Sandia National Laboratories

HyMARC Hydrogen Materials Advanced Research Consortium

H2FC Hydrogen and Fuel Cells Program

SAND2017-4493C

Tailoring Reaction Enthalpies and Activation Energies in Complex Metal Hydrides Doped with Reactive Metal Ions

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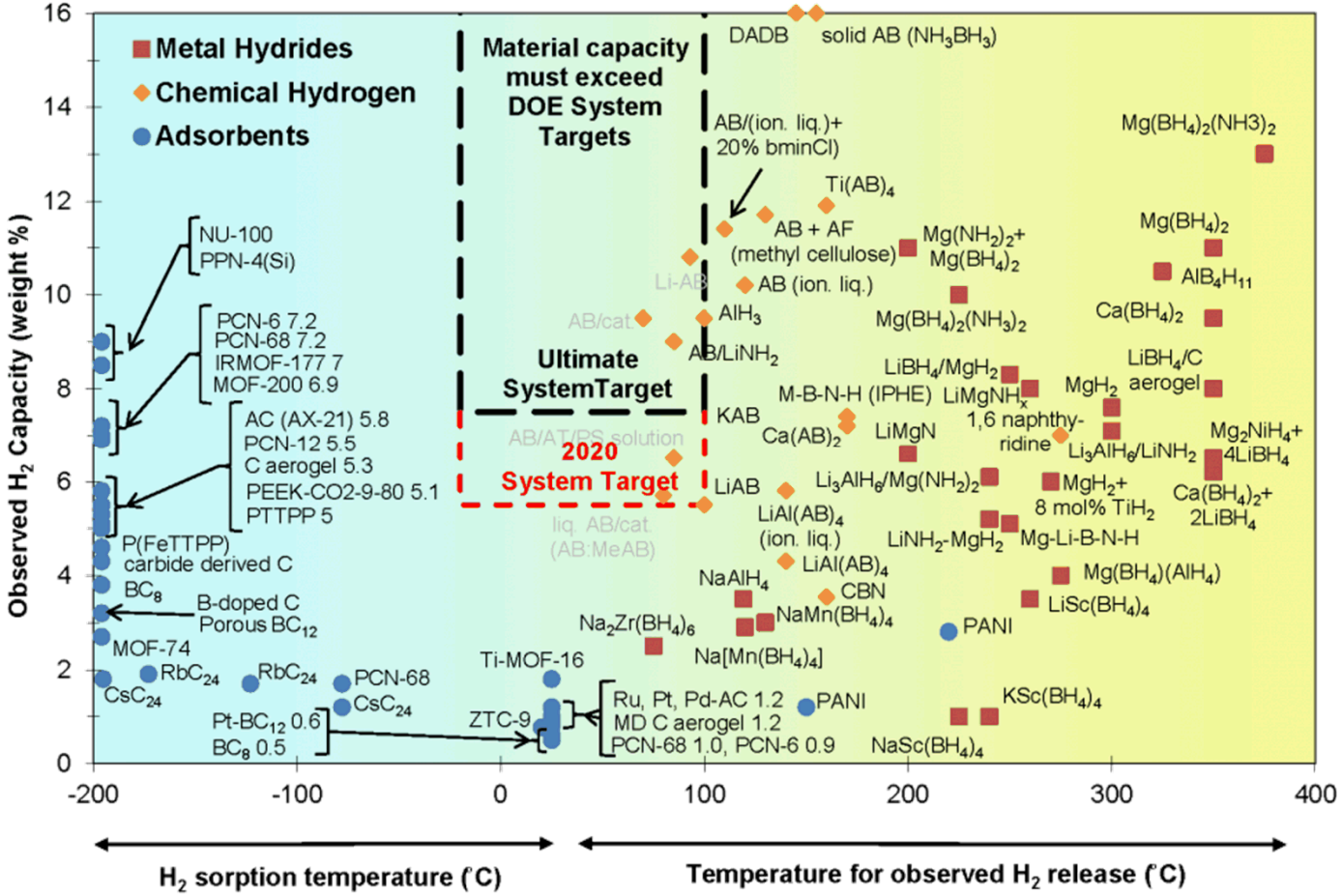
Solid-state hydrogen storage

Solid-state hydrogen storage is one of the critical enabling technologies for creating hydrogen-fueled transportation systems that can reduce oil dependency and mitigate the long-term effects of fossil fuels on climate change.



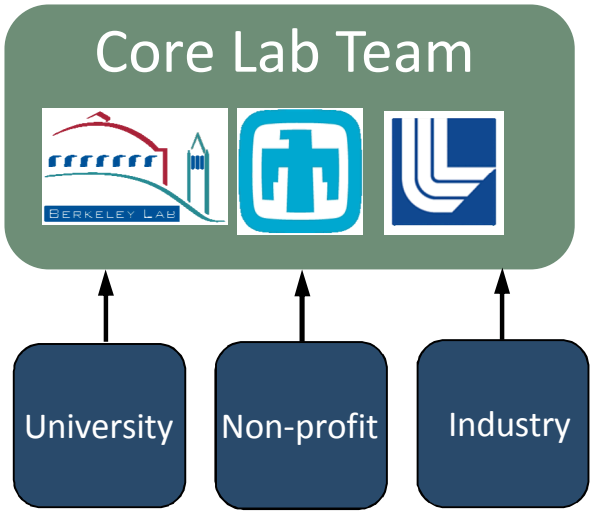
- DOE 2020 Targets:
  - 5.5 wt% H_2
  - 40 g H_2 / L system
  - 85° C max delivery temp. (ΔH≈20-30 kJ/mol H_2)
  - Reversible (1500 cycles)
  - 1.5 kg H_2/min fill rate

DOE EERE FCTO

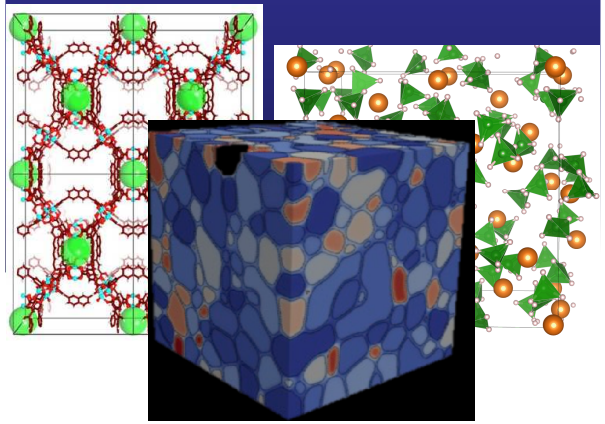
HyMARC: Hydrogen Storage Materials Research Consortium

HyMARC is a DOE-funded consortium established to provide foundational understanding of phenomena governing thermodynamics and kinetics limiting the development of solid-state hydrogen storage materials

