Complex Hydrides – A New Frontier for Future Energy Applications

Mechanochemsitry, Nanostructuring and Potential for Reversibility

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Funding: BES, Materials Sciences Division

New BES-funded research effort

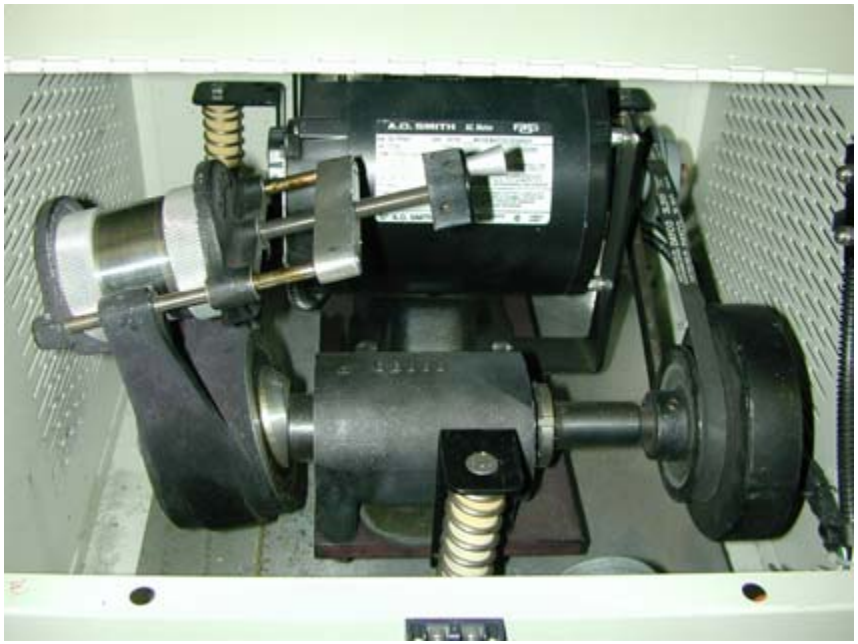
AMES LABORATORY

- Ames Laboratory:
  - Vitalij Pecharsky, Oleksandr Dolotko, Haiqiao Zhang
  - Scott Chumbley, Ozan Ugurlu
  - Marek Pruski, Jerzy Wiench
  - Victor Lin, (Cedric) Po-Wen Chung
- Virginia Commonwealth University:
  - Purusottam Jena, Sa Li

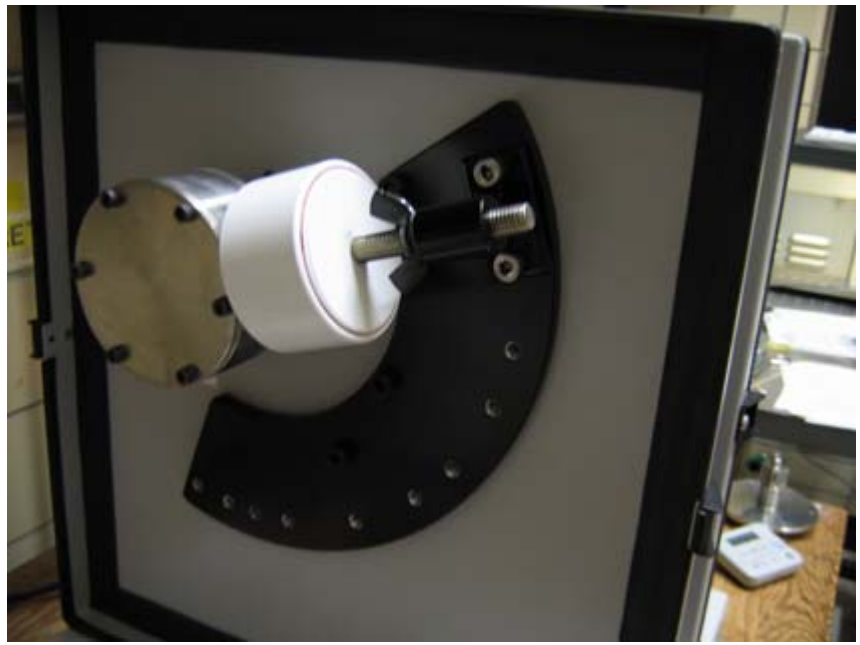
Approach

- Synthesis and processing:
  - Transformations of complex hydrides in solid state
  - Nanostructuring
    - Stochastic (mechanochemistry)
    - Controlled (micelle self assembly in non-polar organic solvents)
  - Solid state synthesis
  - High H-pressure mechanochemistry (near future)
- Characterization:
  - Diffraction and microscopy
  - Solid state NMR
  - PCI (PCT-PRO from HyEnergy LLC, near future)
- Theory and computation:
  - Super-cell band structure methodology
    - Density functional theory
    - Generalized gradient approximation
    - PAW potential
    - VASP code

