# HYDROGEN STORAGE USING COMPLEX HYDRIDES

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# Objective

- Identify a hydrogen storage system that meets the DOE guidelines
  - Complex hydrides have the potential
  - $NaAlH_4$ exciting but will never have capacity
  - Other complex hydrides

# Complex Hydrides

| Hydride | Wt % | Hydride | Wt% |
|---|---|---|---|
| $LiAlH_4$ | 10.5 | $Ca(BH_4)_2$ | 11.4 |
| $LiBH_4$ | 18.2 | $NaAlH_4$ | 7.5 |
| $Al(BH_4)_3$ | 20.0 | $NaBH_4$ | 10.5 |
| $LiAlH_2(BH_4)_2$ | 15.2 | $Ti(BH_4)_3$ | 12.9 |
| $Mg(AlH_4)_2$ | 9.3 | $Ti(AlH_4)_4$ | 9.3 |
| $Mg(BH_4)_2$ | 14.8 | $Zr(BH_4)_3$ | 8.8 |
| $Ca(AlH_4)_2$ | 7.7 | $Fe(BH_4)_3$ | 11.9 |

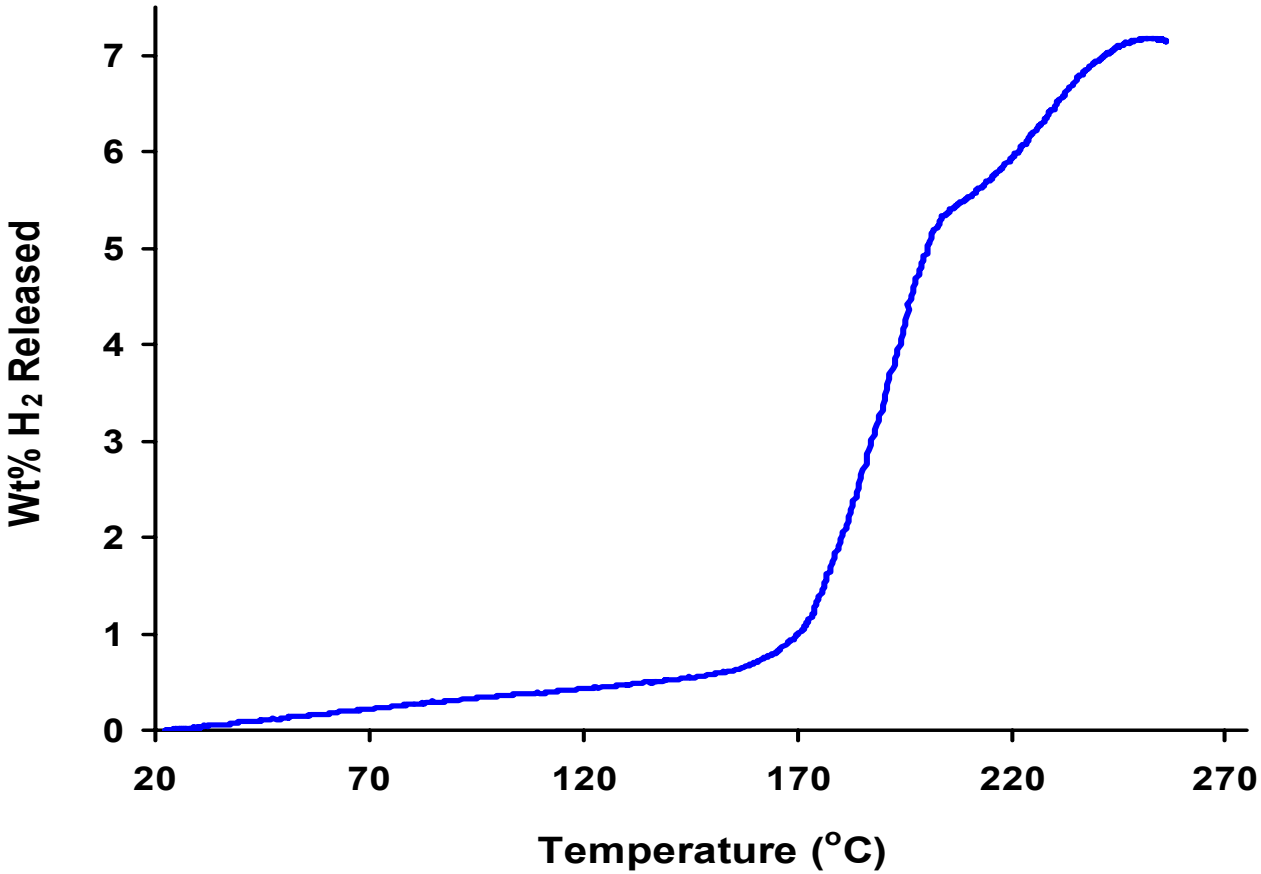
# Timeline - Accomplishments

| Task Designation / Milestone | FY 2002 | | | | 2003 |
|---|---|---|---|---|---|
| | Qtr1 | Qtr2 | Qtr3 | Qtr4 | Qtr1 |
| Acquire commercially available cmpds (1) | ◆ | | | | |
| Synthesize reported cmpds (2) | | ◆ | | | |
| Develop syntheses - unreported cmpds (3) | | | ◆ | | |
| Det. H interaction properties of pure (1) | | ◆ | | | |
| Det. H interaction properties of pure (2), (3) | | | | ◆ | |
| Catalyst incorporation methods study | | | ◆ | | |
| Determination of catalyst effects | | | ★ | | |
| Catalyst mechanism study | | | | ★ | |
| Propose and study other catalysts | | | | | ◆ |

