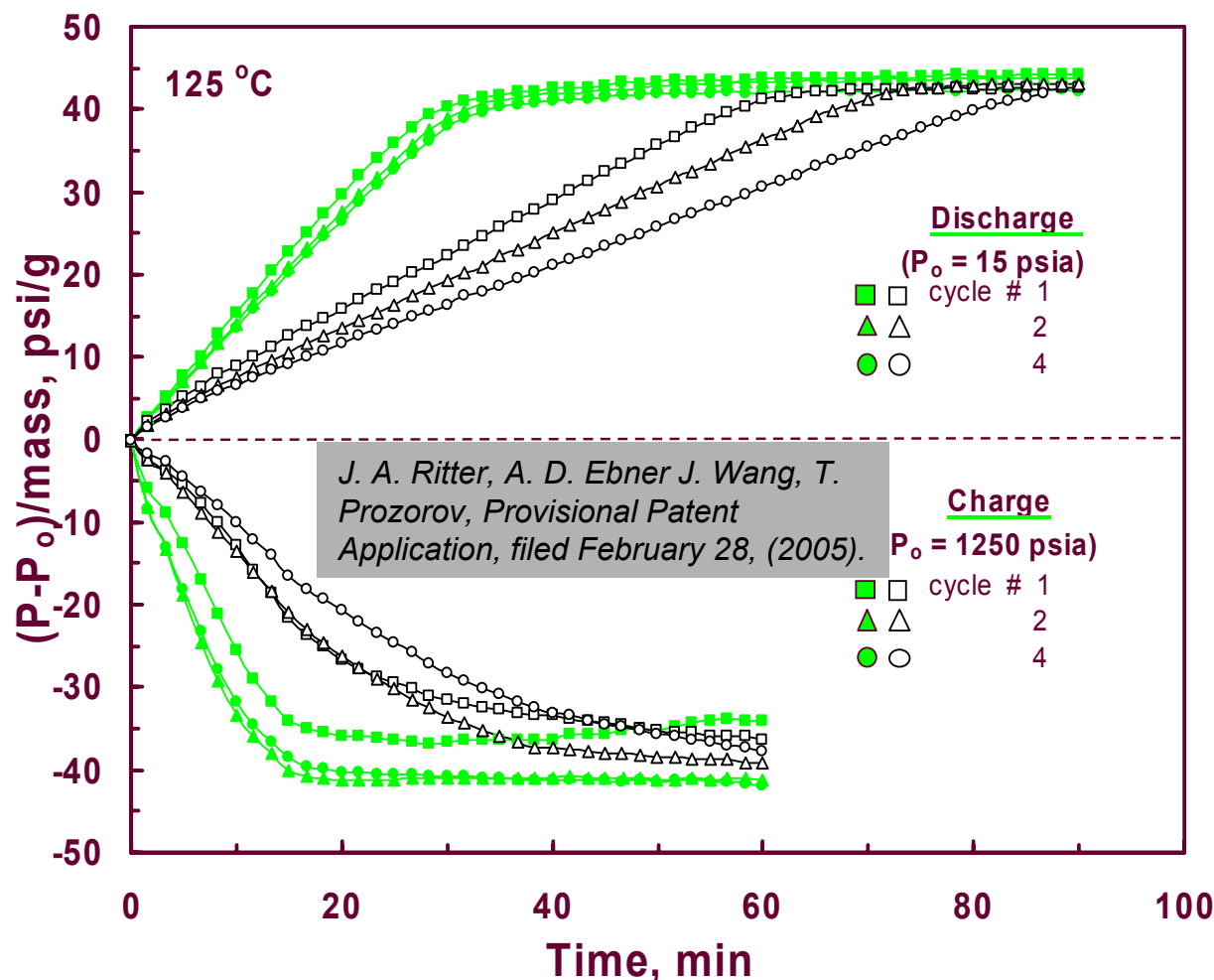
T. Prozorov, J. Wang, A. D. Ebner and J. A. Ritter, *J. Alloys and Compounds*, submitted (2005).





Influence of Sonochemical PreTreatment on Hydrogenation and Dehydrogenation Rates During Cycling

Ball milled samples of NaAlH_4 wet doped and sonochemically doped in decalin with THF, all doped with 2 mol% Ti. Filled symbols correspond to the sonochemically doped sample; empty symbols correspond to the wet doped sample.