Mechanochemistry

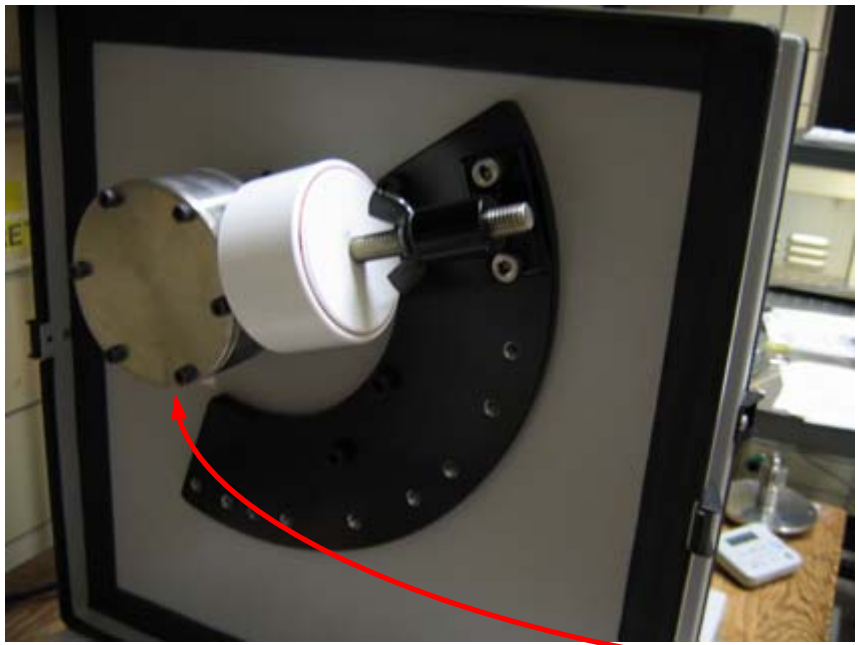


SPEX: high energy; control by balls-to-material mass ratio

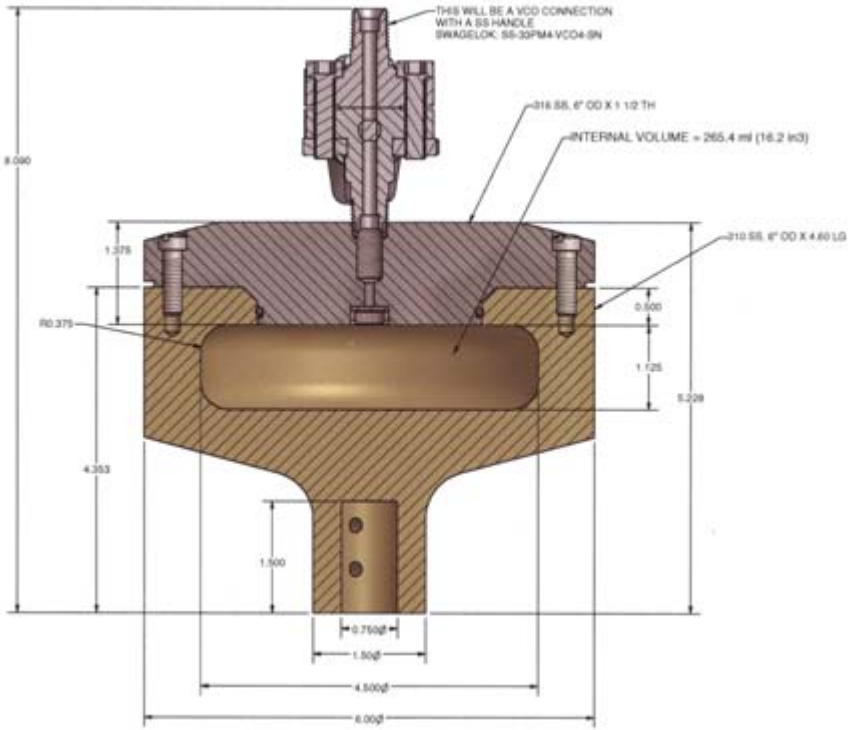


Magnetic: variable energy; control by rpm and positioning of the magnets

High H-pressure mechanochemistry



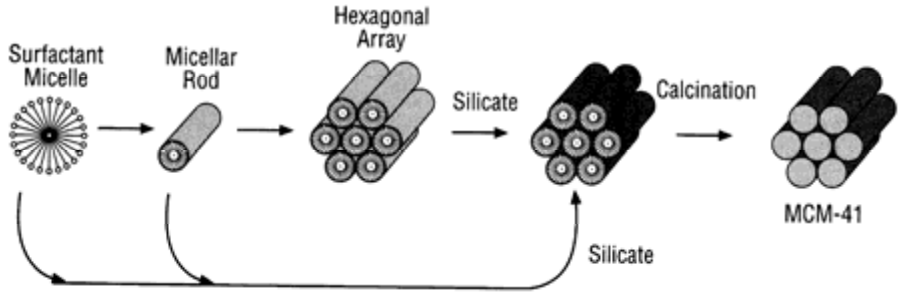
Maximum H-pressure 300 bar



Design completed
Manufacturing will be completed mid-June
Readiness review and operational approval is expected by the end of June

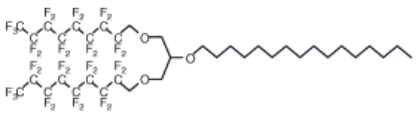
Micelle self-assembly

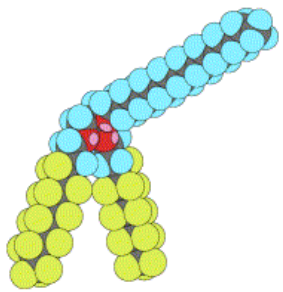
- The conventional strategy of using surfactant micelles as structure-directing templates (e.g., for metal oxide synthesis) can only work in aqueous solutions.



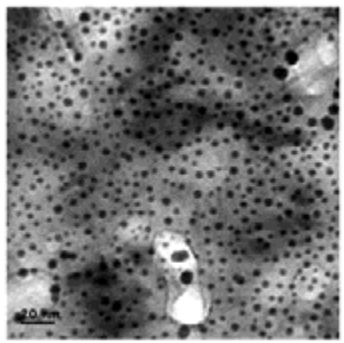
Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, **1992**, *359*, 710.

- Utilizing fluorohydrocarbon molecules that can form micelles in nonpolar organic solvents will facilitate synthesis of nanostructured metal hydride materials.