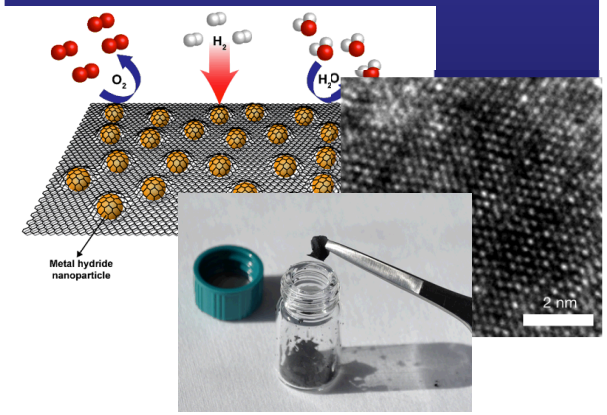
- **Computational models and databases** for high-throughput materials screening
- **New characterization tools and methods** (surface, bulk, soft X-ray, synchrotron)
- **Tailorable synthetic platforms** for probing nanoscale phenomena



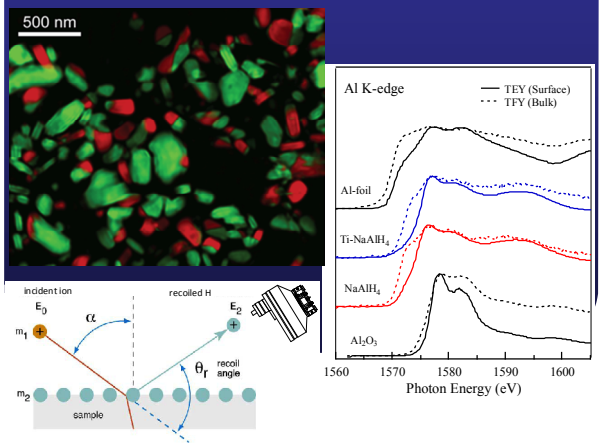
Theory, simulation, & data



Controlled synthesis



In situ characterization

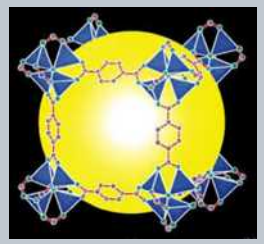


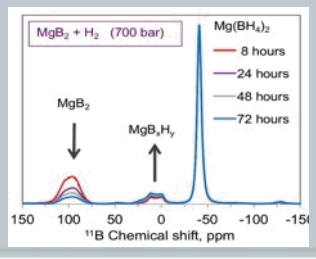
Approach: Mitigate problematic physical phenomena

Energetics

Sorbents: Explore the effect of open coordination sites, polarizable groups, flexibility, gate-opening phenomena, and morphology

Metal hydrides: Control reaction pathways and explore destabilization and doping to tune ΔH and ΔS

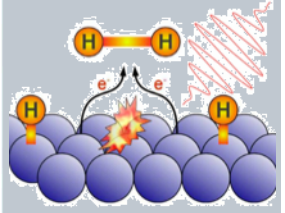


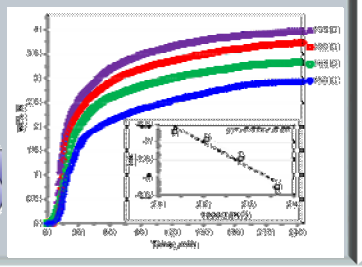


Kinetics

Explore whether surface modifications and nanostructuring can optimize the and kinetics of hydrogen storage reactions

Identify the mechanisms by which catalysts accelerate hydrogenation/dehydrogenation reaction rates

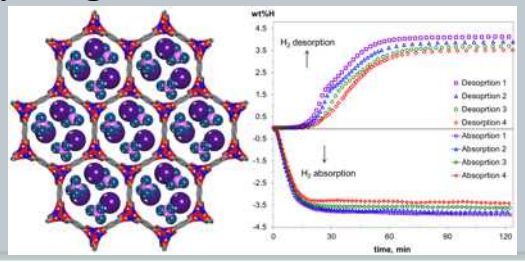




Reversibility

Explore nanostructuring and amorphization as strategies to improve the reversibility and cycle-life in metal hydrides

Test the cycle-life stability of MOFs, porous polymers, and carbons under high-pressure hydrogen



⇒ ***Sorbents:*** ***Develop Quantum Monte Carlo (QMC) and Grand Canonical Monte Carlo (GCMC) tools to identify design rules for materials with H_2-sorbent binding energies of 15-20 kJ mol^{-1} H_2***

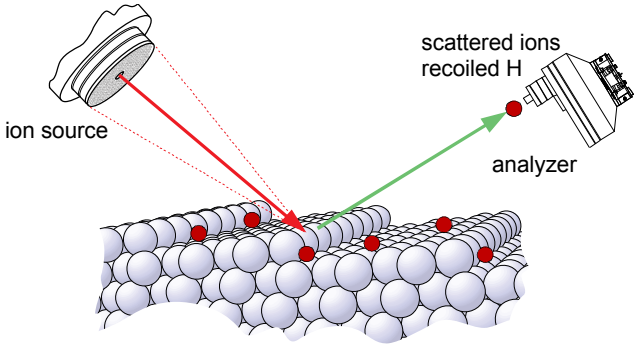
⇒ ***Metal hydrides:*** ***Evaluate doping, amorphization, surface modification and nanostructuring as strategies to improve the kinetics and thermodynamics of complex metal hydrides to achieve $\Delta H \leq 27$ kJ mol^{-1} H_2 and $\Delta E_a \leq 60$ kJ mol^{-1} H_2***

Employ suite of complementary diagnostics to probe phenomena at relevant length-scales

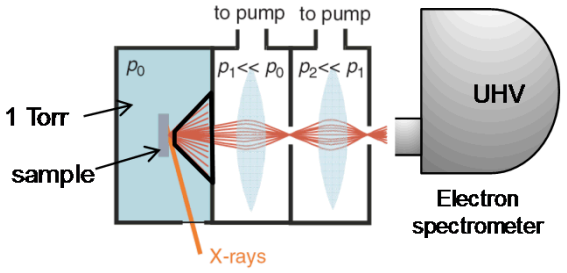
Motivation:

- Surfaces are believed to play an important role in hydrogen storage reaction; exact role remains unclear

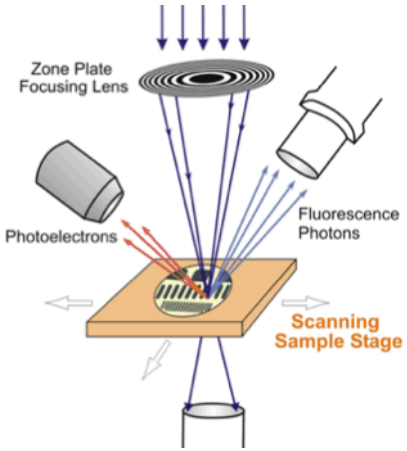
Technical Approach: *In-situ* techniques enable us to probe the surface chemistry for H_2 storage materials



