

# HyMARC: Sandia's Technical Effort

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*Sandia National Laboratories, Livermore, CA, USA*

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*Enabling twice the energy density for hydrogen storage*



# Overview

## *Timeline*

- Project start date: 09/17/2015

## *SNL R&D Budget*

- FY15 Funding Level: \$250K
- FY16 Funds: \$1.205M
- FY17 Funds: \$1.198M
- FY18 Funds: \$1.150M
- Total DOE Funds: \$3.803M

## *Barriers*

- Lack of Understanding of Hydrogen Physisorption and Chemisorption (Barrier O)
- System Weight & Volume (Barrier A)
- Cost, Efficiency, Durability (Barrier F)
- Charge/Discharge Rates (Barrier E)

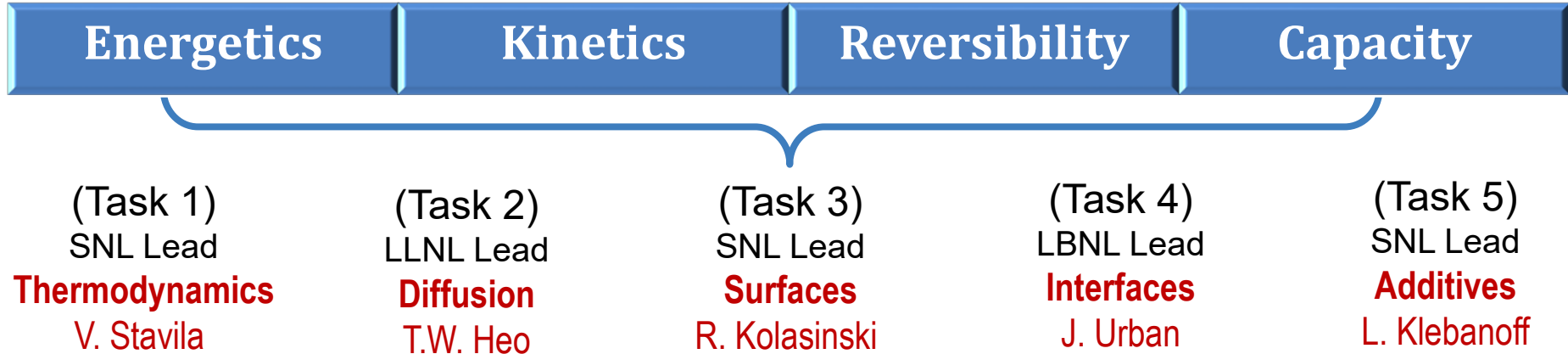


## *Core Team*



# Relevance and impact

Provide the *foundational understanding of phenomena governing thermodynamics and kinetics of hydrogen release and uptake* in all classes of H<sub>2</sub> storage materials



**Sandia's HyMARC activities for the last 12 months:**

- ⇒ Identified and ranked physical and chemical influences that can improve thermodynamics
- ⇒ Obtained experimental data as inputs for the development of hydrogen transport models
- ⇒ Elucidated surface/interface phenomena in NaAlH<sub>4</sub>, Li<sub>3</sub>N, and Mg(BH<sub>4</sub>)<sub>2</sub> that impact H<sub>2</sub> storage
- ⇒ Explored high-hydrogen pressure to mitigate intermediate formation in metal borohydrides
- ⇒ Probed the underlying mechanisms for additive increase in kinetics and reversibility
- ⇒ Applied SNL multiscale codes to discover new materials and new mechanisms of storing hydrogen, provide input for database development

# Approach: Mitigate problematic physical phenomena

## Energetics

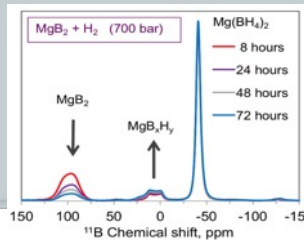
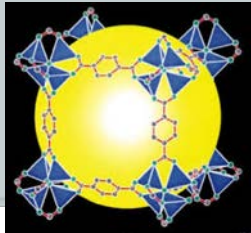
How can we control  $\Delta H$  and  $\Delta S$  of hydrogen adsorption and desorption in sorbents and metal hydrides to enable near-r.t.  $H_2$  storage?

### Sorbents:

- polarizable groups
- flexibility, gate-opening phenomena
- open coordination sites

### Metal hydrides:

- nanostructuring
- destabilization and doping to tune  $\Delta H$  and  $\Delta S$

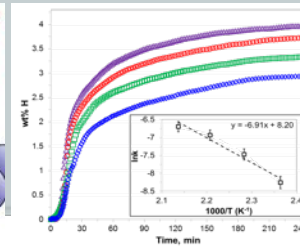
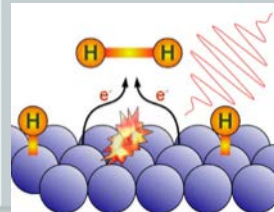


## Kinetics

How can we identify mechanisms by which surfaces and catalysts accelerate reaction rates in reversible metal hydrides?

### Metal hydrides:

- surface modifications to promote  $H_2$  activation
- phase nucleation and interfaces
- nanointerface engineering to optimize transport and diffusion in metal hydrides



## Reversibility

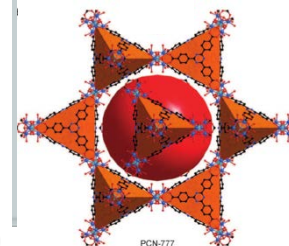
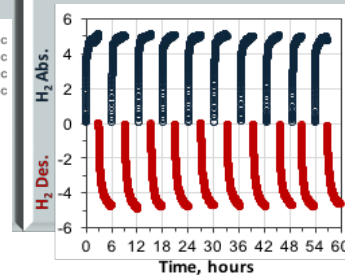
How can we improve the reversibility and cycle-life of metal hydrides and sorbents upon extensive cycling under high  $H_2$  pressure?

### Metal hydrides:

- amorphization and nanostrain to improve reversibility and cycle-life

### Sorbents

- explore cycle-life stability of MOFs, porous polymers, and carbons under high-pressure  $H_2$



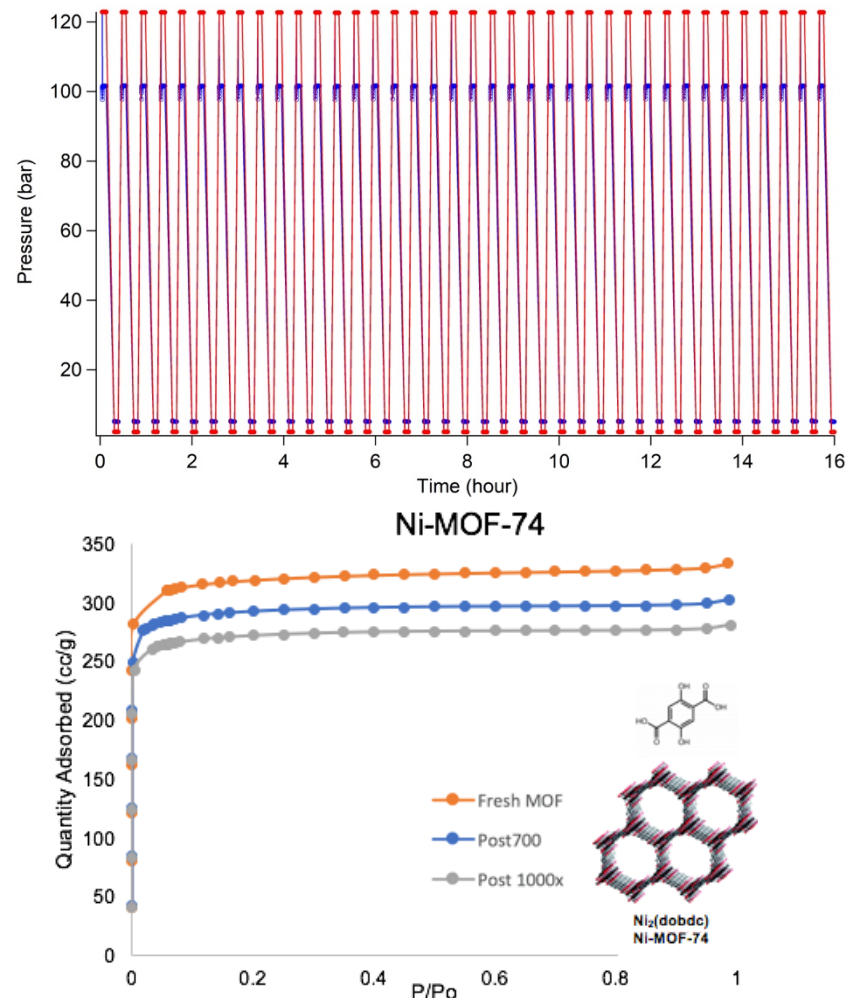
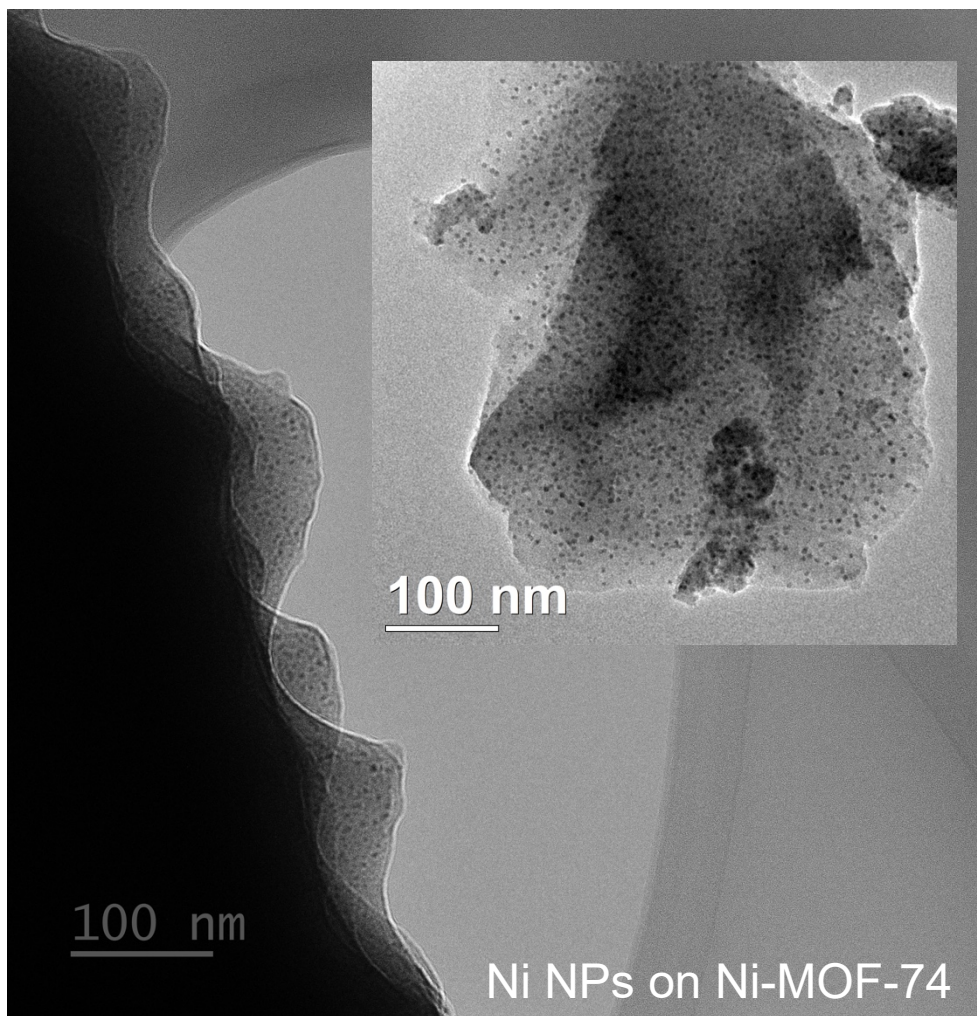
PCN-777