Micelle Formation in dodecane



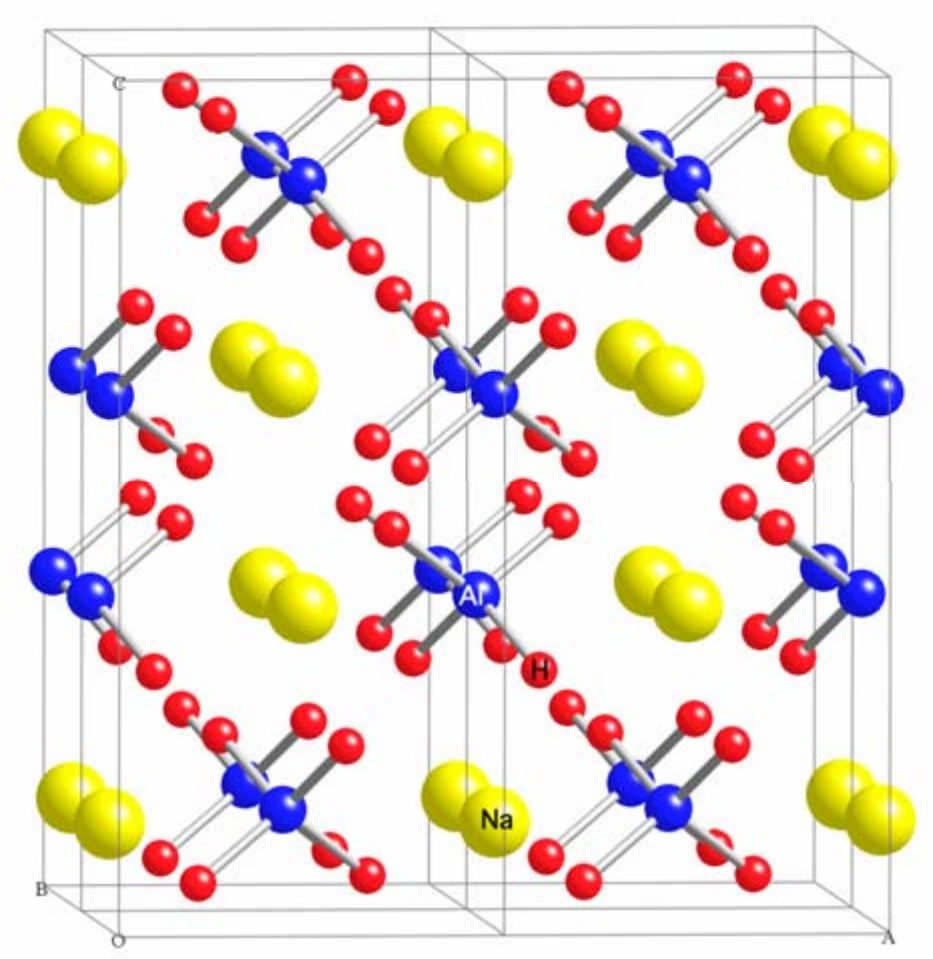
W. Huang , C. Jin , D. K. Derzon , T. A. Huber , J. A. Last , P. P. Provencio , A. S. Gopalan , M. Dugger, and D. Y. Sasaki. *J. Colloid Interface Sci.* **2004**, *272*(2), 457.

Solid state NMR

- **Instruments:**
  - Chemagnetics Infinity and Varian NMR systems operated at 9.4 T and 14.1 T
  - Triple resonance probes capable of MAS at speeds up to 3M rpm
  - Variable temperature capabilities
- **Advanced solid state methods:**
  - High resolution techniques for solids: magic angle spinning (MAS), multiple quantum (MQ) MAS, homo- and hetero-nuclear decoupling
  - Multi-resonance, multi-dimensional experiments for studying the internuclear correlations
  - Nuclei: ^{1}H, ^{7}Li, ^{11}B, ^{23}Na, and ^{27}Al
- **Arsenal used to:**
  - Identify the composition, local environment and structure of complex hydrides
  - Follow the mechanochemically and thermally induced transformations of these materials
  - Study the hydrogen dynamics and solid state hydrogenation-dehydrogenation processes

V.P. Balema, J.W. Wiench, K.W. Dennis, M. Pruski, V.K. Pecharsky, *J. Alloys Comp*. *329* (2001) 108-114
J.W. Wiench, V.P. Balema, V.K. Pecharsky, M. Pruski, *J. Solid State Chem. 177* (2004) 648-653

Super-cell methodology



$NaAlH_4$

2x2x1

96 atoms total

Why complex hydrides?

$LaNi_5H_{6.7}$ – 1.5 wt.% H_2 1960's – 1990's

Mg_2NiH_4 – 3.6 wt.% H_2 1970's – …

MgH_2 – 7.6 wt.% H_2

$NaAlH_4$ – 7.4 wt.% H_2 1997 – …

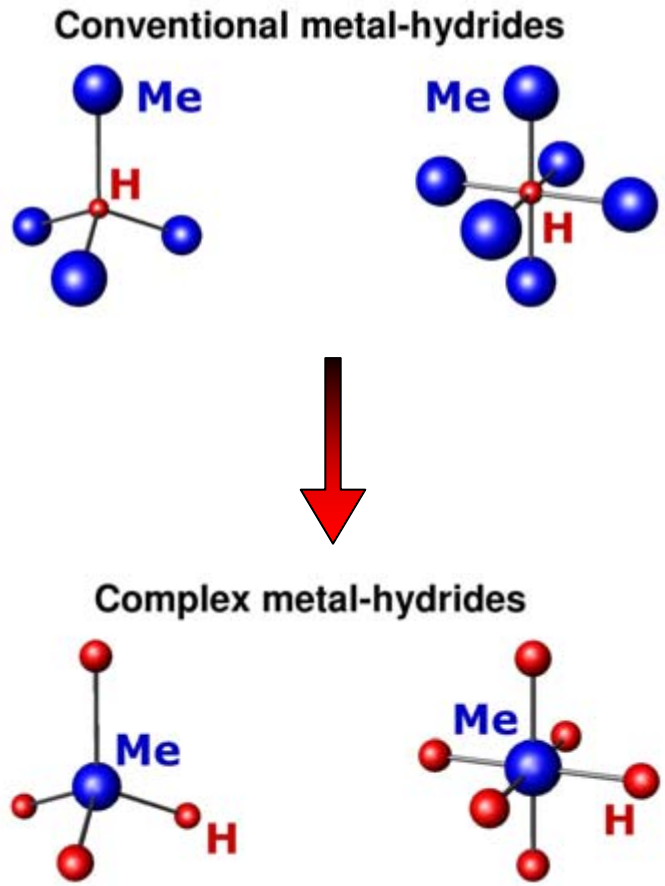
$LiNH_2$ – 8.7 wt.% H_2

$LiAlH_4$ – 10.5 wt.% H_2

$NaBH_4$ – 10.5 wt.% H_2

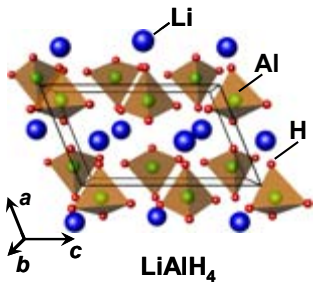
Li_3AlH_6 – 11.1 wt.% H_2

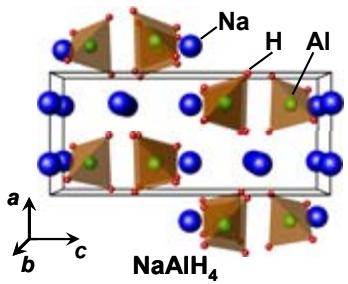
$LiBH_4$ – 18.2 wt.% H_2

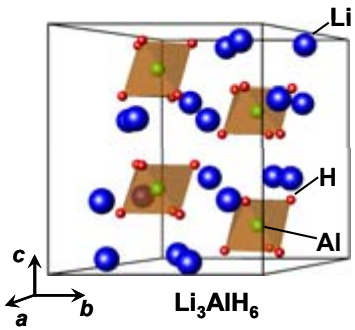


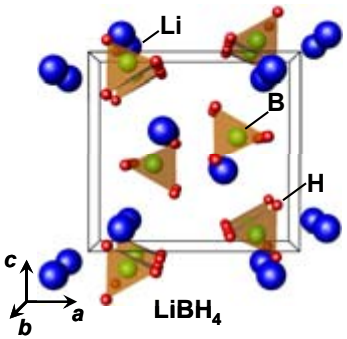
Alanates (aluminohydrides), amides & borohydrides