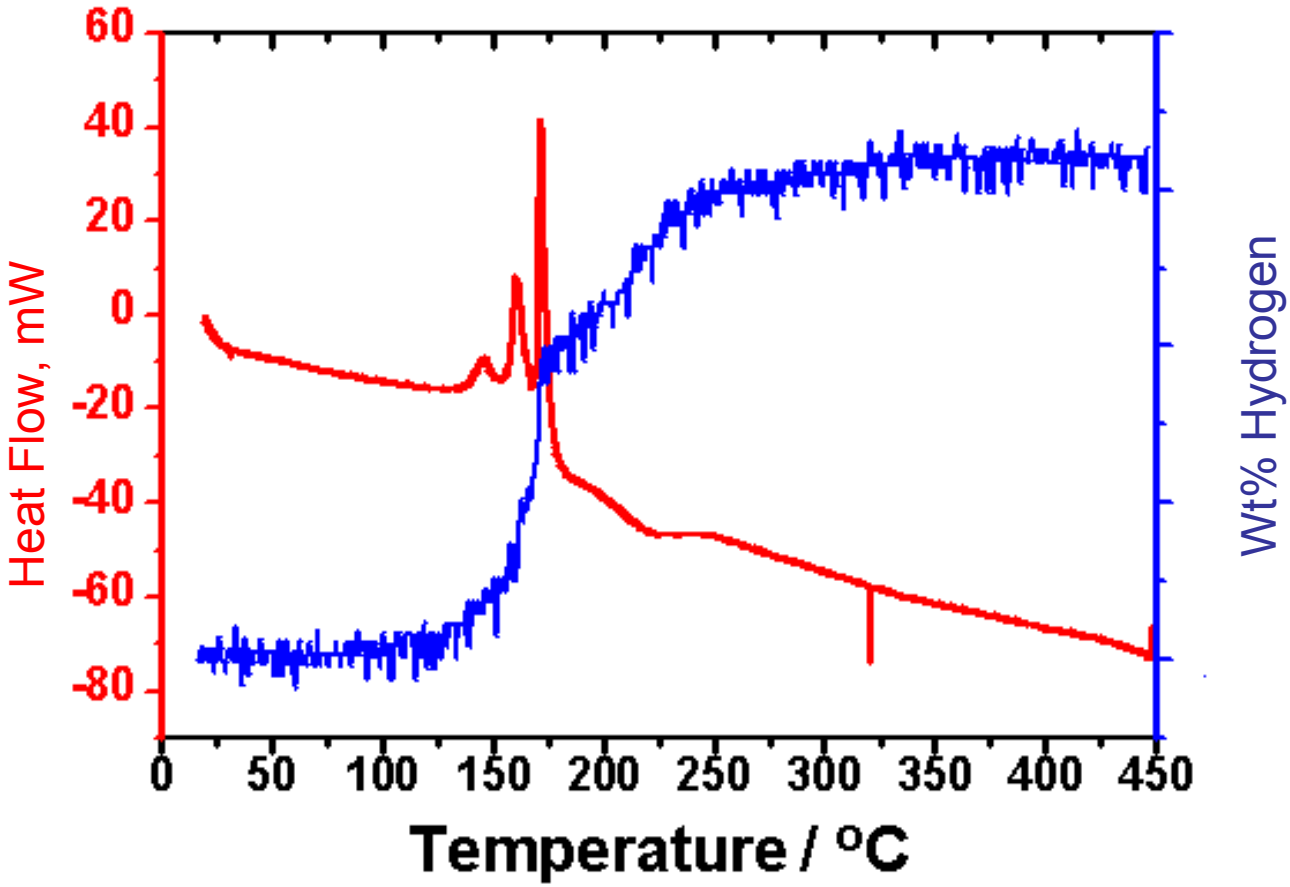
# Accomplishments

- Synthesis
  - $Mg(AlH_4)_2$
  - Other cmpds via chemical and mechanical
  - $Ti(AlH_4)_4$
- Addition of elemental Ti and other catalysts
- Ball milling as an activation method