# Summary of progress over the last 12 months

- Provided experimental input to establish a validated phase diagram for  $\text{Mg}(\text{BH}_4)_2$
- Elucidated the reactivity of various additives with hydrogen and metal hydrides and proposed that B-B and B-H bond activation is the rate-limiting step in borohydrides
- Determined the enthalpy and entropy of hydrogen desorption from bulk  $\text{Mg}(\text{BH}_4)_2$
- Created a new melt-infiltration method for  $\text{Mg}(\text{BH}_4)_2$  incorporation into porous hosts
- Discovered that selected MOFs can be partially decomposed either under high-hydrogen pressure or upon repeated hydrogen cycling
- Probed the surface chemistry of  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Li}_3\text{N}/\text{LiNH}_2/2\text{LiH}$  with AP-XPS and LEIS
- Used Sandia high-pressure (up to 1000 bar) system to reveal the effects of high-pressure hydrogen on stability and reaction pathways of metal borohydrides
- Measured low- and high-pressure hydrogen isotherms for GCMC model validation
- Initiated a comprehensive force-field development effort for Mg-B-H intermediates
- Developed and validated MD models of hydrogen diffusion in magnesium hydride
- Established capabilities to elucidate the effect of surfaces on hydrogen transport using XAS, AP-XPS, STXM, and LEIS techniques

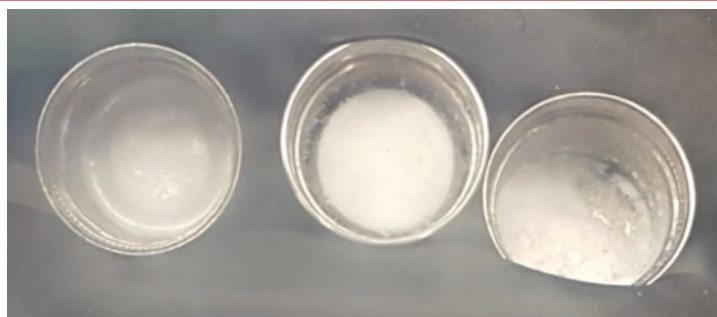
# Accomplishment (Sorbents): Determined stability of MOFs under high-pressure hydrogen



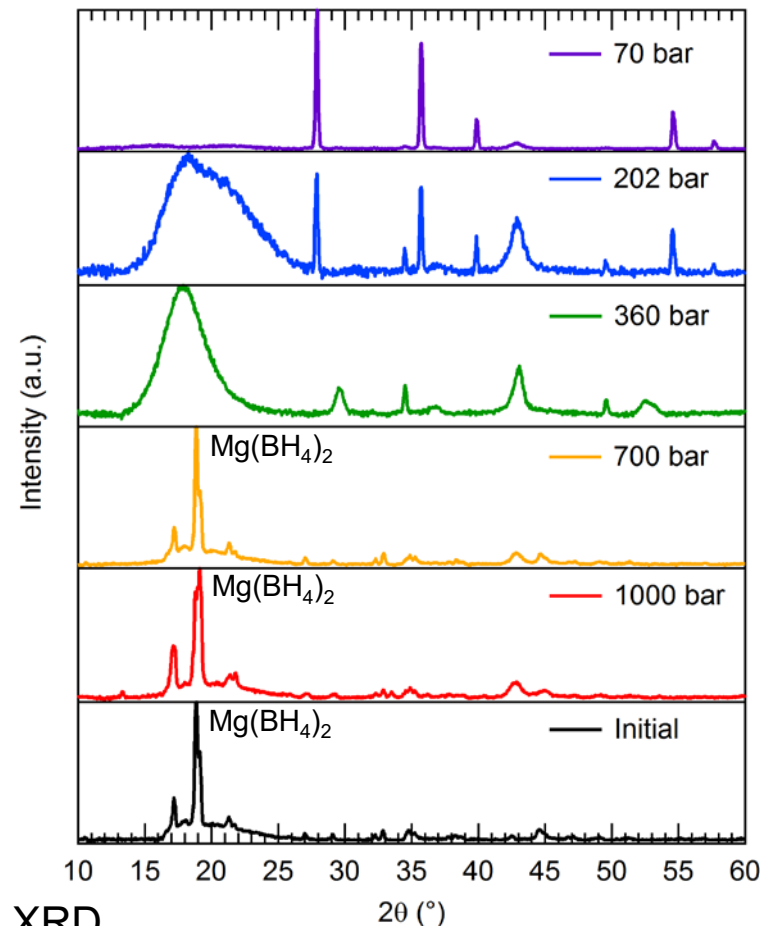
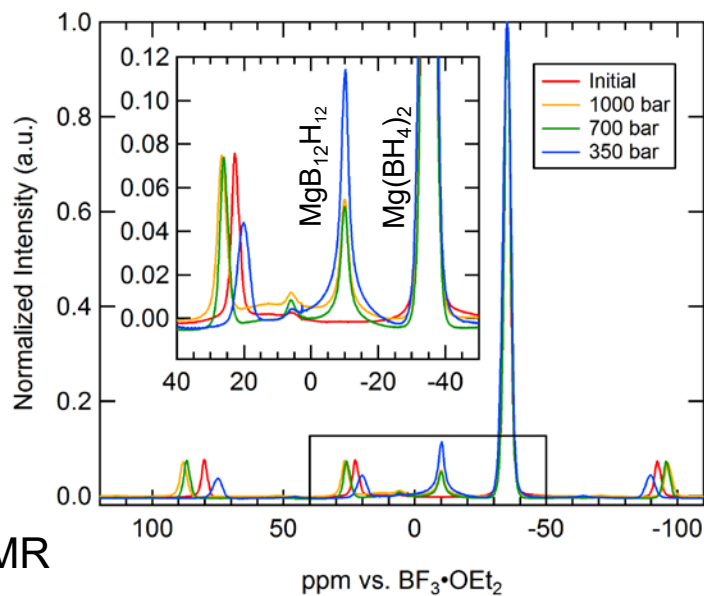
⇒ IRMOF-74-II(Mg) and IRMOF-74(I)-Ni show a significant decrease in the surface area upon high-pressure hydrogen exposure; MOF-5, MOF-177, HKUST-1, Ni(mdobdc) show no degradation

# Accomplishment (Thermodynamics): Building an experimental phase diagram for $\text{Mg}(\text{BH}_4)_2$

- ⇒ Magnesium borohydride melts without decomposition at 365 °C under 1000 bar  $\text{H}_2$
- ⇒ Experiments under  $\text{H}_2$  pressure reveal the limits of thermodynamic stability of  $\text{Mg}(\text{BH}_4)_2$



Melt      Partial melt      Powder

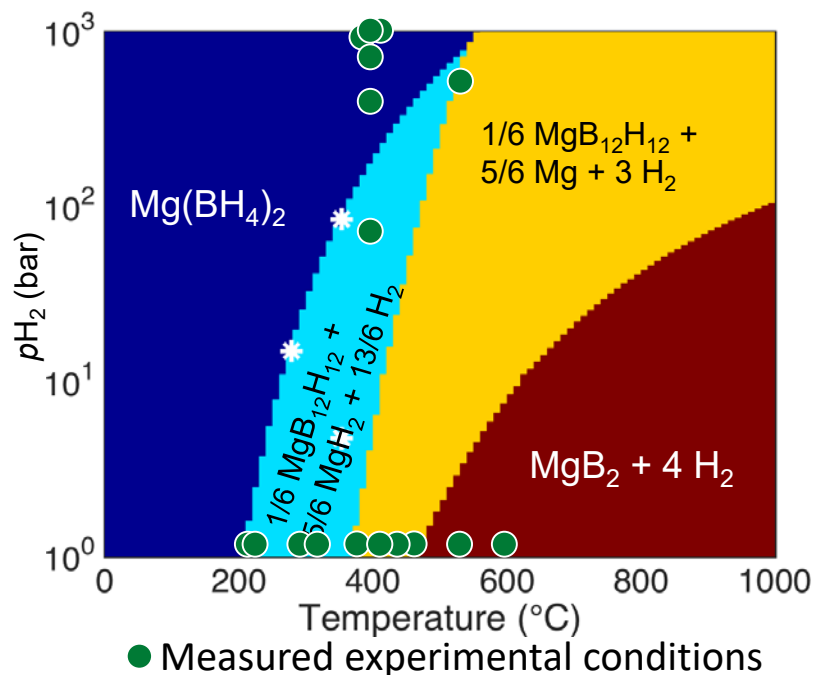


XRD

*manuscript in preparation*

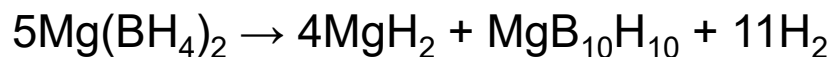
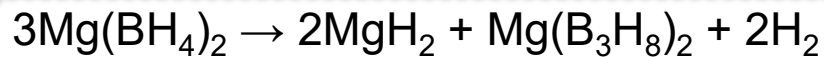
$^{11}\text{B}$  MAS NMR

# Accomplishment (Thermodynamics): Established detailed Mg-B-H phase diagram

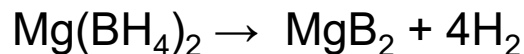
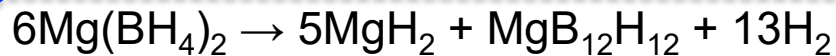


\*Efforts to include  $Mg(BH_4)_2$  melting underway

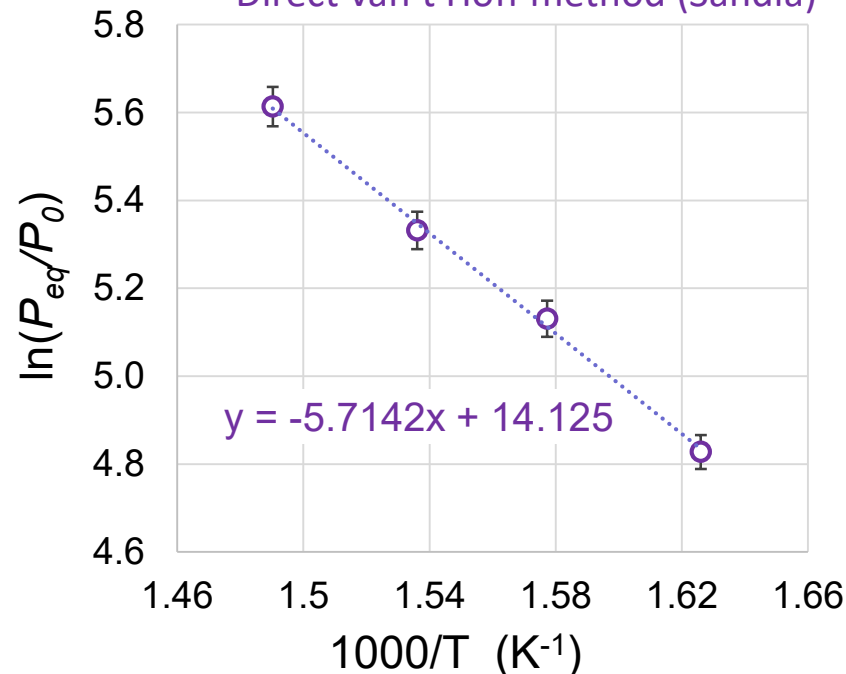
Kinetic products



Thermodynamic products



Direct van't Hoff method (Sandia)



$$\Delta H = 48 \text{ kJ mol}^{-1}$$

$$\Delta S = 117 \text{ J mol}^{-1} \text{ K}^{-1}$$

$\Delta H$  and  $\Delta S$  values measured under high-hydrogen pressure

(see ST129 for additional details)