Fundamental issues









- Covalent M-H bonds are strong
- “Destabilization” is required
- Multiple-stage hydrogenation and dehydrogenation reactions
- Tuning thermodynamics by chemical substitutions is far from trivial
- Long-range mass transport and detrimental kinetics

Destabilization by doping

7.4 wt.% H total,
¾ or 5.6 wt.% usable

9% of H-content
Is irreversibly lost!

$$NaAlH_4 + 0.03TiCl_3 = 0.91NaAlH_4 + 0.09NaCl + 0.09Al + 0.03[Ti]^0 + 0.18H_2$$

6.2 wt.% H total,
¾ or 4.7 wt.% usable: ~16% loss of reversible capacity

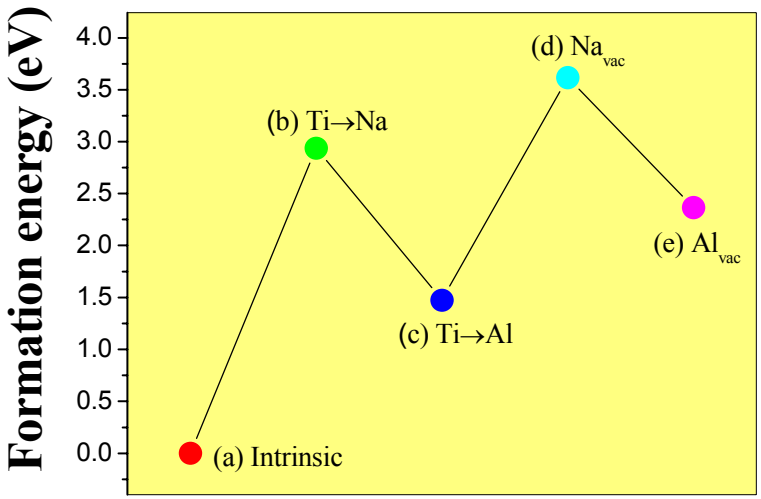
10.5 wt.% H total,
¾ or 7.9 wt.% usable

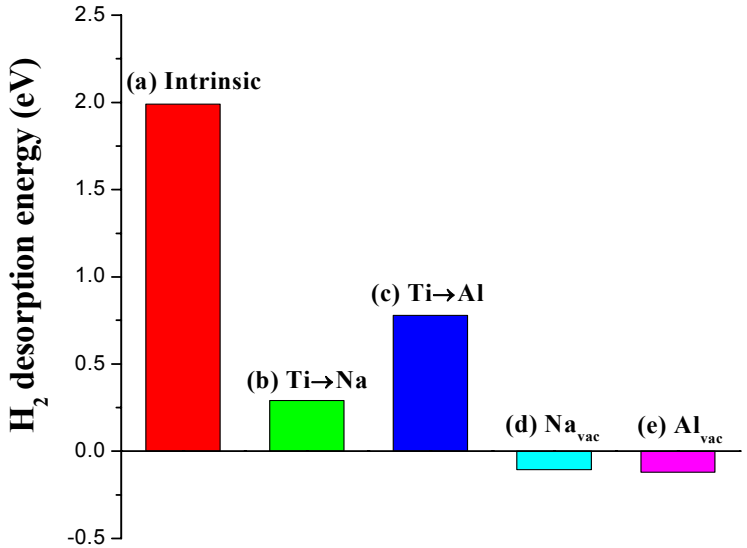
9% of H-content
Is irreversibly lost!

$$LiAlH_4 + 0.03TiCl_3 = 0.91LiAlH_4 + 0.09LiCl + 0.09Al + 0.03[Ti]^0 + 0.18H_2$$

8.5 wt.% H total,
¾ or 6.4 wt.% usable: ~19% loss of reversible capacity

Can Al-H bonds be destablized without Ti-doping?