Low energy ion scattering (LEIS):
Determine surface composition, H surface conc.
(First monolayer only, <1 nm)



Ambient pressure XPS:
Characterize O, Na, Al, and Ti binding
(Surface and near sub-surface, <10 nm)



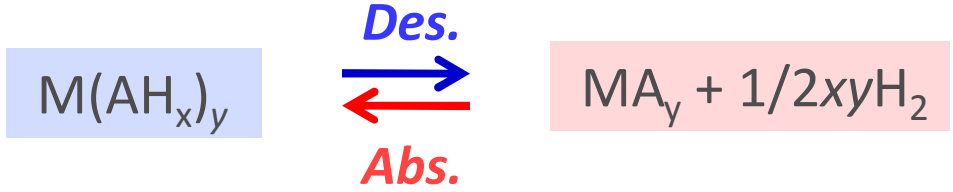
Scanning trans. x-ray microscopy (STXM):
Distribution of Ti within particles
(Bulk)

What we hope to learn:

- What is the exact surface composition of H_2 storage materials
- How do surfaces respond to temperature and H_2 environments
- What is the spatial distribution of species of interest
- *Can surfaces be modified to improve H_2 storage properties*

James White (AP-XPS, STXM)
Farid El Gabaly (AP-XPS, STXM)
Robert Kolasinski (LEIS)
Lennie Klebanoff (XAS)
Jonathan Lee (STXM)
Alexander Baker (STXM)
Brandon Wood (theory)
Yi-Sheng Liu (XAS and XES)
Jinghua Guo (XAS and XES)
David Prendergast (theory)

Reversibility in bulk complex metal hydrides



$2NaAlH_4 \xrightleftharpoons{TiCl_3} 2NaH + 2Al + 3H_2$

$Mg(NH_2)_2 + 2LiH \rightleftharpoons Li_2Mg(NH)_2 + 2H_2$

$2LiBH_4 + MgH_2 \rightleftharpoons 2LiH + MgB_2 + 4H_2$

$Mg(BH_4)_2 \rightleftharpoons MgB_2 + 4H_2$

Bogdanovic *et al. J. Alloys Comp.* **1997**, *253-254*, 1
Bogdanovic, Schwickardi, *U.S. Patent* 6,106,801, **2000**

Cheng *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 5828
Luo *et al. J. Alloys Comp.* **2004**, *381*, 284

Pinkerton *et al. J. Phys. Chem. C* **2007**, *111*, 12881
Vajo *et al. J. Phys. Chem.* C. **2005**, *109*, 3719

Soloveichik *et al. Int. J. Hydrogen Energy*, **2009**, *34*, 916
Severa *et al. Chem. Commun.* **2010**, *46*, 421

- **Gibbs energy minimization calculations** to determine the thermodynamically favored reaction pathways
- Synthesis of metal hydrides in various forms and formats (Graphene oxide supported nanoparticles, hydrides@MOFs, thin films)
- Determine the **effect of impurity phases**, e.g. $[B_{12}H_{12}]^{2-}$ and B_2H_6 in borohydrides
- Explore effects of **nanostructuring** and **additives** on reversibility ($\Delta H°$ and $\Delta S°$)

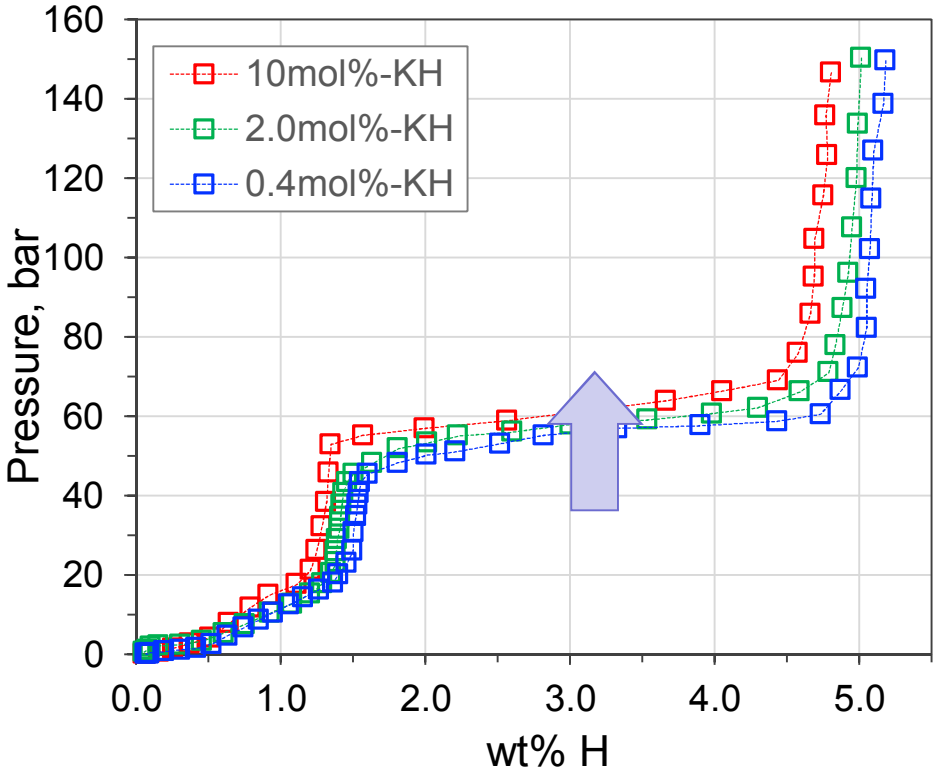
⇒ *Our goal is to understand the critical aspects of enabling reversibility in complex metal by improving thermodynamics and kinetics of solid-state hydrogen storage reactions*

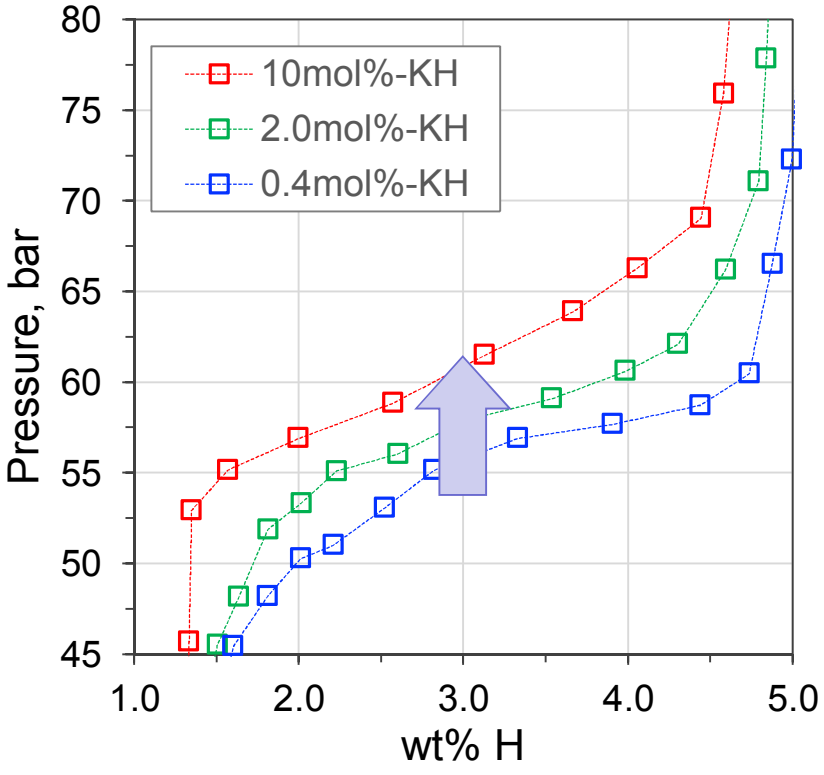
KH doping increases the equilibrium vapor pressure of Li-Mg-N-H