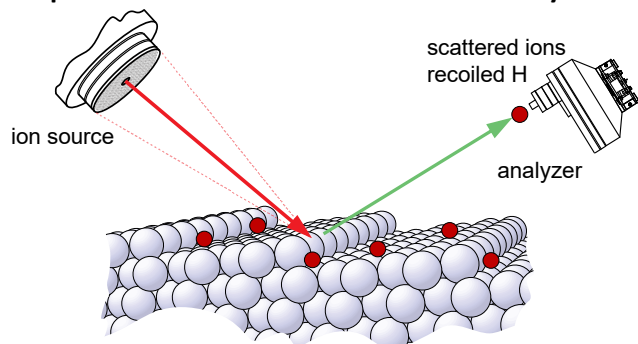


# Approach (Surfaces): Employ suite of complementary diagnostics to explore the role of surfaces

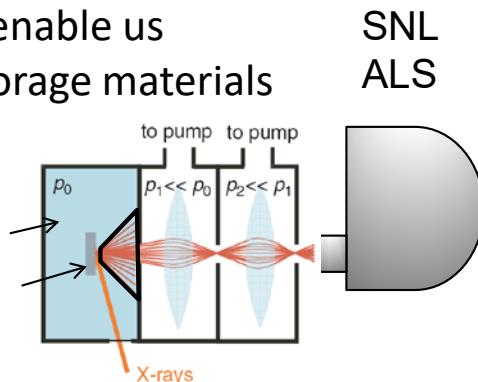
## Motivation:

- Surfaces are believed to play an important role in hydrogen storage reactions; exact role and mechanisms remain unclear

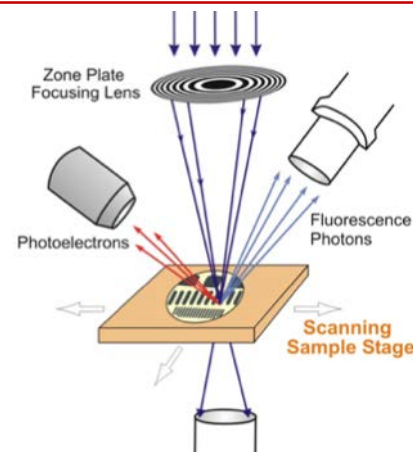
**Technical Approach:** *In-situ* techniques enable us to probe the surface chemistry for H<sub>2</sub> storage materials



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



**Ambient pressure XPS:**  
Characterize chemical environment of  $Z \geq 3$   
(Surface and near sub-surface, <10 nm)



**Scanning trans. X-ray microscopy (STXM):**  
Distribution of chemical species within particles  
(Bulk)

## What we hope to learn:

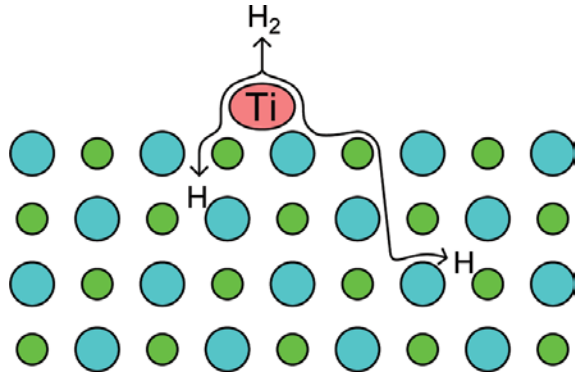
- ⇒ *What is the surface composition of H<sub>2</sub> storage materials?*
- ⇒ *How do surfaces respond to temperature and H<sub>2</sub> environments?*
- ⇒ *What is the spatial distribution of species of interest?*
- ⇒ *Can surfaces be modified to improve H<sub>2</sub> storage properties?*



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)

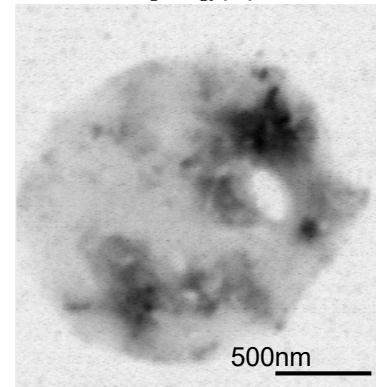
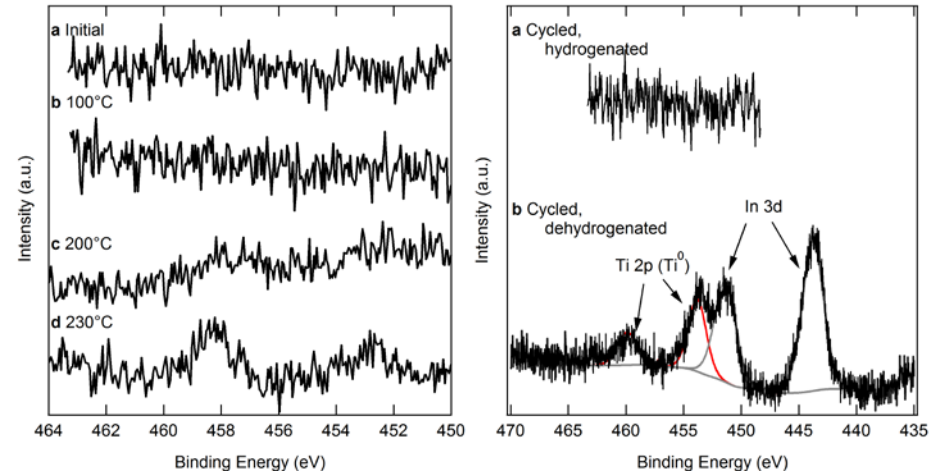
# Accomplishment (Kinetics): Revealed role of Ti in hydrogen desorption from $\text{NaAlH}_4$

## Previously hypothesized mechanisms

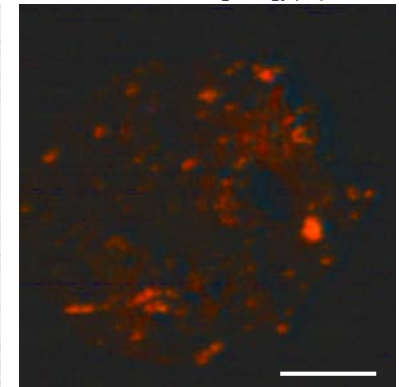


### Pump-Spillover

Ivanov et al. *J. Less-Common Met.* **1987**, 131, 25

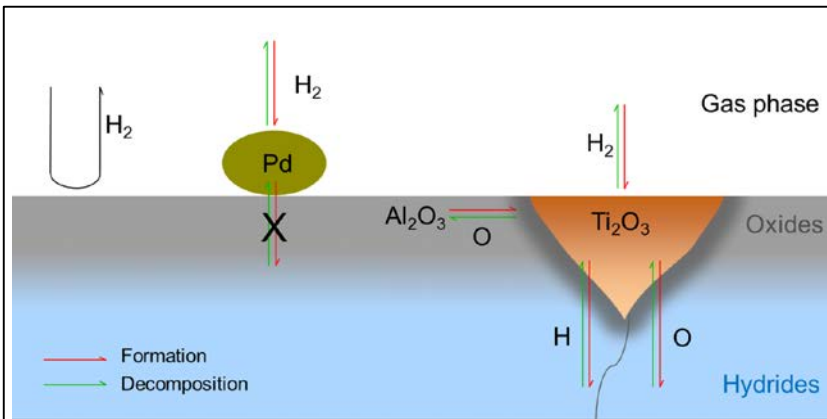


Brightfield image



STXM map

$\text{Ti}^0$  in red,  $\text{TiO}_2$  in blue



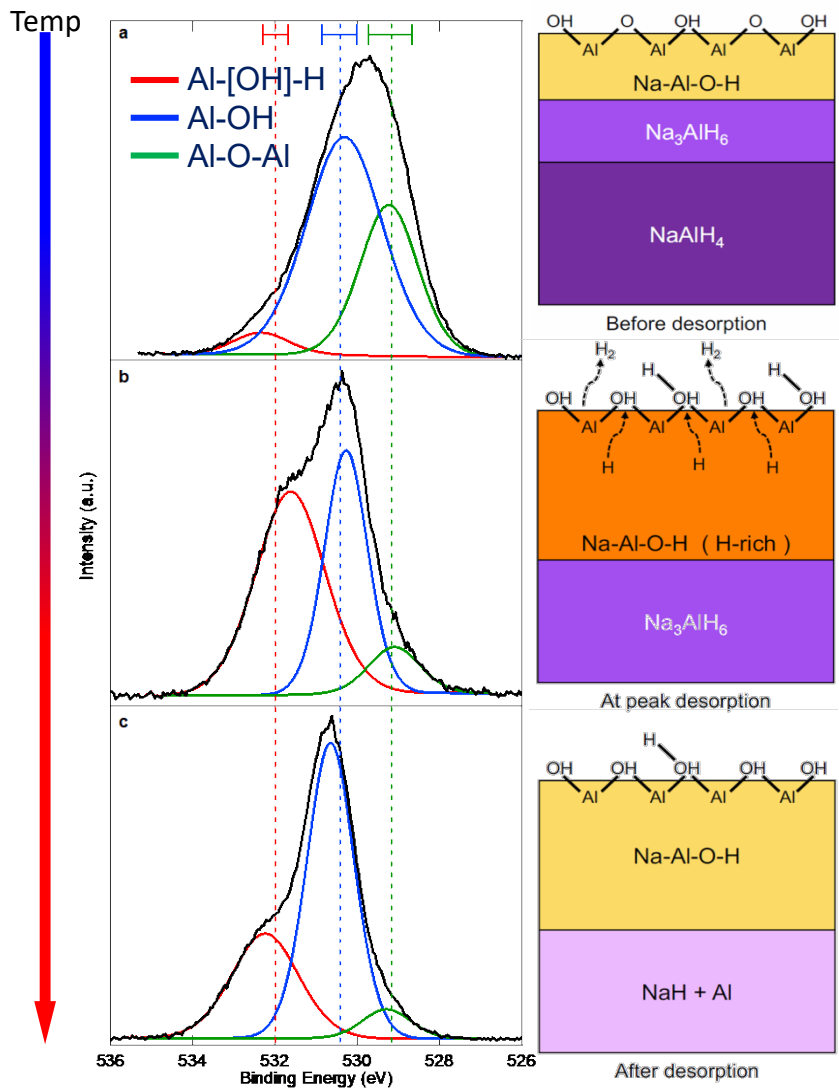
### Ti-Oxide Model

Delmelle, et al. *AIP Advances* **2014**, 4, 127130

⇒ *Ti plays no direct role in surface dehydriding reactions; relegates its role to the bulk*

# Accomplishments (Surfaces): Dynamically evolving surface oxides in $\text{NaAlH}_4$ dehydrogenation

## Interpretation of surface oxide XPS on $\text{NaAlH}_4$ shows dynamically evolving O/OH species



- Correct peak assignment critical to understanding changes *in situ*.
- O 1s XPS can be used to distinguish O species (Al-[OH]-H, Al-OH, and Al-O).
- During desorption, H concentration increases in oxygen layer, and after desorption its concentration decreases, indicating that either H diffusion in oxygen layer or  $\text{H}_2$  recombination is rate-limiting. *(see ST129 for details on calculations)*