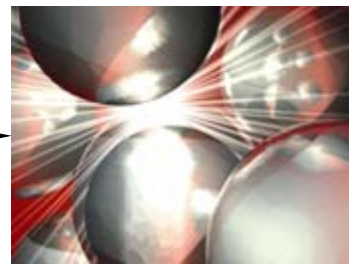


Destabilization by synergy

9.8% H_2 by weight total

$LiAlH_4$ + $LiNH_2$

Mechanochemical



processing

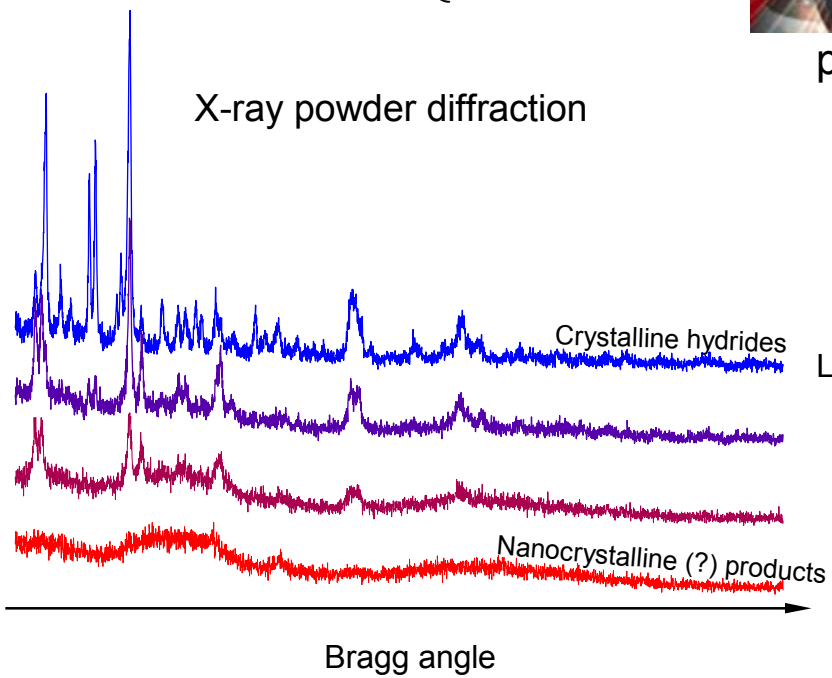
$LiAlH_4$ + $LiNH_2$

4 min

12 min

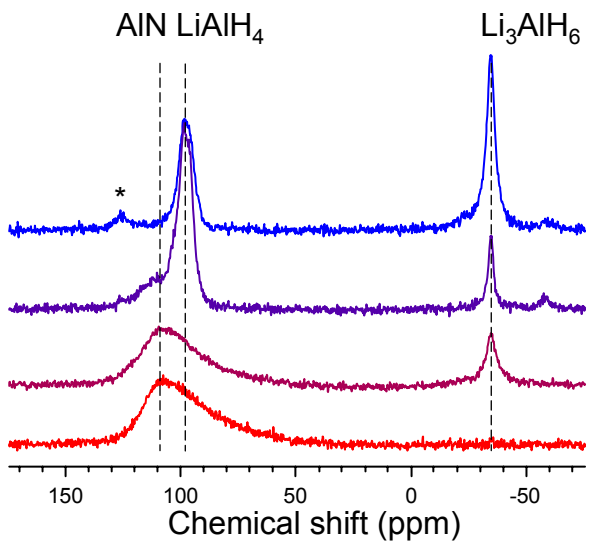
30 min

X-ray powder diffraction

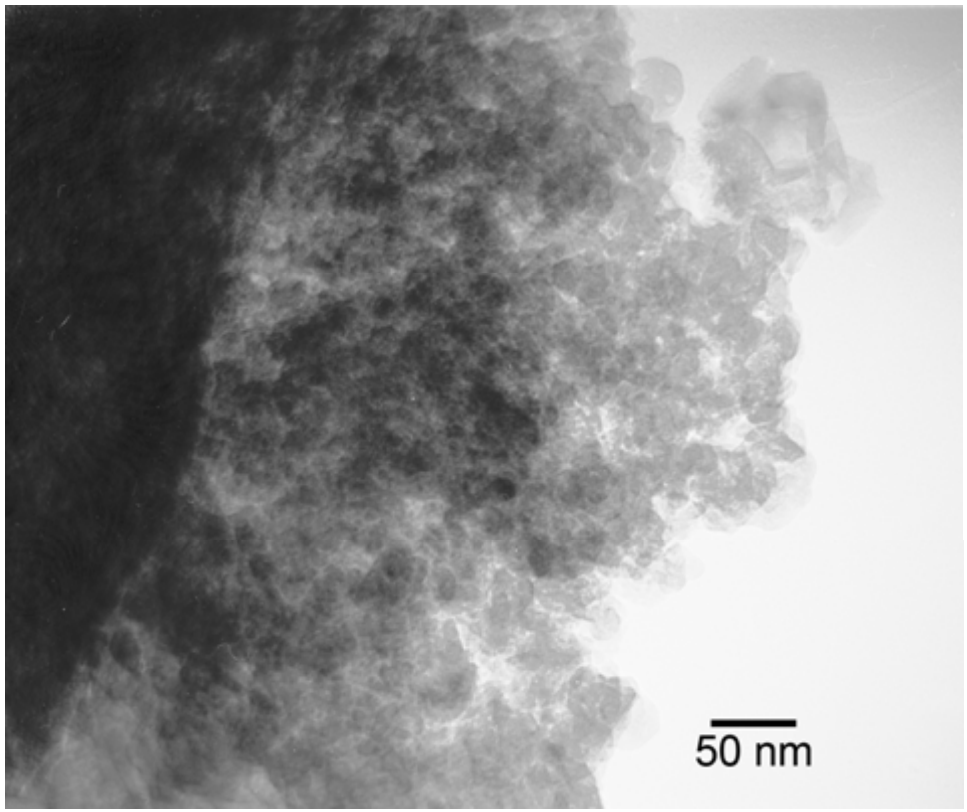


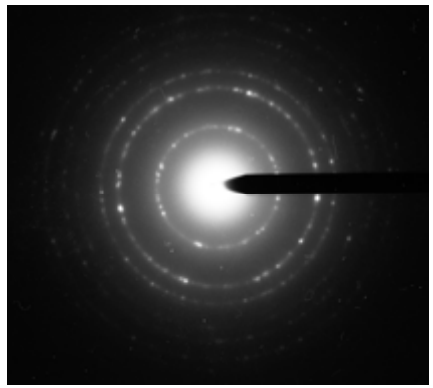
Physical mixture of $LiAlH_4$ and Li_3AlH_6