$$2LiNH_2 + MgH_2\ (+0.03KH) \Leftrightarrow Li_2MgN_2H_2 + 2H_2$$

Cheng *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 5828

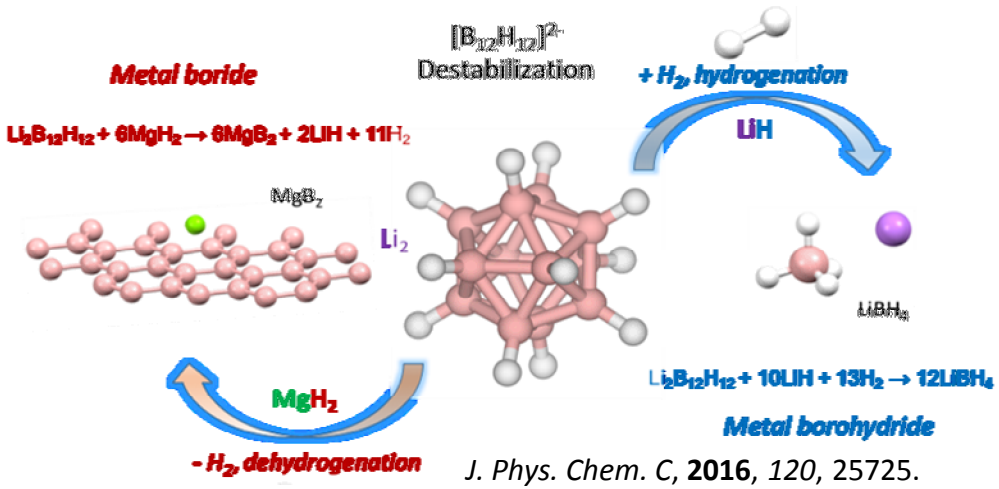
PCT isotherms collected at 237 °C





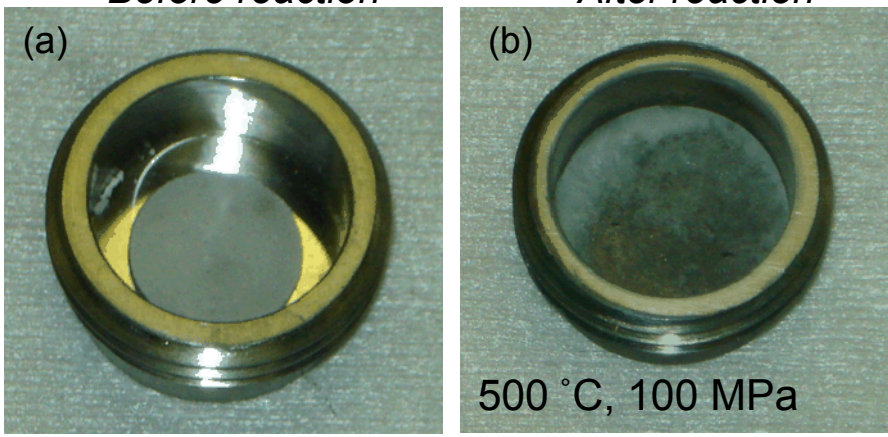
⇒ ***Equilibrium plateau pressure increases with KH-content, suggesting changes in the thermodynamics of hydrogen desorption from Li-Mg-N-H upon KH doping***