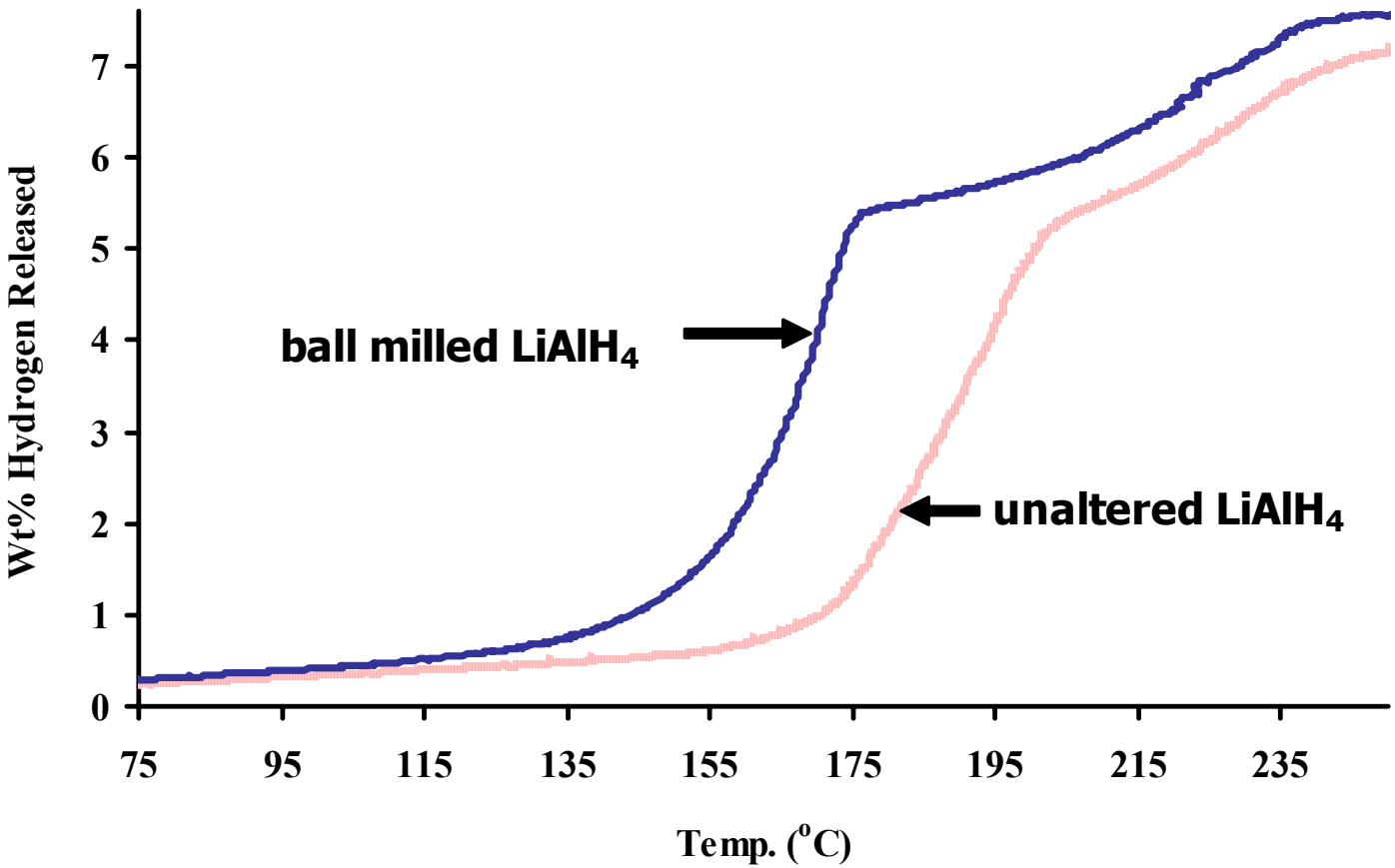
# Dehydriding of $LiAlH_4$



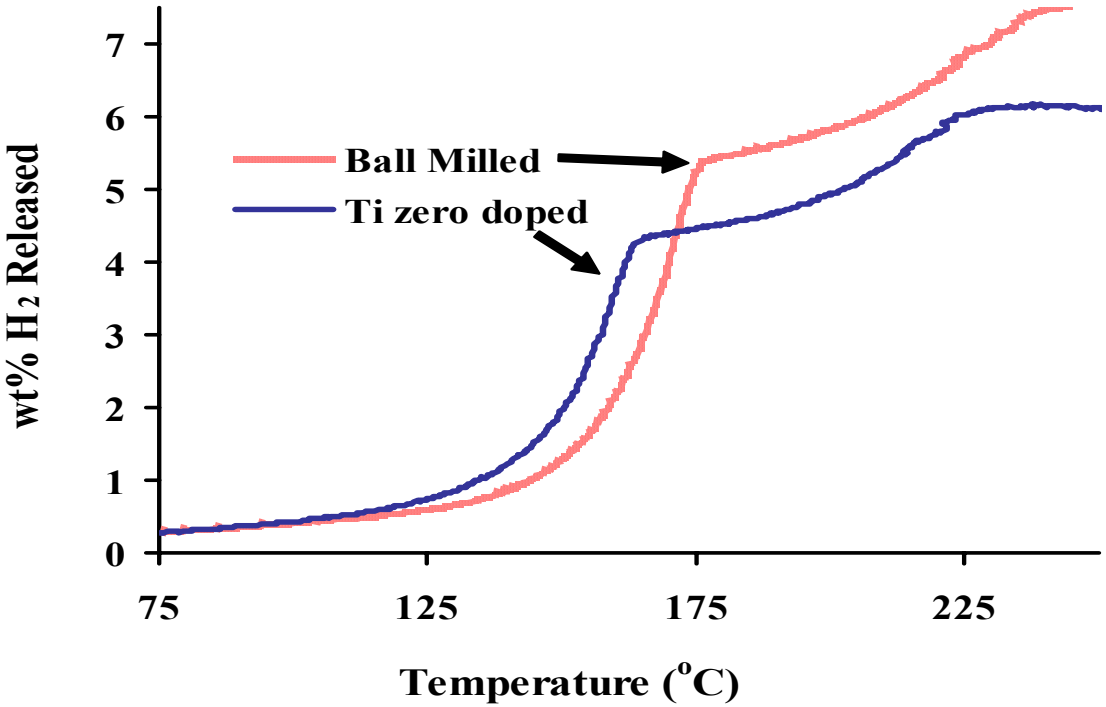
# DSC Thermogram of the Dehydriding