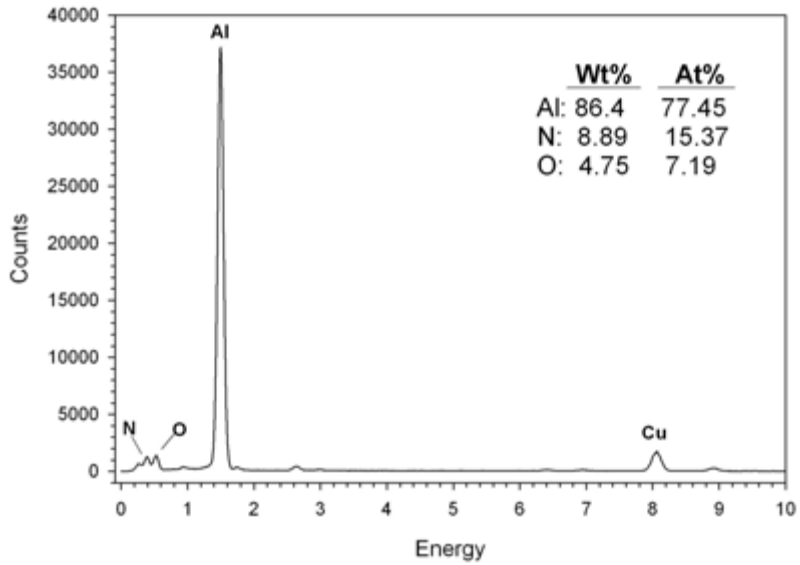
^{27}Al MAS NMR



The products are nanocrystals







Overall dehydrogenation reaction

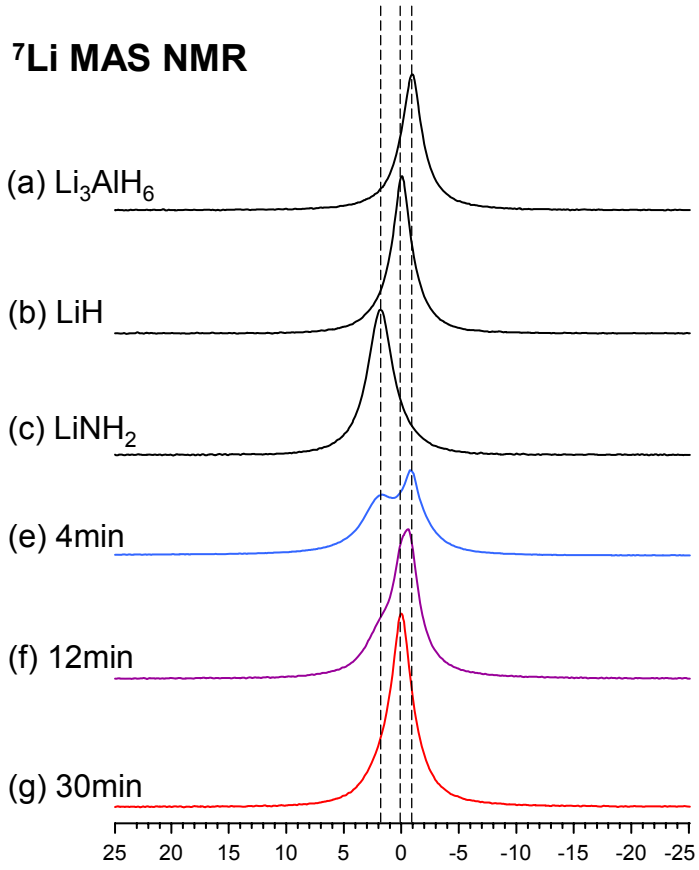
Time of the ball milling, min	$LiAlH_4$	$LiNH_2$	Li_3AlH_6	AlN	LiH	Al
0 min	+	+	–	–	–	trace
4 min	↓	↓	+	+	+	–
12 min	↓	↓	↑	↑	+	–
30 min	–	–	–	+	+	–

30 min in a SPEX

$$LiAlH_4 + LiNH_2 \longrightarrow AlN + 2LiH + \underbrace{2H_2}$$

240 min in magnetic

6.6 wt.% H_2



Only 4.3 wt.% H_2 may be obtained mechanochemically from Ti-destabilized $LiAlH_4$ [Balema et al., Chem Comm. 1665 (2000)]

Possible mechanism

$Al_{(trace)} + LiNH_2 \rightarrow AlN + LiH + {}^1/_2H_2\uparrow$ [2 wt.% H_2 (1:1)]

$LiAlH_4 + 2LiH \rightarrow Li_3AlH_6$

$Li_3AlH_6 + LiNH_2 \rightarrow AlN + 4LiH + 2H_2\uparrow$ [5.2 wt.% H_2]

$LiAlH_4 + LiNH_2 \rightarrow AlN + 2LiH + 2H_2\uparrow$ [6.6 wt.% H_2]

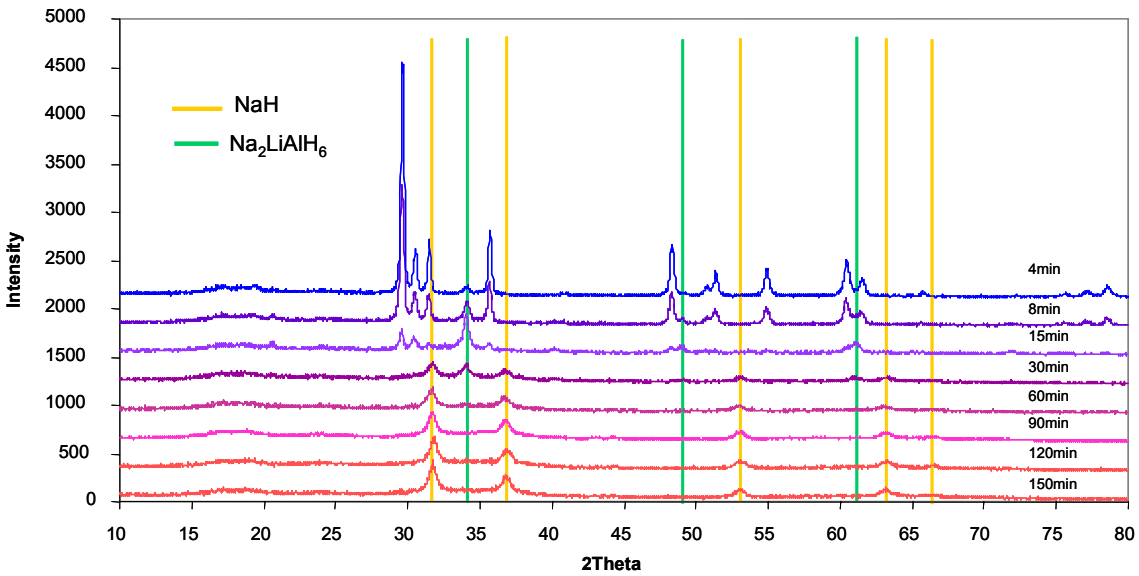
All of these reaction pathways have been verified experimentally
There is a competition between different reaction pathways
Other pathways are possible
Working with theorists in order to establish the most favorable energetics

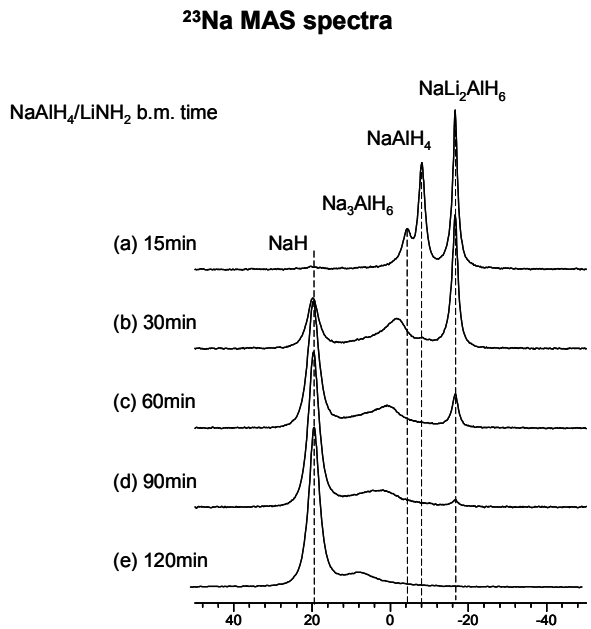
Mechanochemistry of related complex hydride systems

$$NaAlH_4 + NaNH_2 \xrightarrow{\text{SPEX, 60 min}} AlN + 2NaH + 2H_2\uparrow \quad [4.3\ wt.\%\ H_2]$$