⇒ **Surface oxides are active in dehydrogenation of  $\text{NaAlH}_4$ .**

⇒ **Presence of hydroxides catalyzes  $\text{H}_2$  formation at the surface.**

⇒ **Theory is critical for accurate assignment of Al 2p peaks (see ST129).**

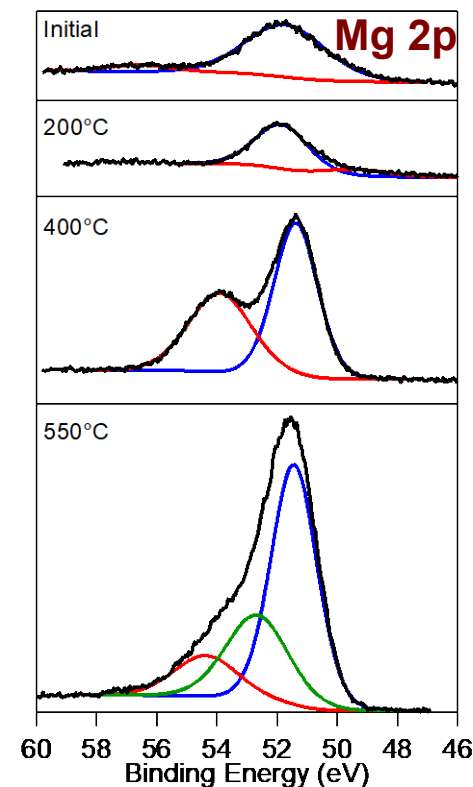
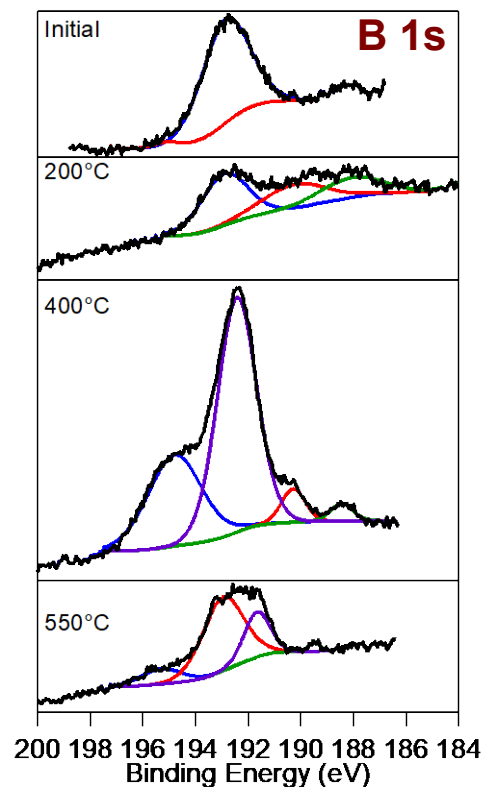
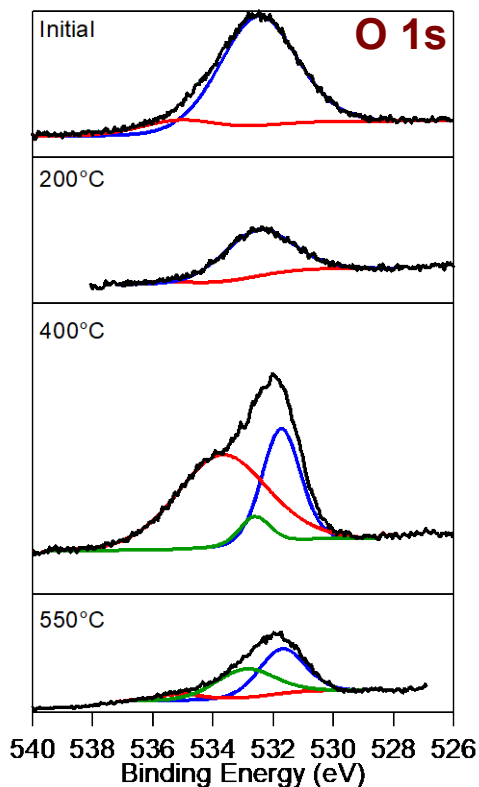
# Accomplishment: First *operando* ambient pressure XPS results on magnesium borohydride

## Boron:

- Concentration elevated at 400 °C, near peak desorption
- Returns to initial level at 550 °C

## Magnesium:

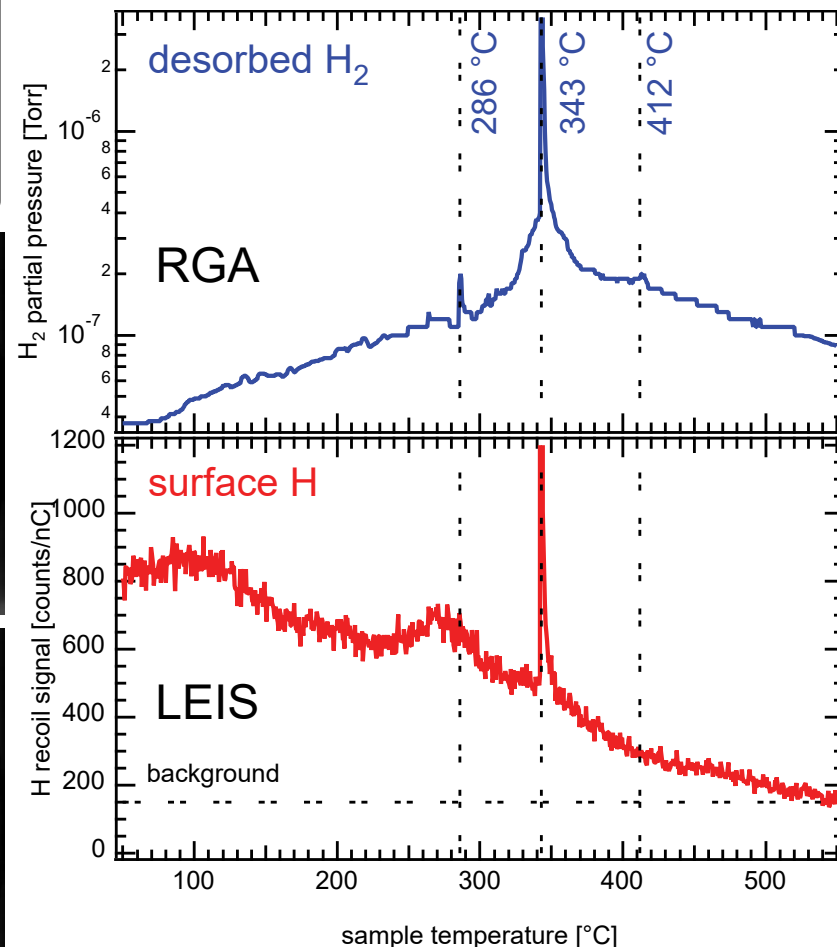
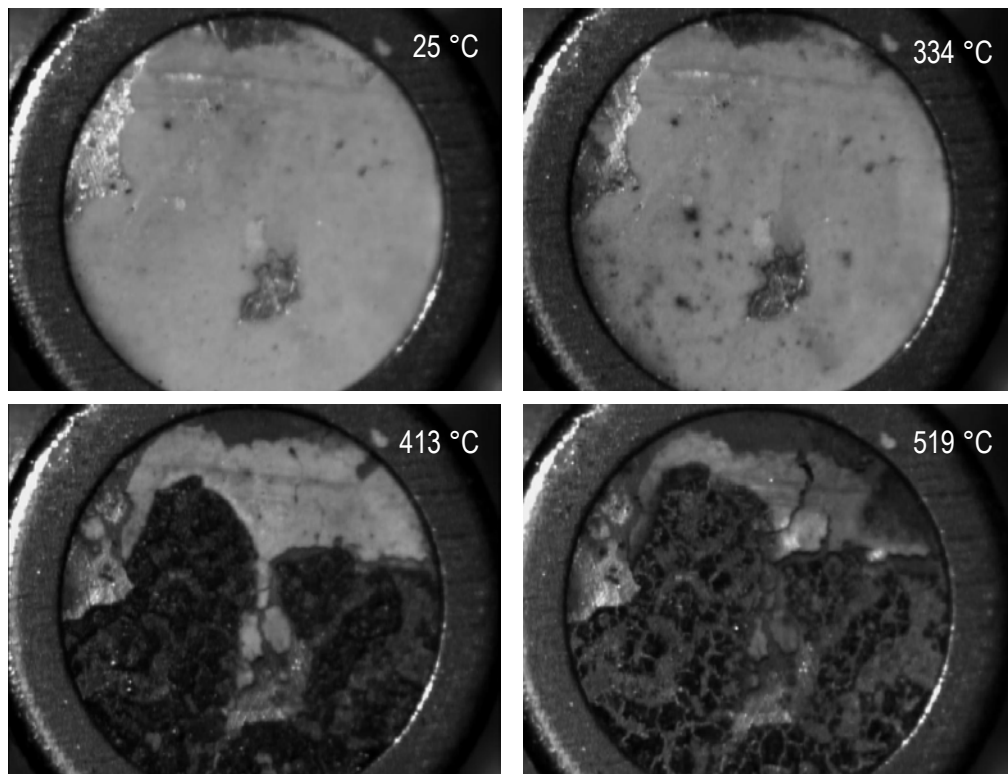
- Segregates to surface – implications for reversibility upon full desorption





# Accomplishment (Surfaces): Detecting H at the surface of $\text{Mg}(\text{BH}_4)_2$ using LEIS

- 2 keV  $\text{Ne}^+$  scattering parameters optimized for H detection (less sensitive for O, B)
- H, Mg and 2 background channels monitored to provide absolute peak height



manuscript in preparation

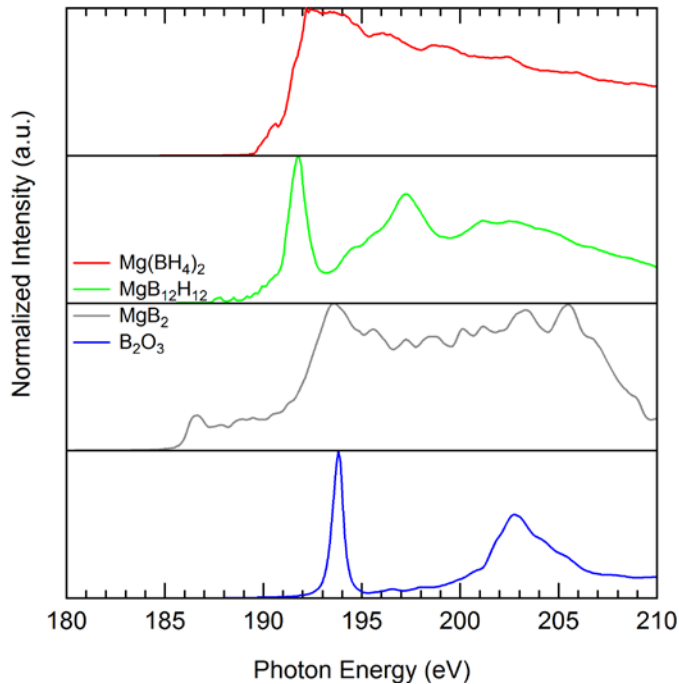
⇒ LEIS results are being used to inform and validate the  $\text{Mg}(\text{BH}_4)_2$  surface model development

# Accomplishment (Interfaces): STXM of Mg-B-H Materials

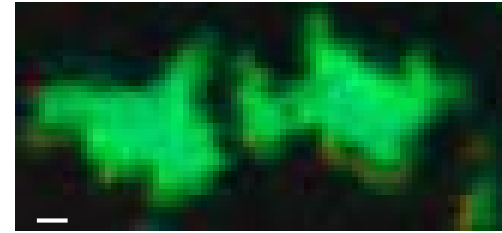
Knowledge of phase nucleation and growth is essential for understanding and improving cycling reactions.