Destabilization of stable $[B_{12}H_{12}]^{2-}$ species

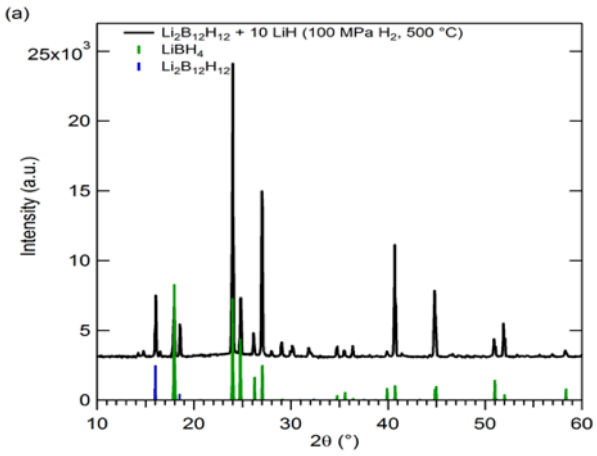


J. Phys. Chem. C, **2016**, *120*, 25725.

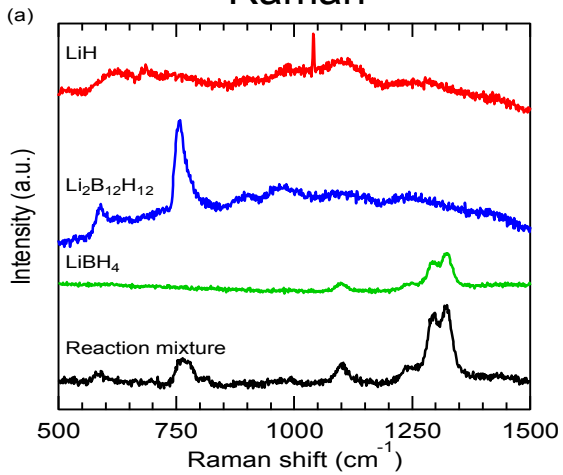
$Li_2B_{12}H_{12}$ + 10LiH



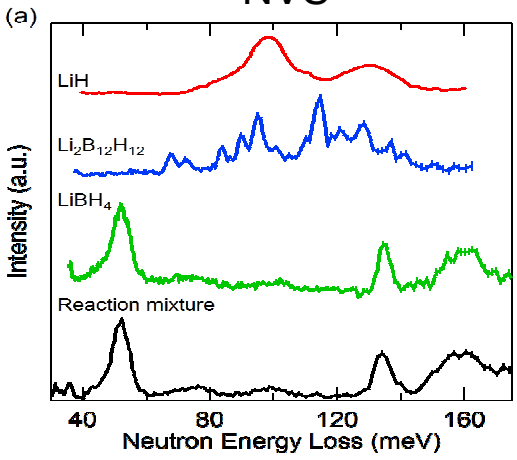
XRD



Raman



NVS

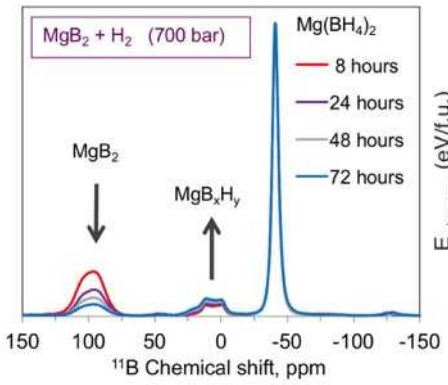


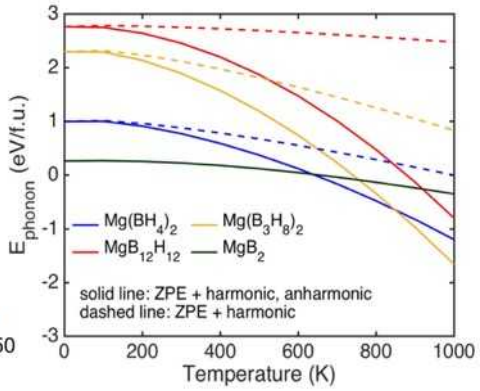
⇒ ***We demonstrated that metal $B_{12}H_{12}$-species can be destabilized through hydrogenation under high-pressure H2 to form borohydrides or through dehydrogenation to form metal borides***

Reversibility of $Mg(BH_4)_2$ under high-pressure H_2

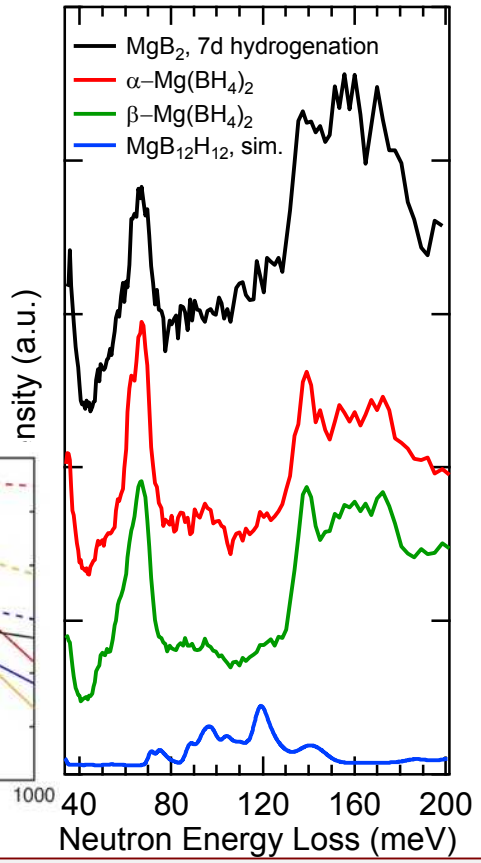
Sandia National Laboratories · Lawrence Livermore National Laboratory · Berkeley Lab · Pacific Northwest National Laboratory · NIST · NREL National Renewable Energy Laboratory · UMSL · University of Hawai'i Mānoa · LiOx · HRL Laboratories

1. $MgB_2 + H_2 \rightarrow MgB_{12}H_{12} + MgH_2 \rightarrow Mg(BH_4)_2$
2. $MgB_2 + H_2 \rightarrow Mg(BH_4)_2 \rightarrow MgB_{12}H_{12} + MgH_2$

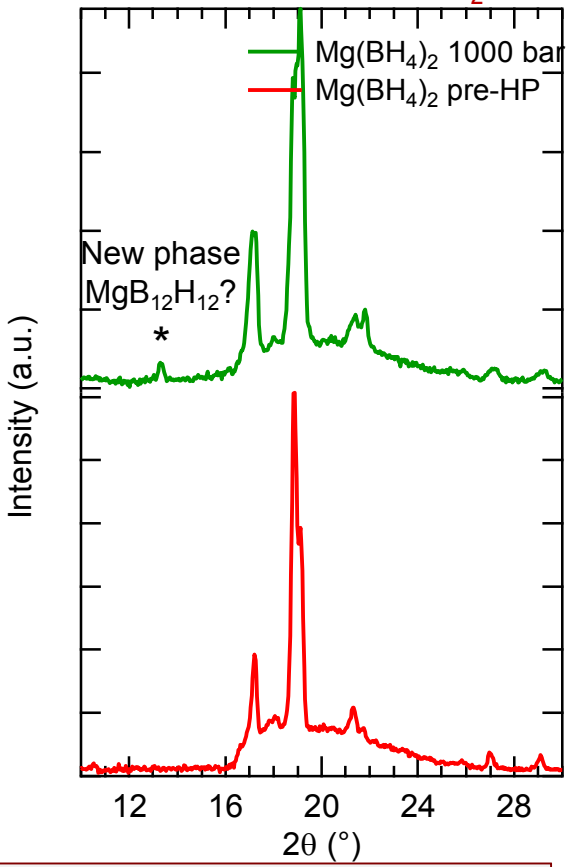




Neutron vibrational spectroscopy (NIST)



XRD of $Mg(BH_4)_2$ at 400 °C and 1000 bar H_2



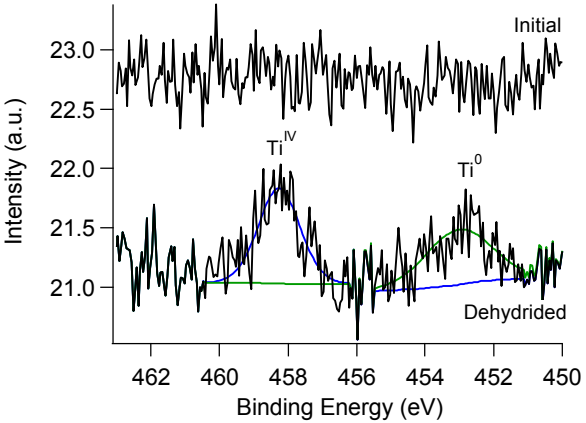
⇒ ***High-pressure hydrogenation of MgB_2 leads to increasing amounts of intermediates with time***

⇒ ***Under similar conditions pure $Mg(BH_4)_2$ generates a small amount of a new crystalline phase, possibly $MgB_{12}H_{12}$ or some other intermediate species***

In situ spectroscopy of Ti-doped $NaAlH_4$ model system with AP-XPS

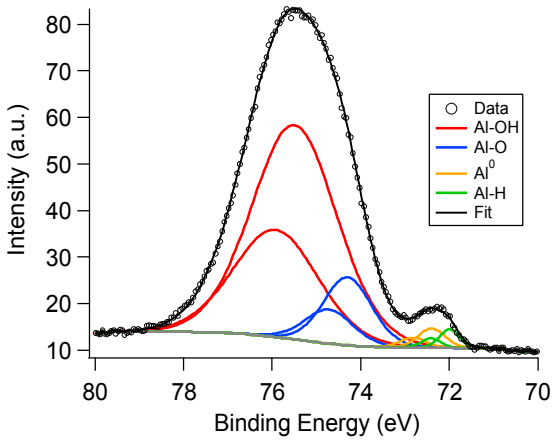
Why $TiCl_3$-doped $NaAlH_4$?