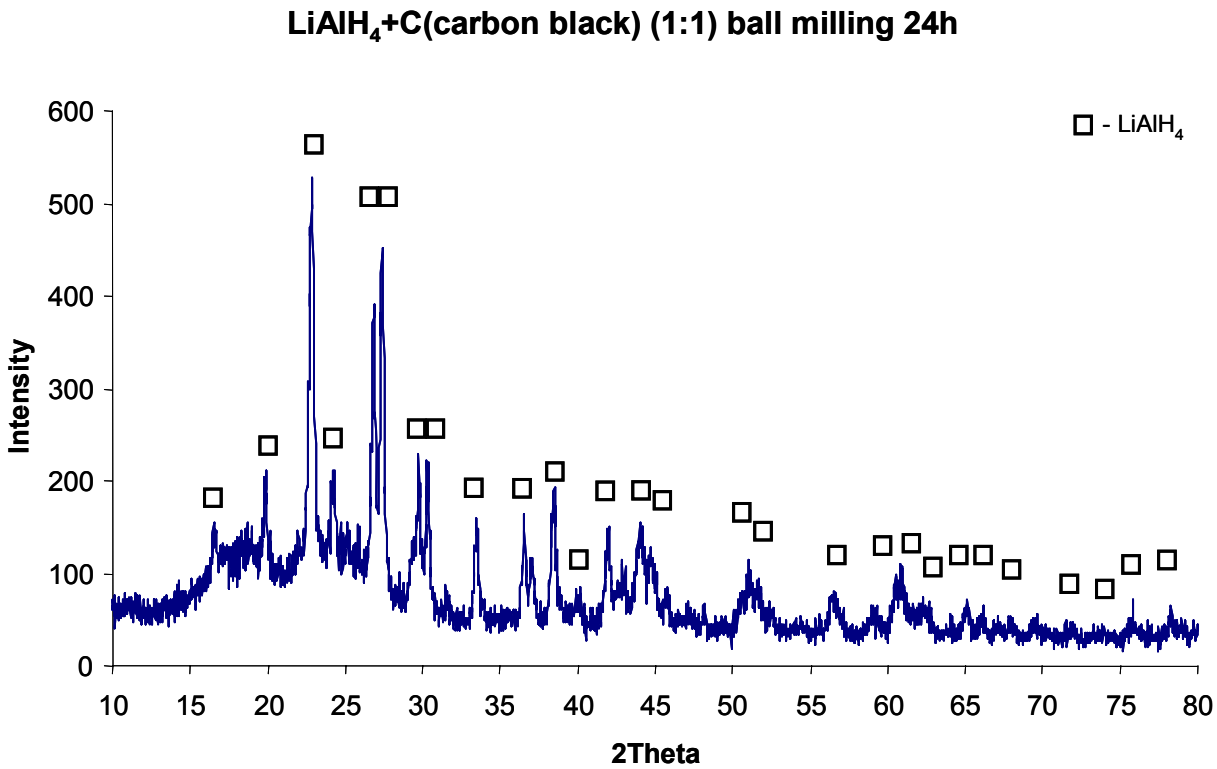
$$LiAlH_4 + NaNH_2 \xrightarrow{\text{SPEX, 90 min}} AlN + NaH + LiH + 2H_2\uparrow \quad [5.2\ wt.\%\ H_2]$$

$$NaAlH_4 + LiNH_2 \xrightarrow{\text{SPEX, 120 min}} AlN + NaH + LiH + 2H_2\uparrow \quad [5.2\ wt.\%\ H_2]$$





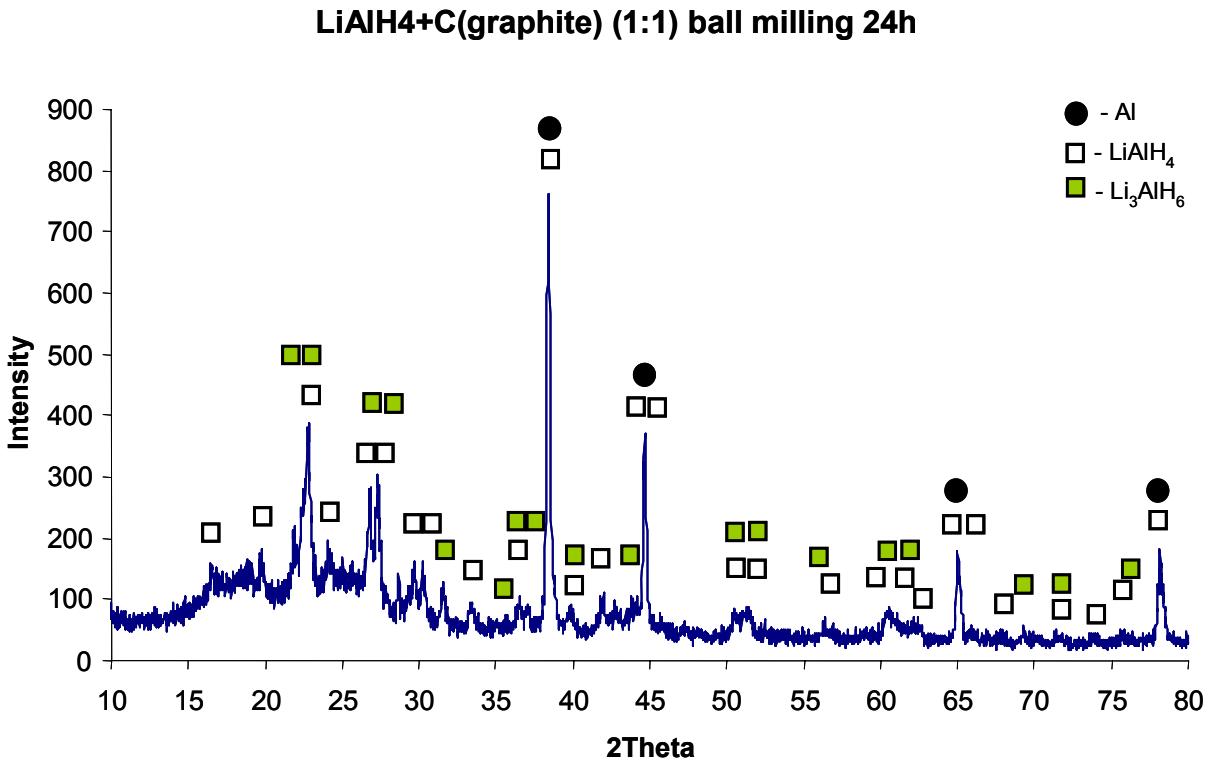
Mechanochemsirty of alanate-carbon systems