↳ Look at microscopic chemical changes at various points in (de)hydrogenation reactions through XAS-based STXM.

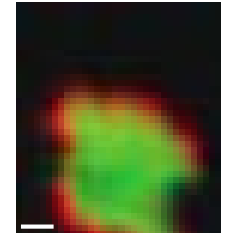
⇒ *Hydride is present on the exterior after partial decomposition of borohydride and hydrogenation of boride.*  
⇒ *Dehydrogenated phase propagates from inside outward, rather than outside inward as initially proposed.*



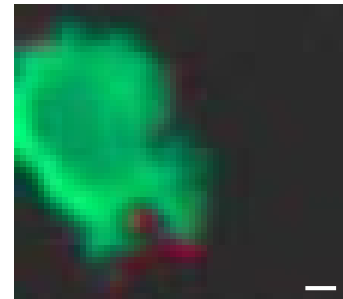
Simulated XAS B K edge spectra



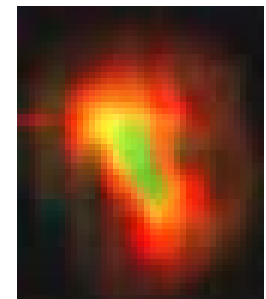
$\text{MgB}_2$ , 202 bar



$\text{Mg}(\text{BH}_4)_2$ , 202 bar



$\text{MgB}_2$ , 700 bar



$\text{Mg}(\text{BH}_4)_2$ , 360 bar

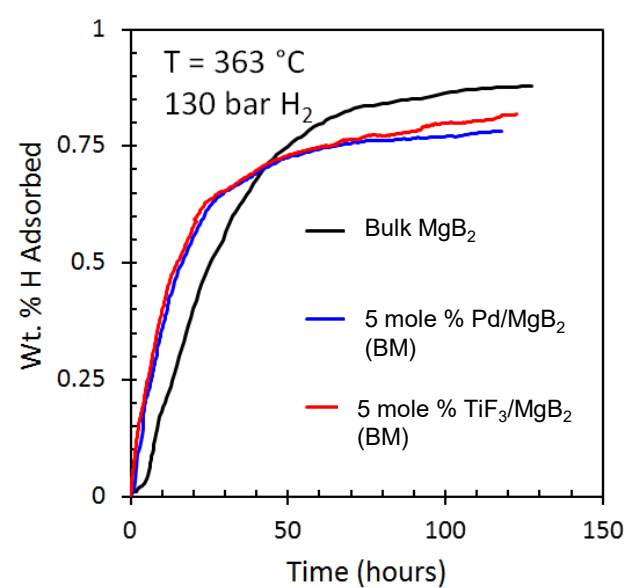
Red:  $\text{Mg}(\text{BH}_4)_2$   
Green:  $\text{MgB}_{12}\text{H}_{12}$   
Blue:  $\text{B}_2\text{O}_3$   
Scale bar=200 nm

Measurements performed at UVSOR, IMS, Japan

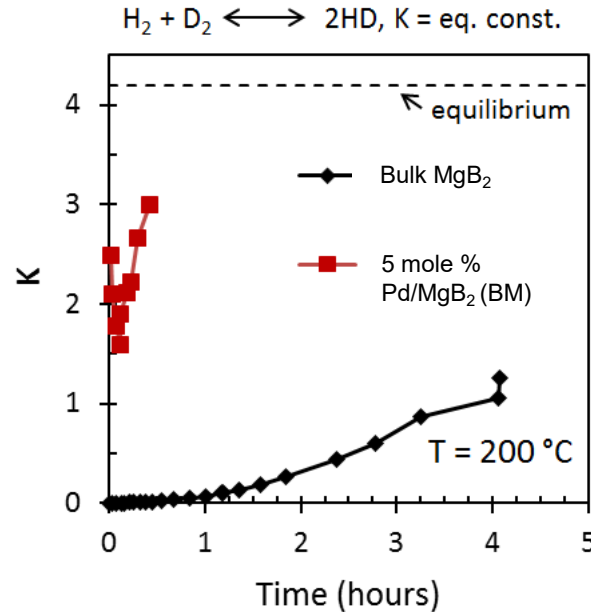


B. Wood et al. *Adv. Mater. Interfaces* **2017**, 4, 1600803

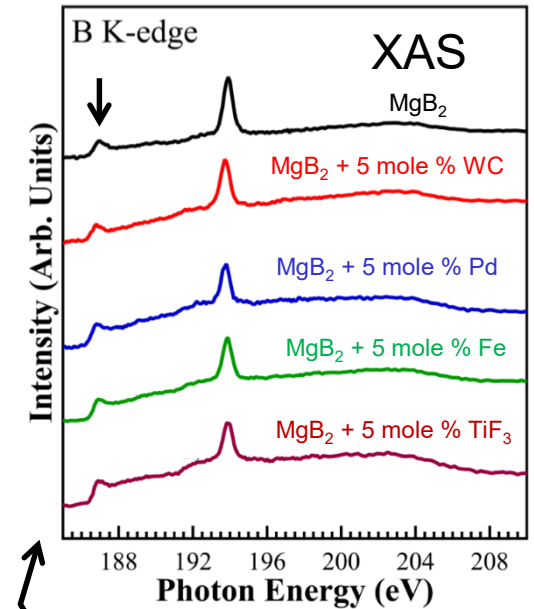
# Accomplishment (Kinetics): H-H bond breaking does not limit bulk $\text{MgB}_2$ hydrogenation rate



Initial  $\text{MgB}_2$  H uptake is slow...



Even though H-H bond dissociation is relatively fast.....



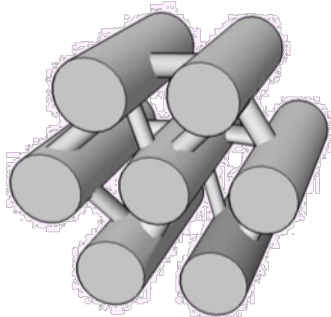
$\text{MgB}_2$  materials with intact B-B rings hydrogenate slowly...

By 10 hours, both bulk  $\text{MgB}_2$  and  $\text{MgB}_2$  with 5 mole % additives dissociate a lot of  $\text{H}_2$ , yet the hydrogenation still proceeds slowly over many tens of hours.

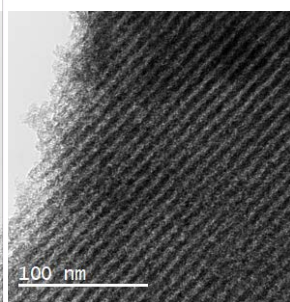
- $\Rightarrow$  H-H bond breaking is NOT the rate-limiting step for bulk  $\text{MgB}_2$  hydrogenation.
- $\Rightarrow$  H-H bond breaking may be important for nano- $\text{MgB}_2$  or nanoconfined  $\text{MgB}_2$
- $\Rightarrow$  Or the additive needs to disrupt the hexagonal B-B ring system.
- $\Rightarrow$  Or the additive needs to form a different type of H ( $\text{H}^+$  or  $\text{H}^-$  but not H atoms).

# Nanoporous templates for $\text{Mg}(\text{BH}_4)_2$ infiltration

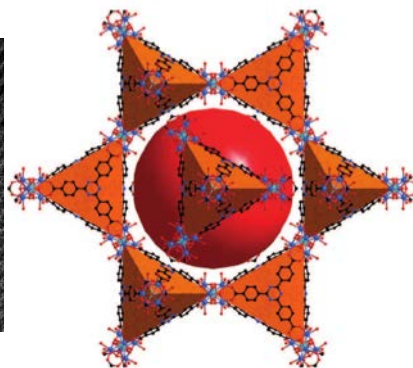
Porous Host	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Type	Stability	Avg. Pore Size (nm)
Graphene aerogel	1338	4.2	Carbon	High	8.2
CMK-3	782	1.0	Carbon	High	4.8
NPC	1556	1.8	Carbon	High	2.3
PCN-777	2008	2.7	MOF	Low	3.8
CTF-1	886	0.4	Covalent framework	Moderate	1.9
PPN-4	6461	3.0	Covalent framework	Moderate	1.9



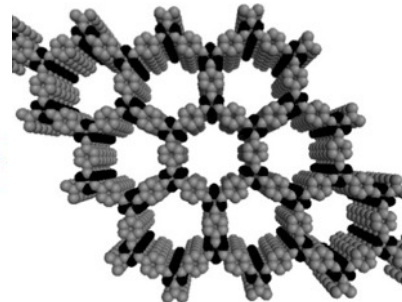
CMK-3



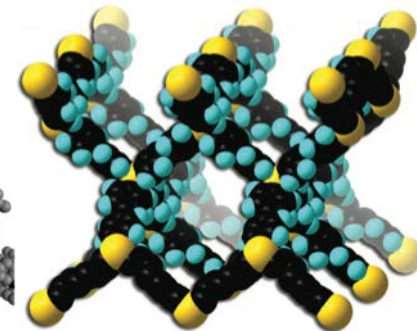
NPC



PCN-777



CTF-1



PPN-4

⇒ Synthesized and characterized a library of nanoporous hosts for metal hydride infiltration

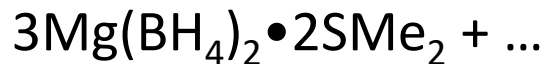
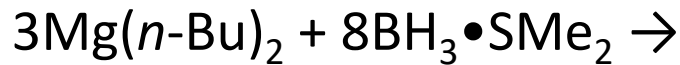


# Accomplishment: $\text{Mg}(\text{BH}_4)_2$ in nanoporous hosts

- Evaluated three approaches to infiltrate  $\text{Mg}(\text{BH}_4)_2$  into porous hosts:

- I. Solution infiltration using  $\text{Me}_2\text{S}$

- II. In-pore reaction

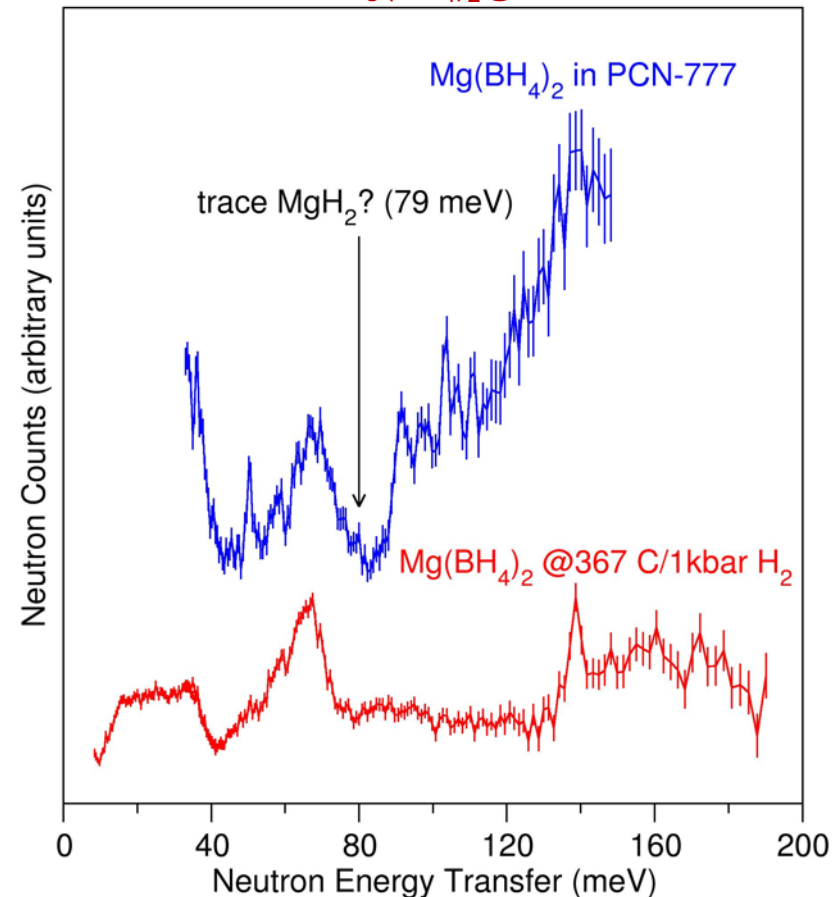


- III. Melt infiltration: unique capability

- Heat to  $400^\circ\text{C}$  under 1000 bar  $\text{H}_2$  to melt

- Capillarity draws melt inside pores

NVS for  $\text{Mg}(\text{BH}_4)_2$ @PCN-777



⇒ *Developed a new method of infiltrating magnesium borohydride into porous hosts by melt infiltration under high-pressure hydrogen*

T. Udovic

**NIST**  
National Institute  
of Standards  
and Technology

# Accomplishment: Supporting Seedling Projects

## SNL high-pressure system



- More than **50** samples measured under high-pressure hydrogen (sorbents and hydrides)
  - **43** magnesium diborate etherate samples for the U. of Hawaii project
  - **7** samples for the Liox/HRL project
- **15** samples from UMSL (*Chem. Mater.* MS published\*) for XPS and **7** samples from Penn State for porosimetry measurements
- Go/No-Go validation for the ANL and HRL seedling projects (measured hydrogen purity and overall capacity for 5 samples)

\* *Majzoub et al.*, DOI: [10.1021/acs.chemmater.8b00305](https://doi.org/10.1021/acs.chemmater.8b00305)



# Milestones

Project Milestone	Type	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	% Complete	
Evaluate additive/composite strategies for improving effective $\Delta E$	PM	9/30/17	9/30/18		75%	Evaluation of multiple strategies in progress
Prototype hydride surface and interface chemistry kinetic models	M	9/30/17		9/30/17	100%	
Amorphous phases and defects model formalism	PM	12/31/17		12/31/17	100%	
Sensitivity analysis of morphology and microstructure	PM	3/31/18		3/31/18	100%	Completed analysis, reported in LLNL AMR slides
Rank improvement strategies for hydrides. Decision criterion: select 2 with greatest potential for reducing effective $\Delta H$	GNG	3/31/18		3/31/18	50%	Nanoscaling and Dopants addressed experimentally
Parameterize integrated kinetic model for representative B-N-Al-hydrides	PM	6/30/18			75%	Thermodynamic parameters completed. Some kinetic parameters have been calculated for Na-Al-H and Mg-B-H
Compute sorbent isotherms from QMC data using CoRE database of MOFs Milestone delayed until Phase 2	PM	9/30/18			0%	Not started
Revised language: Public release of databases, synthetic protocols, characterization methodologies optimized for storage materials	M	9/30/18			0%	Not started. Release of codes is a time-consuming process that will be difficult to complete for codes that as of the date of this report are not ready.

# Remaining Challenges and Future Work

## Modeling

- Apply newly-established Mg-B-H bond order potentials to reveal H-transport mechanisms in magnesium borohydride
- Build a “machine learning” framework to reveal the underlying structure-property relationships in complex metal hydrides, which often defy scientific intuition

## Synthesis

- Optimize synthetic approaches to achieve pure nanoparticles of  $\text{MgB}_2$  and  $\text{Mg}(\text{BH}_4)_2$
- Synthesize amorphous materials to test the thermodynamics theory framework
- Develop new encapsulation approaches to improve metal hydride loading inside “non-innocent” hosts and improve  $\text{H}_2$  storage properties

## Characterization

- Use newly developed *in-situ* capabilities to elucidate surface chemistry and transport in high-capacity metal amides and borohydrides
- Measure hydrogen transport under various reaction conditions in  $\text{Mg}(\text{BH}_4)_2$
- Collect reliable temperature-dependent hydrogen desorption and absorption isotherms for both metal hydride and sorbent theory model validation
- Apply XAS, XPS, and neutron diffraction to gain insights into the degradation mechanisms of MOFs extensively cycled under hydrogen

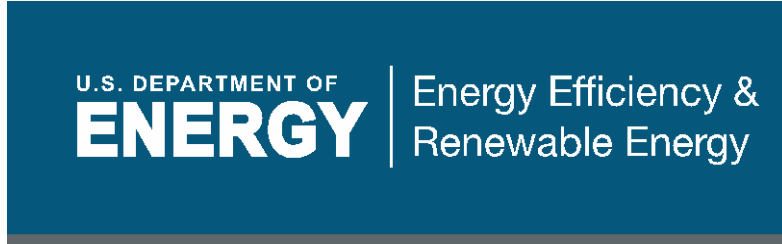
Any proposed future work is subject to change based on funding levels



# Collaboration & Coordination

- T. Udovic and C. Brown (NIST): neutron diffraction/spectroscopy
  - *Exchanged 14 samples for neutron diffraction and NVS studies*
- T. Autrey and M. Bowden (PNNL): NMR on metal borohydrides and intermediates
- K. Hurst, P. Parilla and T. Gennett: Validation of MOF H<sub>2</sub> adsorption isotherms
- M. Head-Gordon (LBNL): DFT computations of H<sub>2</sub> physisorption sites in MOFs
- Timmy Ramirez (ORNL): small angle neutron scattering, neutron diffraction
- Viktor Balema, Vitalij Pecharskij (AMES): metal hydrides, mechanochemistry
- D. Chandra (University of Nevada, Reno): CALPHAD calculations and phase diagrams
- Martin Dornheim (Helmholtz-Zentrum Hamburg, Germany): high-pressure calorimetry
- T. Jensen (Aarhus University, Denmark): nanoscale effects in metal hydrides
- S. Orimo (Tohoku University, Japan): hydrogen and ion transport in metal *closo*-borates
- P. Chen (Dalian University, China): synthesis and characterization of ternary metal amides
- S. Kaskel (Technische Universität Dresden, Germany): high-surface area MOFs

# HyMARC Partners and Funding



<https://hymarc.org/>



# Technical Back-Up Slides

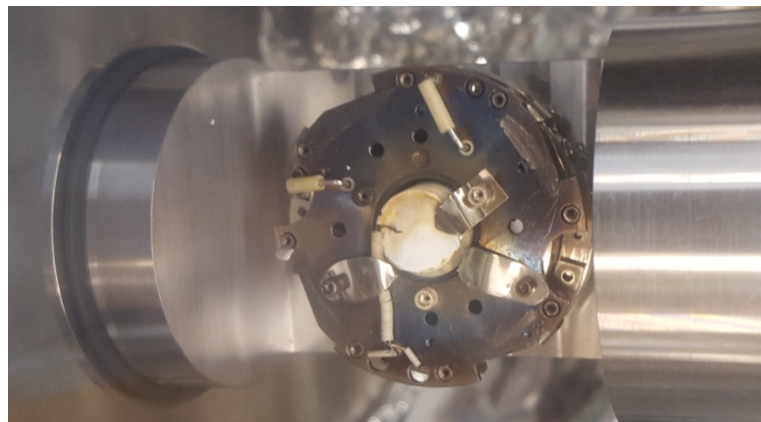
# Approach (Surfaces): Comprehensive effort initiated to elucidate surface science of $\text{Mg}(\text{BH}_4)_2$

- AP-XPS user proposal accepted for 2 sessions (100 h total beamtime) in March 2018 (BL 11.0.2)

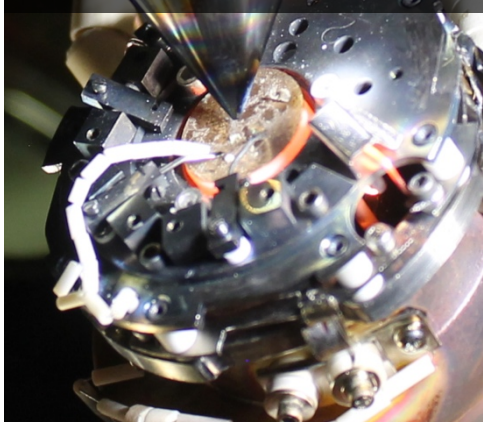
## Technical Challenge:

- Prior attempts unsuccessful due to sample charging
- Mitigated by using only thin layer, flooding chamber with 50 mTorr Ar

Synthesized  $\text{Mg}(\text{BH}_4)_2$  mounted in Au foils and cleanly transferred



*In situ* heating at  $\sim 600^\circ\text{C}$  in APXPS chamber



## Two experimental sessions:

- 3 samples analyzed in each set of runs
- Step-wise heating in 50 – 100  $^\circ\text{C}$  increments ( $\sim 1$  h for each set of spectra)

*Batch 1:* Heating rate varied

*Batch 2:* Examined effect of exposure to  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and air

**Acquired and analyzed over 1500 spectra!**

# Accomplishment (Thermodynamics/Kinetics): XAS study of element-specific electron states



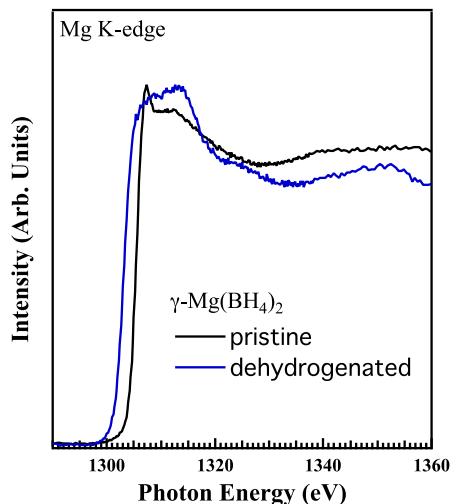
Sandia National Laboratories



Lawrence Livermore National Laboratory

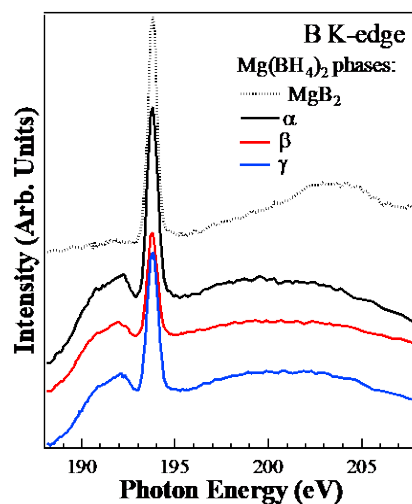


Ex-situ:  $\text{Mg}(\text{BH}_4)_2$



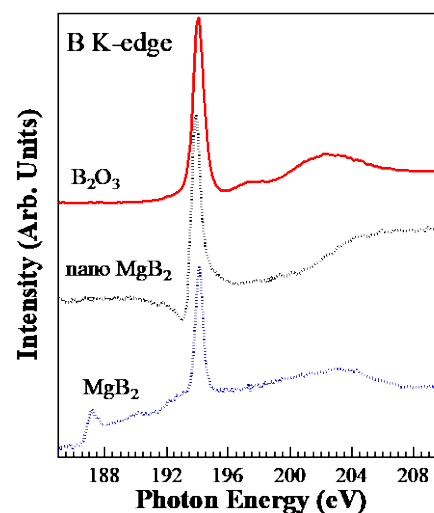
Mg K-edge spectra reveal the footprint of dehydrogenated phase.