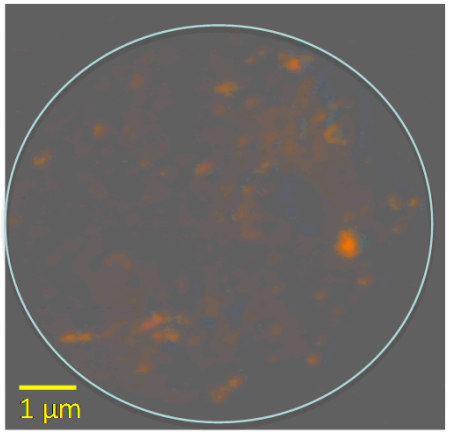
- Realistic material: extensively milled, cycles well
- Well-studied: abundance of experimental data in literature to validate new characterization techniques
- Established models: lots of theory work has been done to which results can be correlated
- Still new things to learn:
  - No Ti on the surface (Ti, Ti_2O_3, or $TiCl_x$) during H_2 desorption
  - Zipper mechanism for dehydrogenation, involving subsurface Ti, is most consistent with our experimental observations



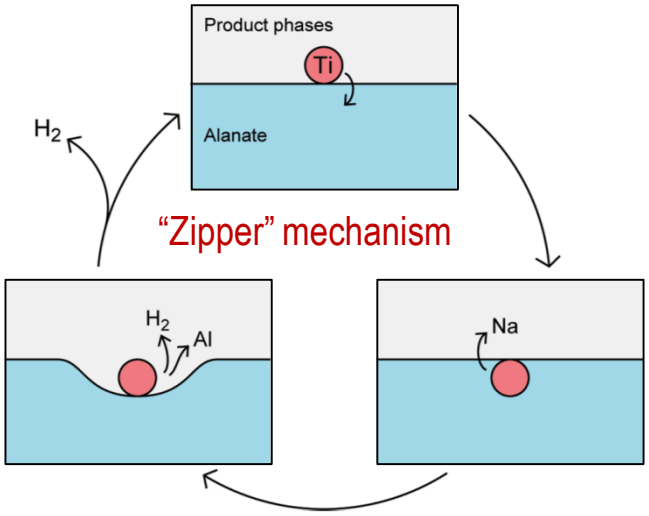
No evidence of surface Ti before or during desorption using XPS, LEIS, or Auger electron spectroscopy.

Four Al species detected by AP-XPS during dehydrogenation





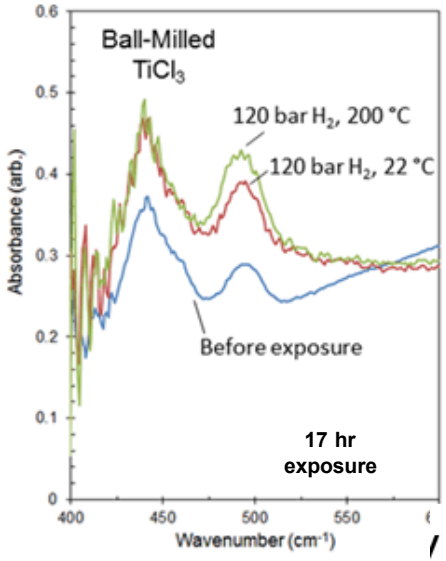
STXM of doped particle
Ti^0 in orange



Chem. Rev. **2012**, *112*, 2164-2178

Found that pure TiF_3, $TiCl_3$ are inactive towards H_2 and don't promote H_2 dissociation

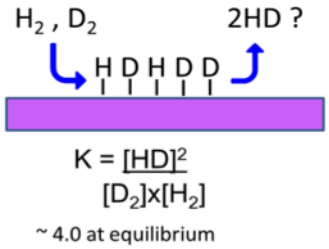
FTIR study of Ti-Cl bonding



Bulk or ball-milled $TiCl_3$ does not react with H_2.

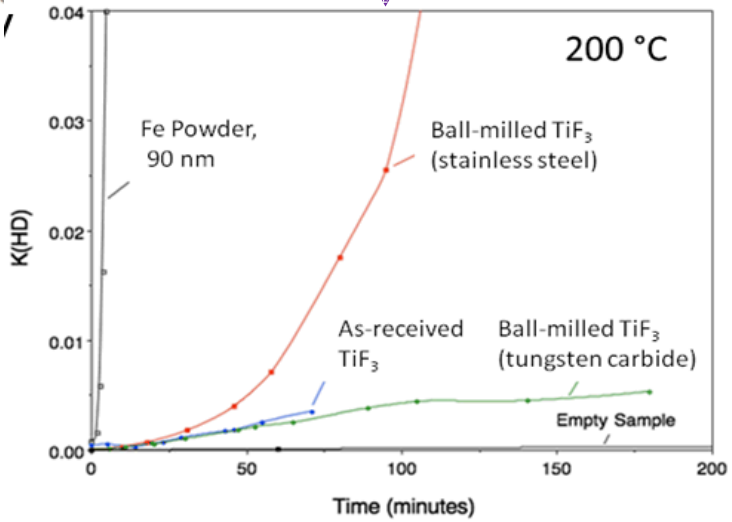
Bulk or ball milled TiF_3 does not react with H_2

TiF_3 does not promote H_2 dissociation.