$LiAlH_4 \xrightarrow[B.M.24h]{C(carbon\ black)}$ *No reaction observed*

Covalent-only C-C bonds

Mechanochemisrty of alanate-carbon systems



$$3LiAlH_4 \xrightarrow[B.M.24h]{C(graphite)} Li_3AlH_6 + 2Al + 3H_2\uparrow \ (\textit{incomplete})$$

Covalent plus π C-C bonds

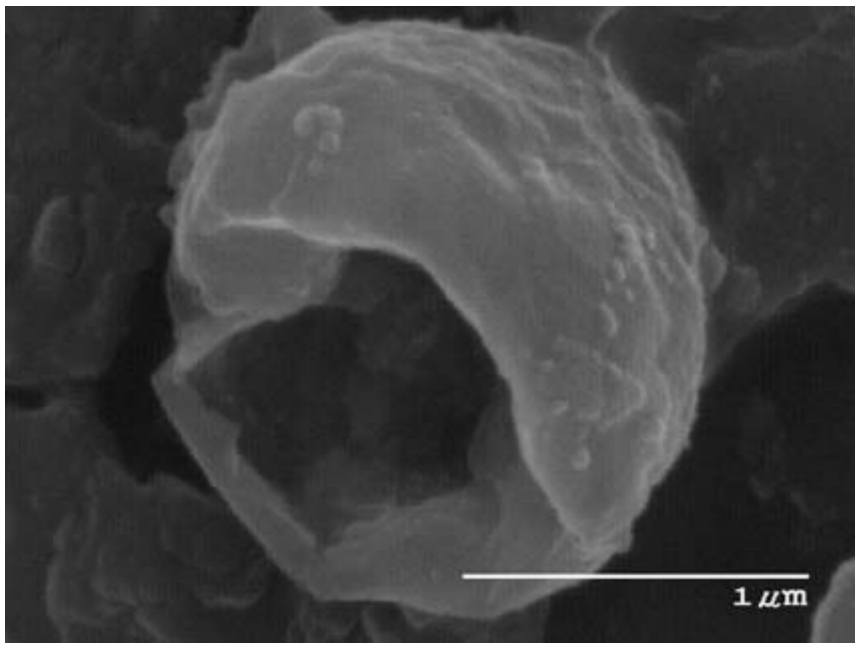
Working with theorists to understand the role of C-C bonding in the activity of carbon

Mechanochemical advantage

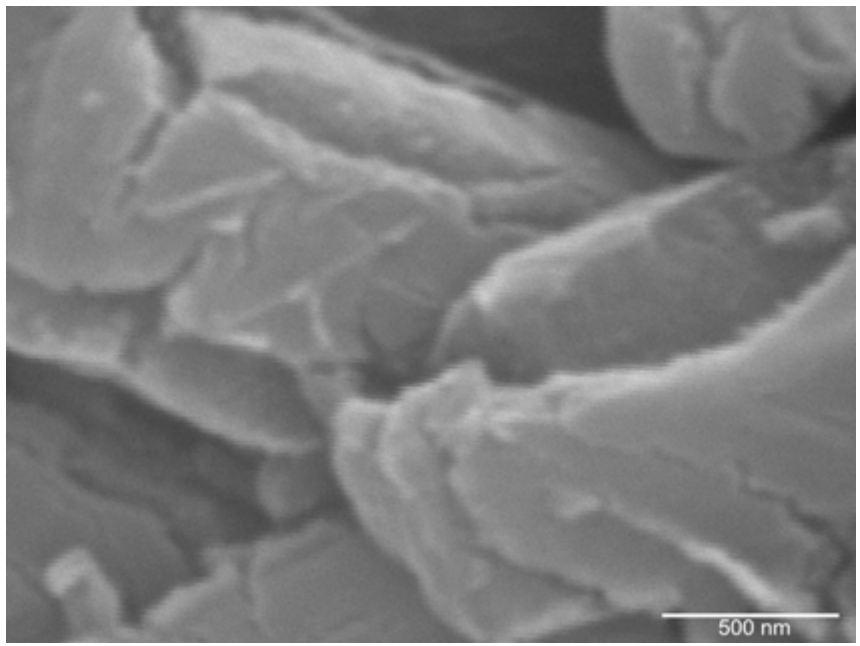
- Doping (e.g., with $TiHal_3$) not needed
- Synergy between $LiAlH_4$ and $LiNH_2$
- Related systems exhibit similar effects
- Nearly 33% more hydrogen released quickly and in a “single” step compared to $TiCl_3$-doped $LiAlH_4$
- No heating, easy control of hydrogen release by controlling mechanical energy
- Hydrogen release/uptake is fundamentally reversible
- Nanocrystallinity = short diffusion paths
- Mechanochemically promoted rehydrogenation offers a possibility to maintain nanocrystallinity of a fully hydrided material

Controlled nanostructuring

- Initial difficulties in synthesis of the needed fluorohydrocarbon molecules
- Demonstrated effect of fluorohydrocarbon molecules as structure-directing templates



Fluorohydrocarbon-templated



Without the fluorohydrocarbon template

Future work

- In concert with theoretical predictions, explore mechanochemistry of novel mixed complex hydride systems
- In collaboration with theoretical and computation effort establish reaction mechanisms
- Thermodynamic and kinetic studies using (PCT PRO delivery is scheduled at the end of May, safety and readiness review is scheduled at the end of June)
- High H-pressure mechanochemical processing to establish reversibility of the most interesting systems