Ex-situ:  $\text{Mg}(\text{BH}_4)_2$

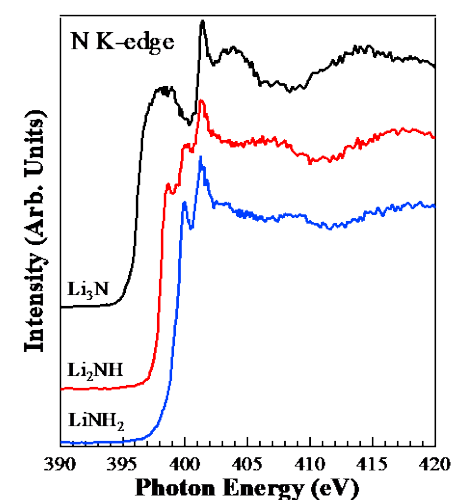


Low-energy XAS feature at  $\sim 192$  eV in the B K-edge spectra is assigned to the  $\text{BH}_4^-$  anion in borohydrides.

Nano  $\text{MgB}_2$

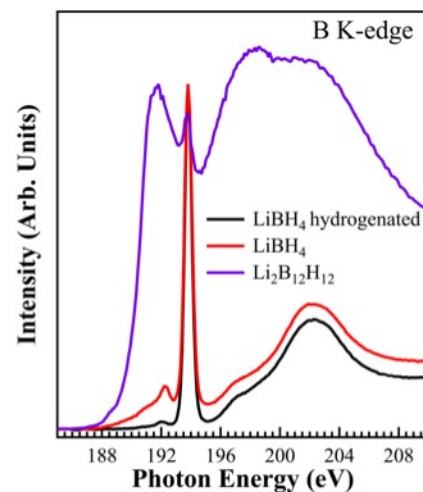
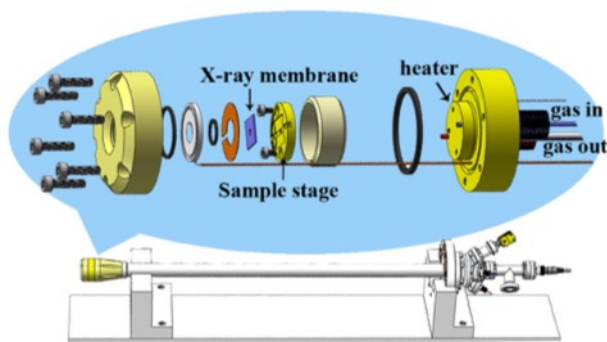


Lithium Amide



B K-edge XAS spectra of nano  $\text{MgB}_2$ , Lithium amide with related compounds, and lithium borohydride will be used to characterize intermediates in future *in-situ* XAS experiments.

Lithium borohydride

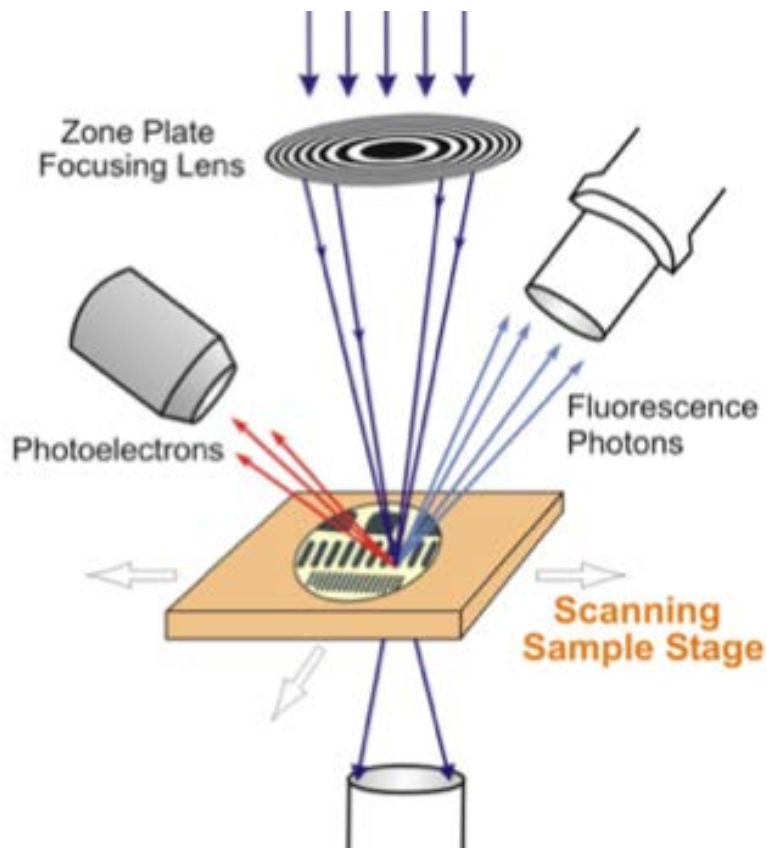


*manuscript in preparation*



# Accomplishment (Interfaces): STXM data provides insights into Li-N-H interfaces during H<sub>2</sub> uptake and release

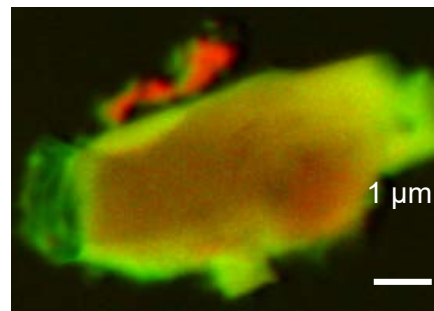
## Scanning trans. X-ray microscopy (STXM)



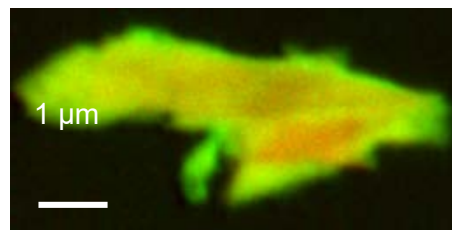
Red: Li<sub>3</sub>N

Green: LiNH<sub>2</sub>/Li<sub>2</sub>NH

Pixel size is 30 nm



Li<sub>3</sub>N, cycled  
Hydrogenated

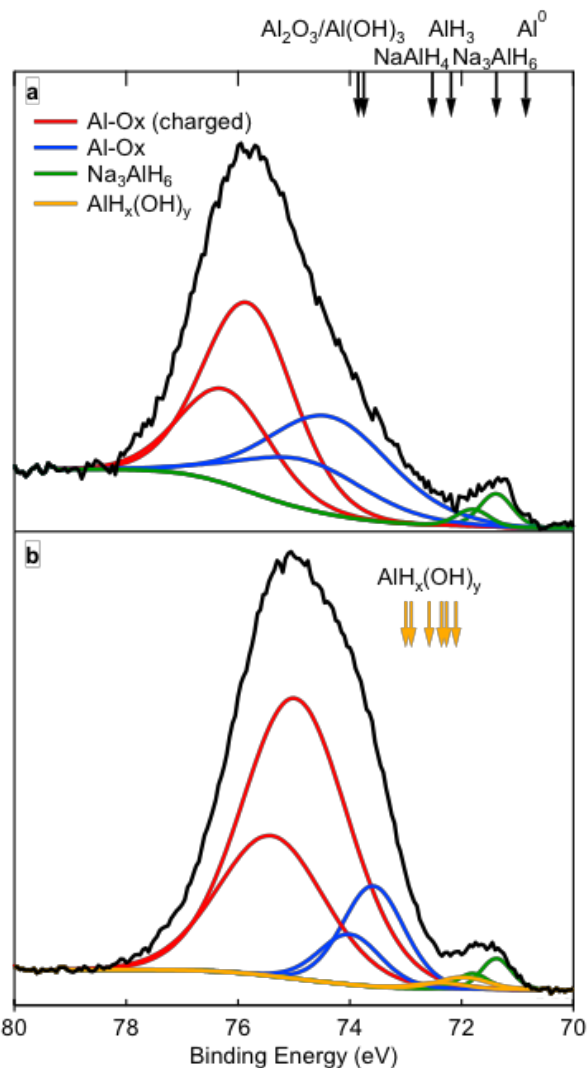


Li<sub>3</sub>N, cycled  
Dehydrogenated

*manuscript in preparation*



# Accomplishment (Kinetics): Analysis of surface and bulk Ti-doped $\text{NaAlH}_4$ reveals Ti role in $\text{H}_2$ desorption



We devised a new scheme based on *ab initio* molecular dynamics + XPS simulations to provide reliable standards and unambiguously interpret AP-XPS experiments

- The binding energy generally progresses in the order Al metal <  $\text{Na}_3\text{AlH}_6$  <  $\text{AlH}_3$  <  $\text{NaAlH}_4$  <  $\text{Al}(\text{OH})_3 \sim \text{Al}_2\text{O}_3$
- In previous studies, assignment of Al-chemical species using Al 2p BE was based intuitively on Al oxidation state (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{NaAlH}_4$  vs. Al metal)
- Ambiguity in previous XPS studies regarding peak assignment for Al-hydrides
  1. Zuttel *et al.* reported  $\text{Al}^{3+}$  2p BE > 75.1 eV for  $\text{NaAlH}_4$ <sup>a</sup>
  2. Splinter *et al.* reported Al 2p BE of Al-H to be 72.4 eV. (w.r.t. 72.9 eV for Al metal)<sup>b</sup>
- Our simulations of Al 2p BE provide standards for Na-Al-H compounds

- a. *Zuttel et al.* *Journal of Applied Chemistry*, 2001, 51, 1211-1218
- b. *Splinter et al.* *Journal of Applied Chemistry*, 2001, 51, 1211-1218

Theory approach shows that past work has incorrectly assigned chemical species. XPS binding energies do not merely follow oxidation state!