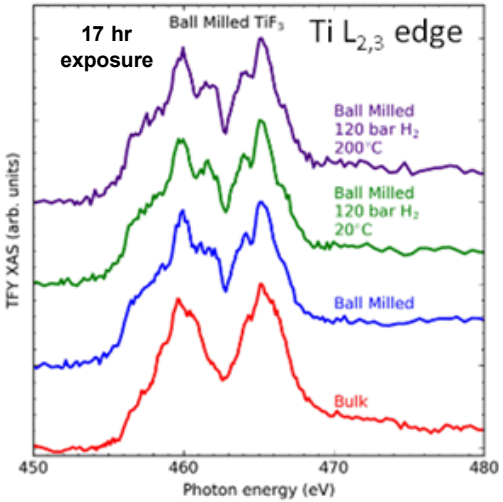


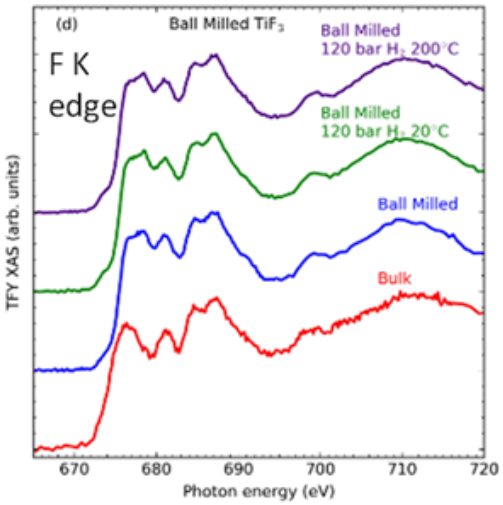
$$K = \frac{[HD]^2}{[D_2]x[H_2]}$$

~ 4.0 at equilibrium



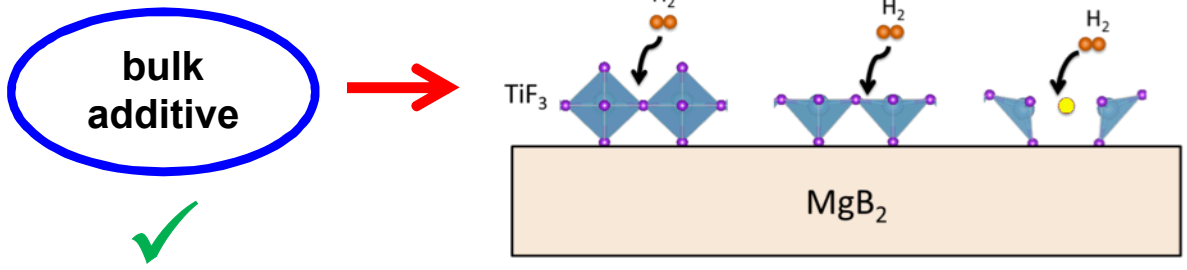
XAS study of Ti, F electronic structure



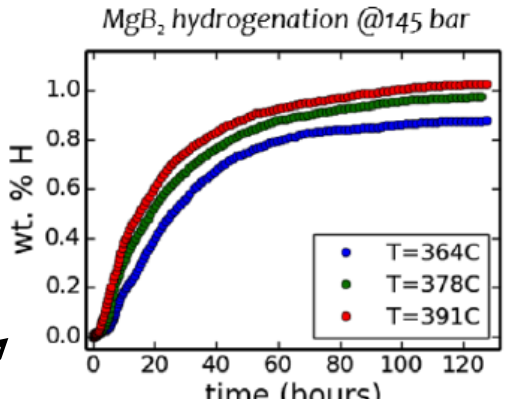


TiF_3 doping into high-capacity B materials

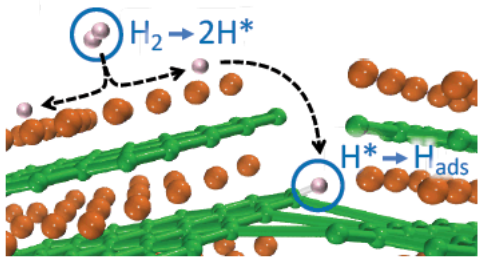
Next Step: Introduce hydrogen storage material, and create additive/host material interface.

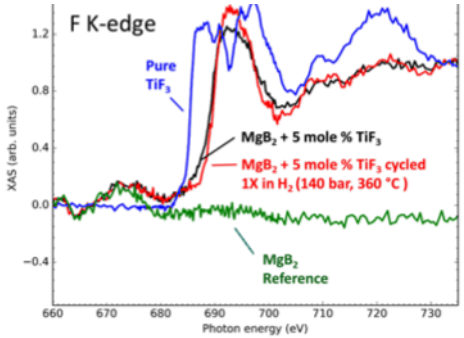


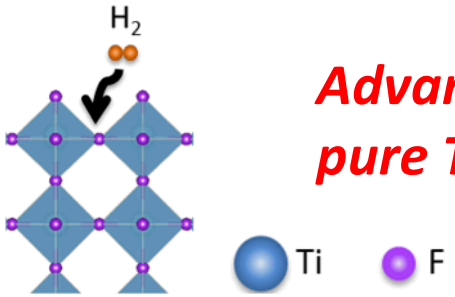
-- from the independent LLNL/Sandia Project on $Mg(BH_4)_2/MgB_2$ --



Investigate reactivity of TiF_3/MgB_2 with H_2 in the two kinetic regimes of initial MgB_2 hydrogenation (H_2 dissociation, diffusion). Understand reaction products, modifications to activation barriers (XRD, FTIR, XAS). XAS indicates reaction between TiF_3 and MgB_2.







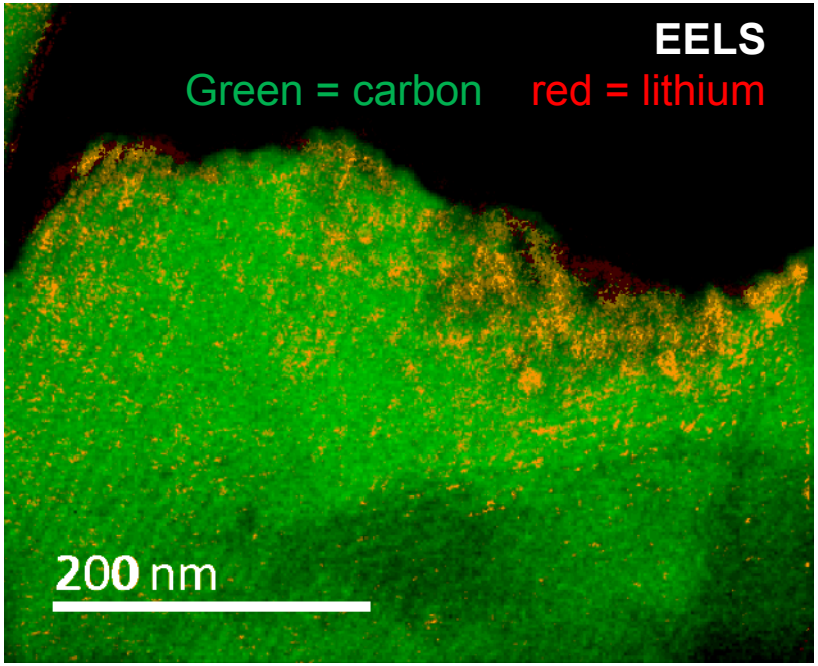
Advance additive model from pure TiF_3 to TiF_3/MgB_2

Demonstrated Li-N-H improved kinetics, reversibility, and intermediate suppression at nanoscale