of $LiAlH_4$



# Effect of Ball Milling $LiAlH_4$



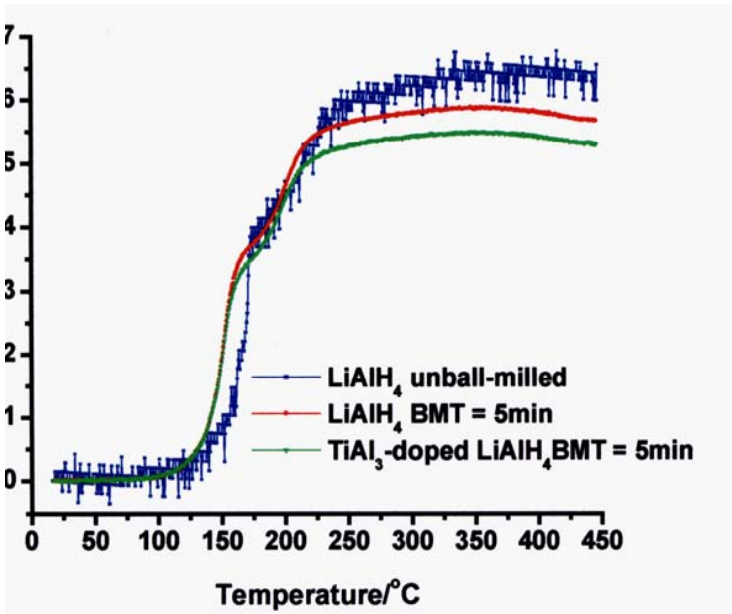
# The Addition of Elemental Ti to $LiAlH_4$