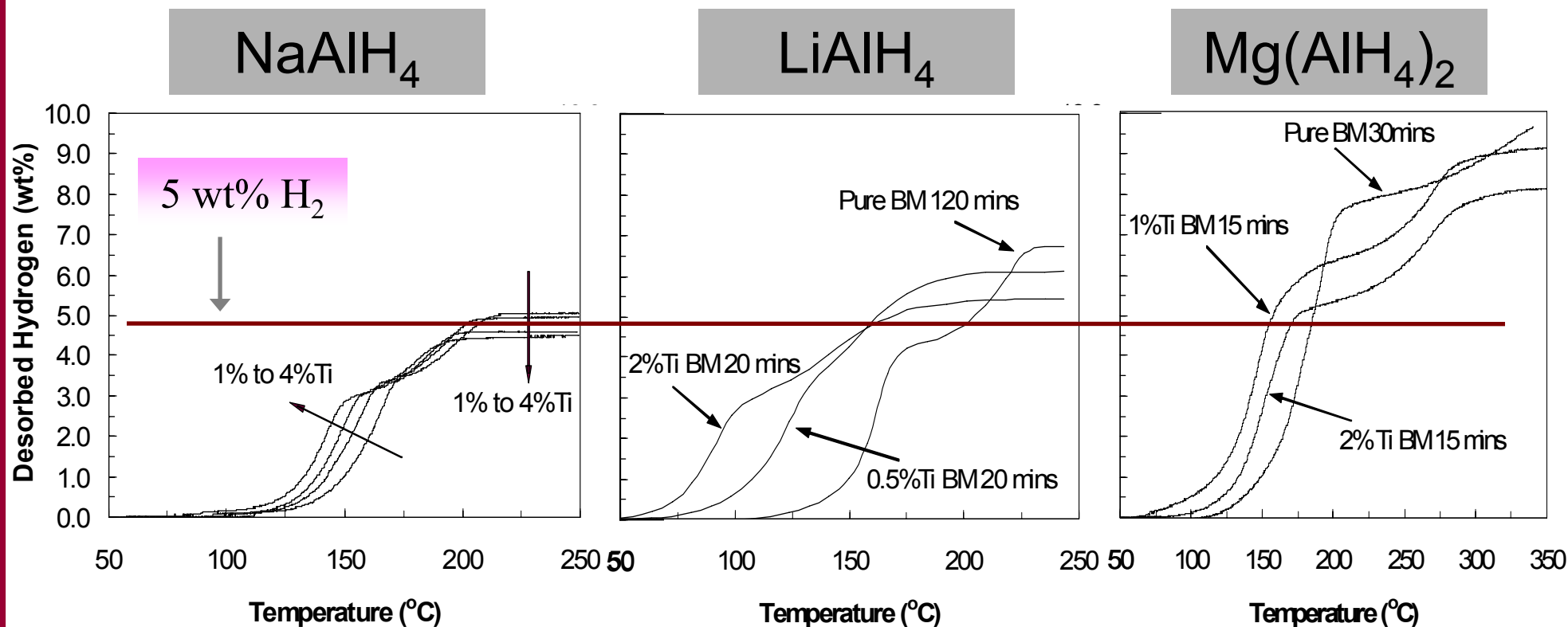


Influence of sonochemical PT on both dehydrogenation and hydrogenation kinetics, is clearly observed. The time for charging is markedly decreased again by a factor of four, from about 60 to 15 min.

Again, these results may represent the best charge kinetics to date for a sample of NaAlH_4 doped with as little as 2 mol% Ti.