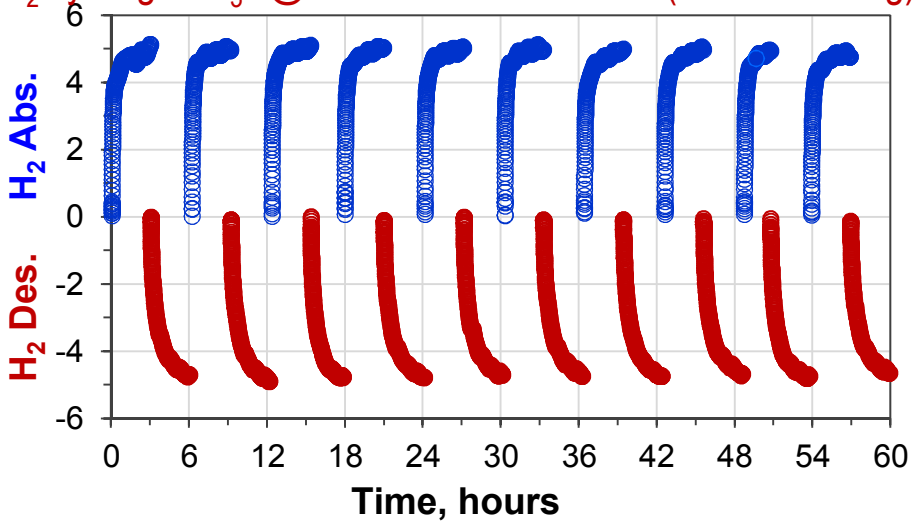
Bulk (2-step reaction pathway)

$$Li_3N + H_2 \rightleftharpoons Li_2NH + LiH \rightleftharpoons Li_3N + 2H_2$$

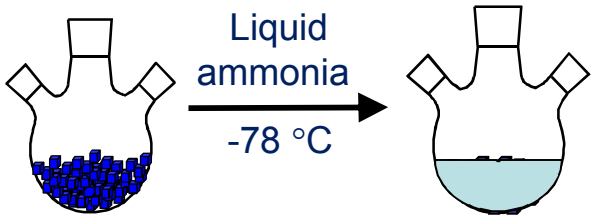
Nano(<12 nm, 1-step reaction pathway)

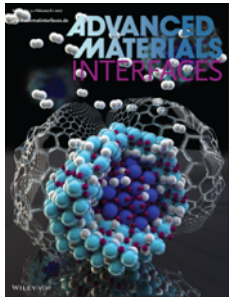


H_2 cycling in Li_3N@6nm-Carbon at 250 °C (52wt% loading)



US Patent Application # 62/235,930





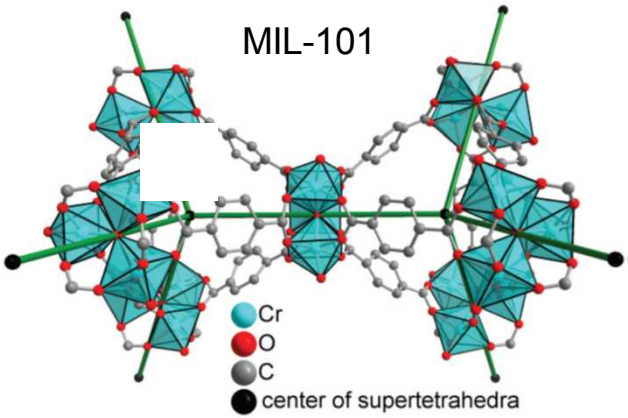
Adv. Mater. Interfaces **2017**, *4*, 1600803 (*Journal Cover*)

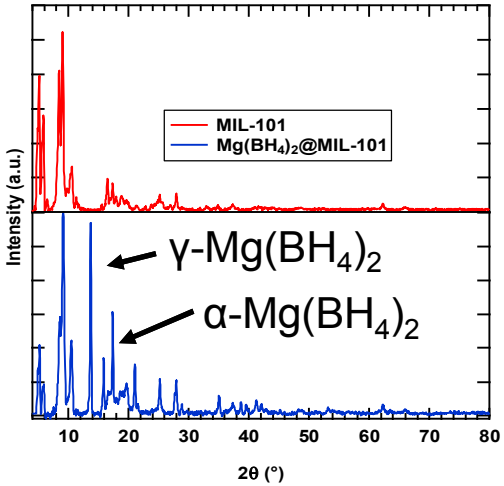
- Developed an improved infiltration approach for metal amide/nitride infiltration into porous hosts using liquid ammonia which enables high loadings (>50% by weight) of Li_3N in porous carbons
- Demonstrated 5wt% reversible H_2 cycling and Li_2NH intermediate suppression in Li_3N@6nm-Carbon

New method for in-pore synthesis of nanoscale $Mg(BH_4)_2$ inside MOFs and graphene aerogels

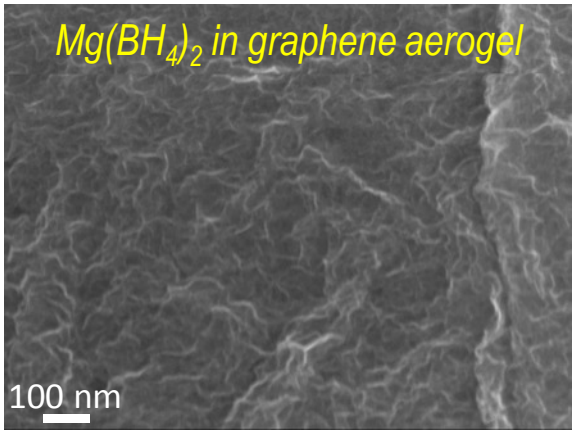
$$3\ Mg(n\text{Bu})_2 + 8\ BH_3{\bullet}S(Me)_2 \rightarrow 3\ Mg(BH_4)_2{\bullet}2S(Me)_2 + 2\ B(n\text{Bu})_3{\bullet}S(Me)_2 + \ldots$$

$$3\ Mg(BH_4)_2{\bullet}2S(Me)_2 \xrightarrow{\Delta,\ vac} 3\ Mg(BH_4)_2 + 6\ S(Me)_2$$

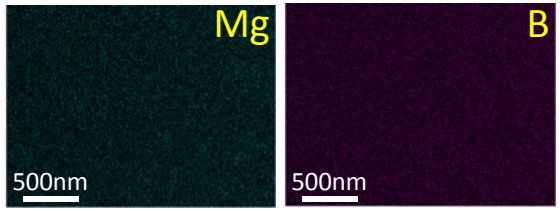




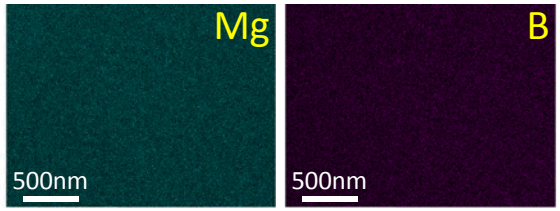
	BET Surface Area (m^2/g)	Pore Volume (cc/g)
Uninfiltrated	1628	0.800
Infiltrated	288	0.16



EDS maps, as-synthesized



EDS maps, after desorption



- Developed an in-pore synthetic approach to incorporate $Mg(BH_4)_2$ into MOFs and nanoporous carbons
- SEM and EDS mapping shows Mg and B are evenly distributed within the sample, confirming $Mg(BH_4)_2$ is inside the pores

Acknowledgements

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Thank you!