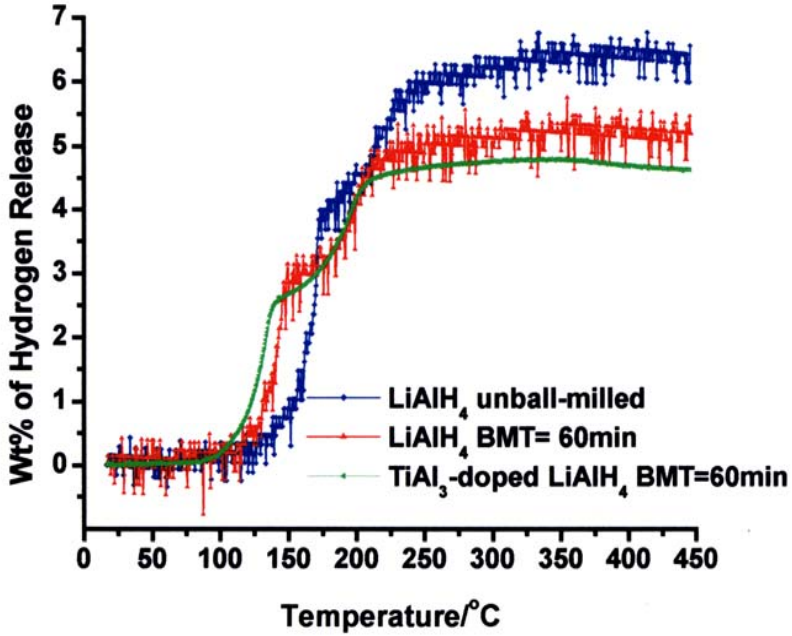


# Reversibility

- Ti catalyzed $NaAlH_4$
- Rehydrided at 120 $^oC$, 45 atm.
- Second cycle,
  - $1^{st}$ decomp step at ~ 90 $^oC$
  - $2^{nd}$ decomp at ~ 220 $^oC$
- Total hydrogen released on second cycle was 4 wt%