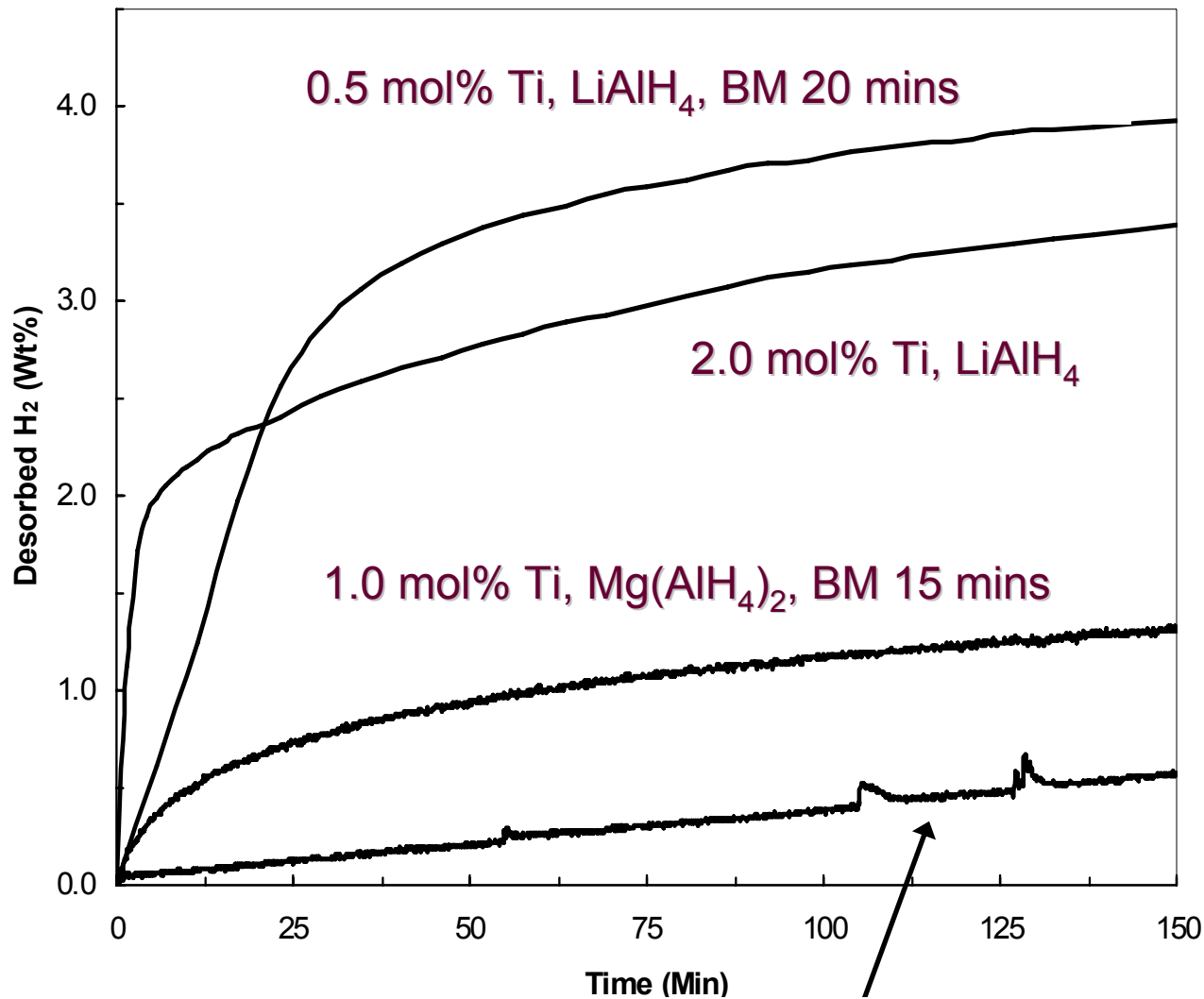
TPD: Comparison of Desorption Capacities of Ti-Doped NaAlH_4 , LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$



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



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



Significant release of H_2 from Li alanate BM for 20 min.

Only small amount of Ti needed for dramatic effect on Li alanate.