# Additional Dopants



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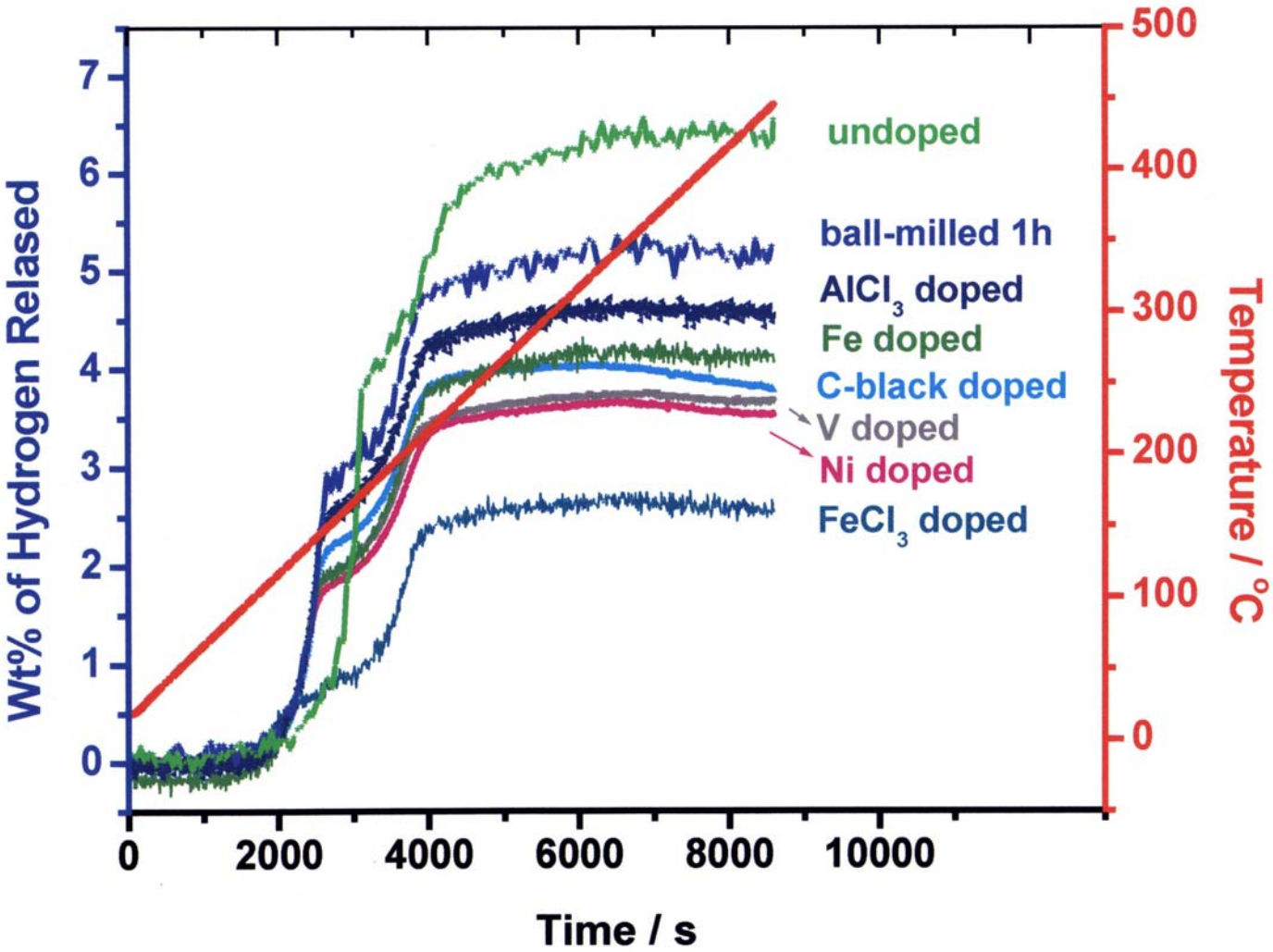

# Reviewers Concerns

# "participant has warned about unstable compounds"

**Sent: Tuesday, May 14, 2002 6:21 AM**

**After our presentation at the Hydrogen Program Review last week, you mentioned that you had had an explosion during the heating of $LiAlH_4$... Can you tell us anything more about what happened...**

**Hi Darlene,**

**Thanks for your concern. There was no accident. We were trying to do a burn rate test according to a UN test procedure...At the DOE Review there are usually 2-3 conversations going on at the same time. I'm sorry you thought we had an accident. Thanks again for your concern.**

# "….fairly broad plan."

- Narrowed scope to look at most promising materials
- Focused on experiments suggested by the research
- Limited catalyst work to using what others had already identified

# Interactions & Collaborations

- Collaboration with Karl Gross – Sandia

- D.K. Slattery, M.D.Hampton, J.K.Lomness, N.Najafi-Mohajeri, M. Franjic, "Hydrogen Storage Using Complex Hydrides", Fuel Chemistry Division Preprints, **2002**, 48(1), 277.
- M. Franjic, J. Lomness, J. Gilbert, M. Hampton, D. Slattery, "Effect of Ti Catalyst on Hydrogen Storage Properties of $LiAlH_4$", 67th Annual

  Meeting Florida Academy of Sciences, Orlando, FL, March 21–22, 2003.

- M.D. Hampton, D.K. Slattery, N. Jafafi-Mohajeri, M.Franjic, J.K. Lomness, "Complex Hydrides as Hydrogen Storage Media", Symposium P1, "Hydrogen Electrochemistry and Generating Systems", Proceedings of the 203rd Meeting of the Electrochemical Society, Paris, France, April 27 – May 2, 2003.

# Goals for Continuation Project

- Complete $LiAlH_4$ investigation
- Synthesize 5 g quantity of $Mg(AlH_4)_2$
- Investigate reversibility of borohydrides

# Conclusions

- $LiAlH_4$ exhibits an exothermic decomp.
- Ball milling $LiAlH_4$ changes dehydriding characteristics
- Catalyzing with elemental Ti was shown to decrease release temp and improve kinetics without significantly decreasing capacity
- $NaAlH_4$ catalyzed with elemental Ti was shown to be reversible

# Acknowledgements

Post docs:

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Mirna Franjic