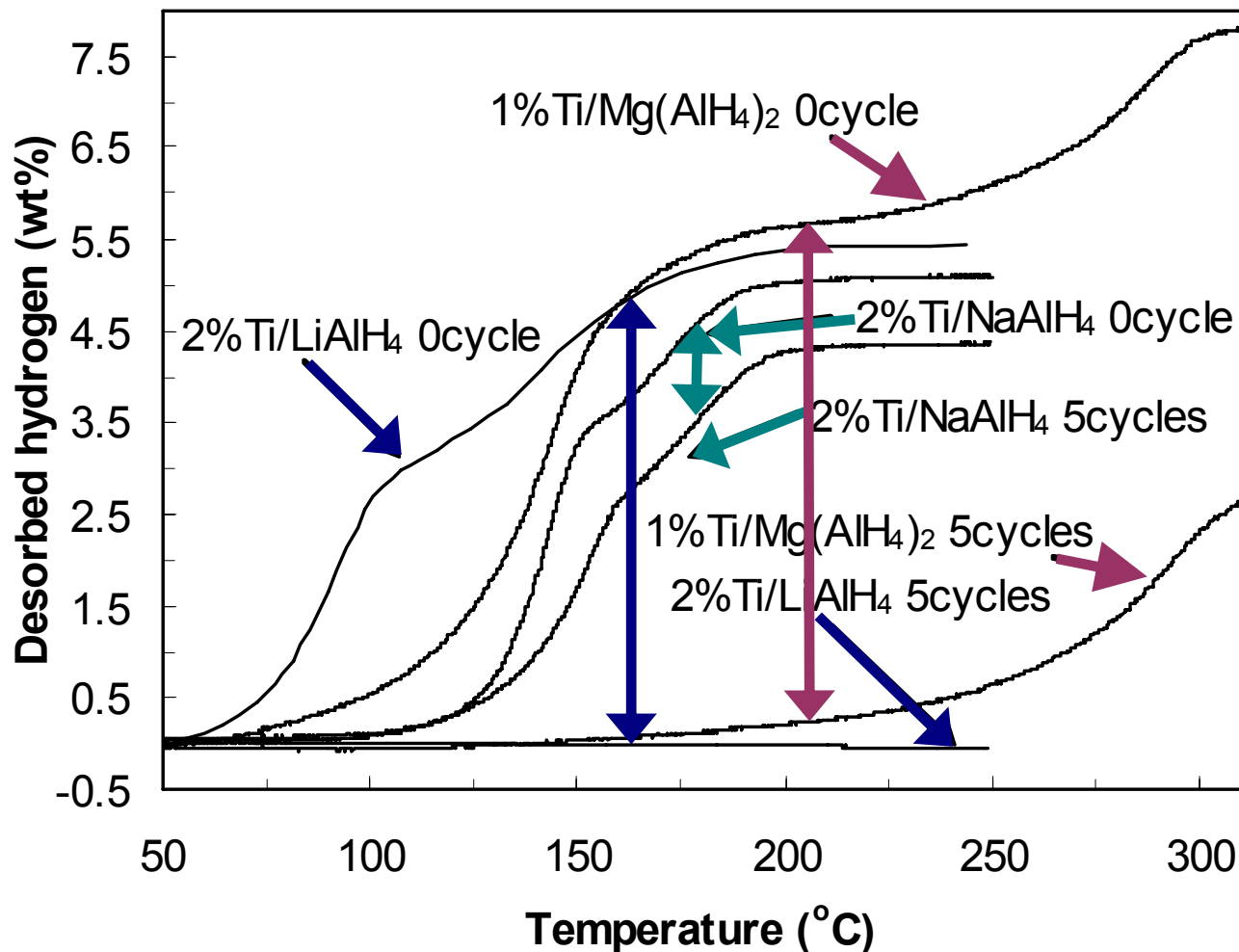
Ti-doped LiAlH_4 exhibits about 20 times higher H_2 production rates than Na and Mg alanates.



Comparison of 0th with 5th Discharge Cycle of Ti-Doped NaAlH₄, LiAlH₄ and Mg(AlH₄)₂

Rate = 5 °C/min

J. Wang, A. D. Ebner and J. A. Ritter,
Adsorption, 11, 811-816 (2005).



Five discharge (4 hrs) and charge (8 hrs) cycles carried out **between 50 and 1,200 psig at 125 °C for Na alanate BM 120 min**, **between 50 and 2,100 psig at 140 °C for Li alanate BM for 20 min**, and **between 50 and 1,500 psig at 150 °C for Mg alanate BM 15 min**.

Under these conditions, only the Na alanate system is observed to be reversible! The Li and Mg alanates systems do not exhibit any reversibility.



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*, in press (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*, submitted (2005).
5. J. Wang, R. C. Petty, A. D. Ebner, T. Prozorov and J. A. Ritter, "Low Temperature Performance of Ti-Doped Sodium Aluminum Hydride with Single Wall Carbon Nanotubes as a Co-Catalyst," *Nanotechnology*, submitted (2005).

Presentations

1. J. Wang, T. Prozorov, A. D. Ebner and J. A. Ritter, "Novel Complex Hydrides for Reversible Hydrogen Storage," AIChE 2004 Annual Meeting, Austin, TX, November 2004.

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).



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

FY05 – FY06

- complete Raman study of Ti-doped NaAlH_4 with Dr. Williams
- continue to explore bimetallic and metal-carbon catalyzed alanates
- continue to explore new sonochemical pretreatment method possibly as an alternative to ball milling metal-doped alanates
- continue to work with Dr. Angerhofer at UF on carrying out high field EPR studies with doped alanates
- continue to work with Dr. Rasolov at USC on *ab initio* studies of TiCl_3 - NaAlH_4 clusters
- continue to synthesize and study the reversibility of other metal doped alanates and boronates, and to carry out a thermodynamic analysis to explain their inherent stability



Technical Barriers and Targets

Hydrogen Storage

DOE Targets:

2005 – 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:

- higher 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



2004-2005 Budget

- Total Funding (18 mo Period Beginning 06/04)
 - \$335,000 + \$83,759 cost share
- Personnel
 - PI: 1.35 academic and 2 summer months
 - Research Professor: 8.5 calendar months
 - Postdoctoral Associate: 9 calendar months
 - Two PhD Students plus Tuition: 36 calendar months
- Travel
- Materials and Supplies