(see ST129 for additional details)

# Approach (Diffusion): Low Energy Ion Scattering experiments on $\text{Mg}(\text{BH}_4)_2$ films

In-situ desorption of  $\text{Mg}(\text{BH}_4)_2$  film:

- Sample charging affects measured surface concentrations
- Mitigated by using an electron flood gun to compensate for charge deposited by incoming ions

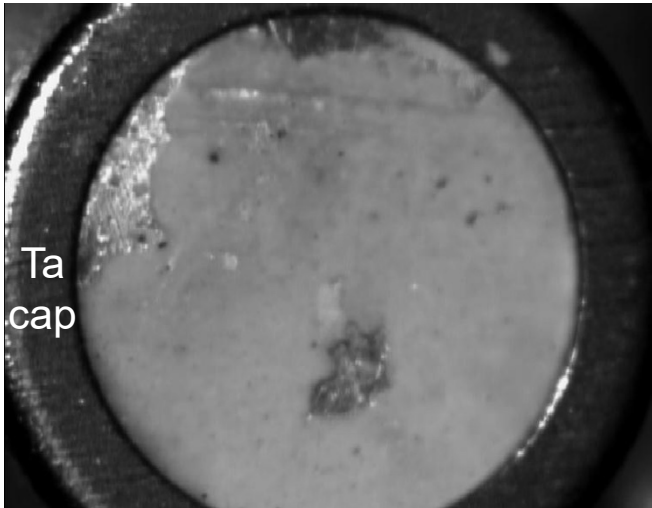
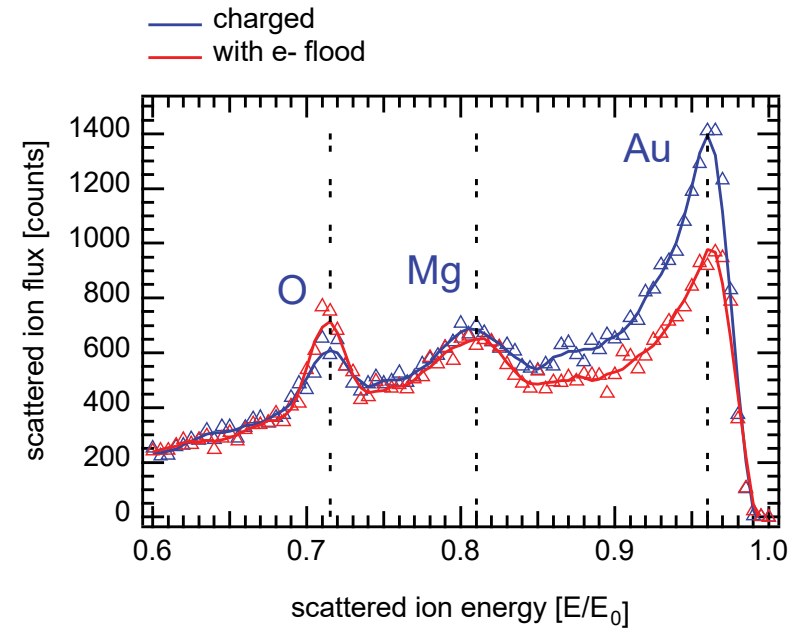


Image of continuous film of  $\text{Mg}(\text{BH}_4)_2$  pressed into Au substrate



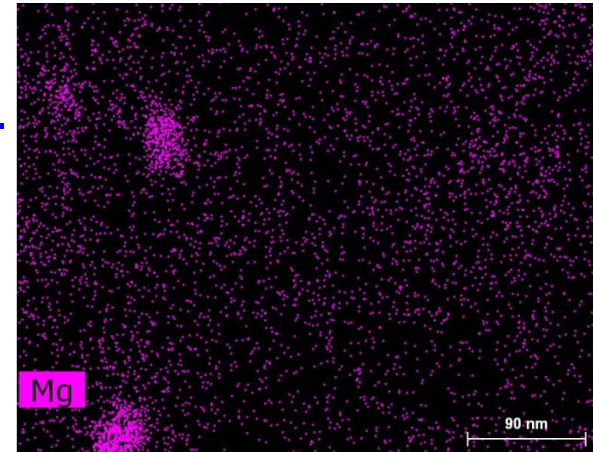
Ion energy spectrum showing how surface charging affects measured concentrations

## Experiments:

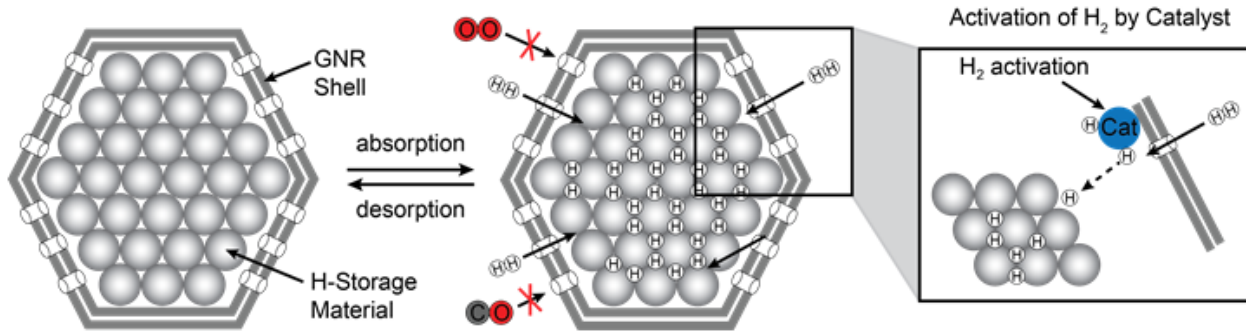
- Heating to 600 °C, linear profile (1.5 °C/s)
- Surface concentration of H monitored with LEIS
- Evolved species detected with line-of-sight mass spectrometer

# Accomplishment (Kinetics): Nanosizing and additive functionality for nanohydride encapsulation

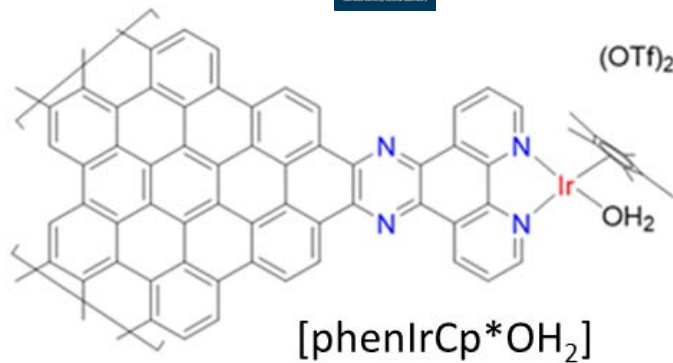
We successfully synthesized free-standing  $MgB_2$  nanoparticles,  $H_2$  uptake measurements are imminent.



Toward nanoconfined  $MgB_2$  in functionalized GNRs:



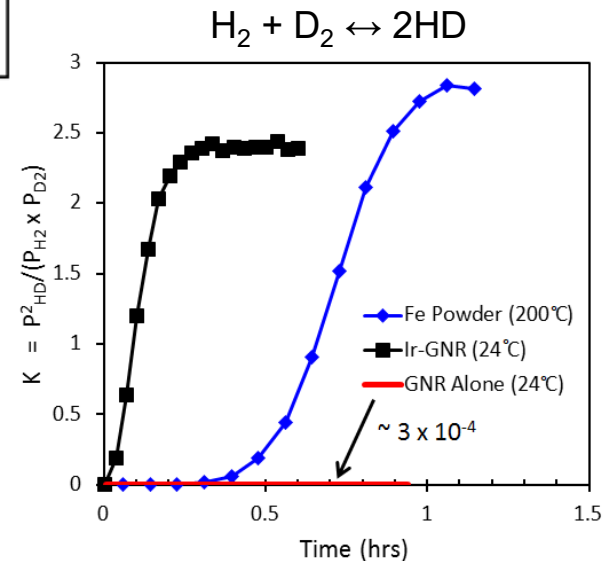
Fischer Group



Ir-cat may be a source of  $H^+$  and  $H^-$  (not  $H^\bullet$ )

$H_2$  activity confirmed

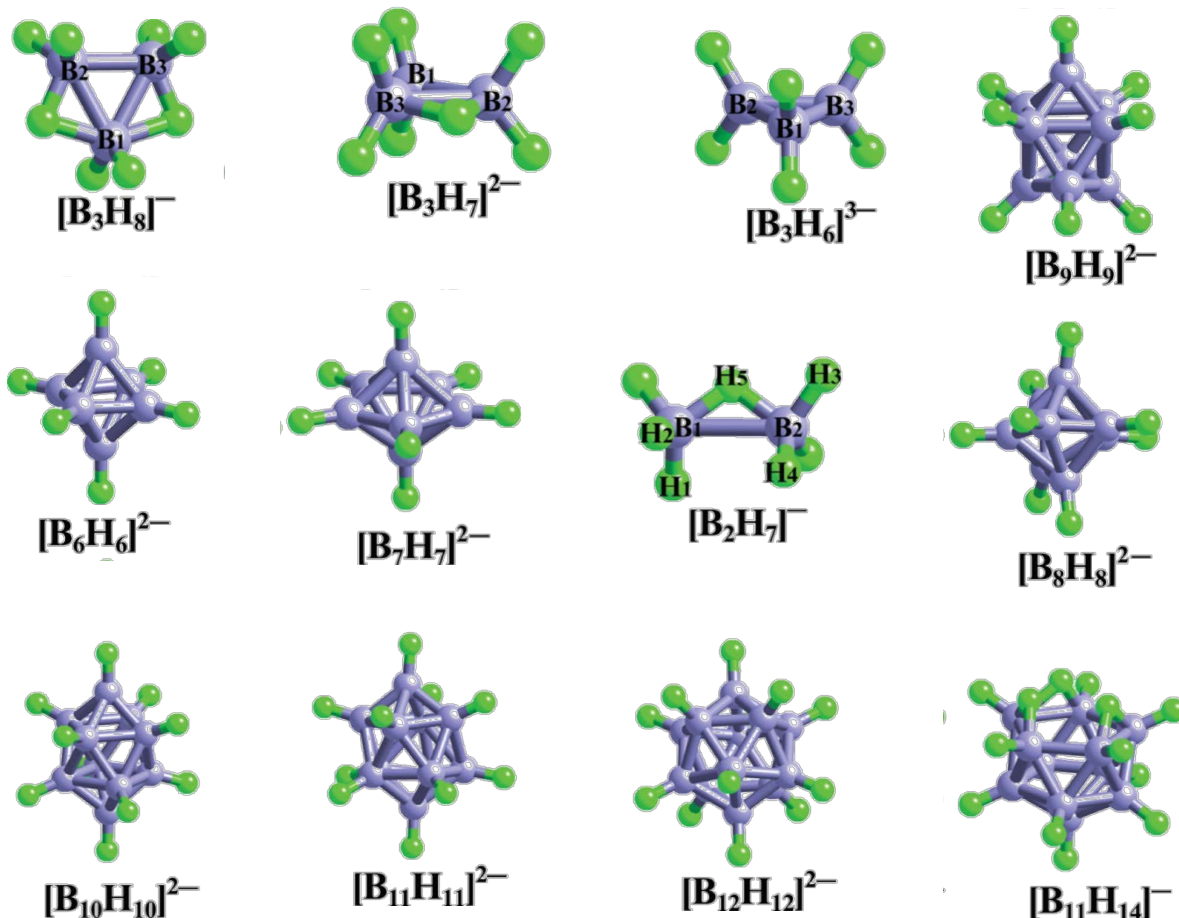
Next step is  $MgB_2$  nanoconfinement



(see ST130 de additional details on GNR synthesis)

# Accomplishment: Force-Field development for Mg-B-H

⇒ *Reliable force-fields are needed to assess the thermodynamic and kinetic properties of  $Mg(BH_4)_2$*

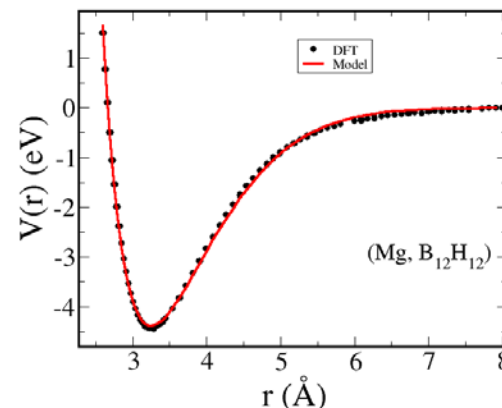


## Approach

1. A quadratic force-field is used for intra-molecule atoms. The molecule can be stabilized by multiple bond lengths
2. A Morse type force-field is fitted to DFT results for inter-molecule atoms

## Results

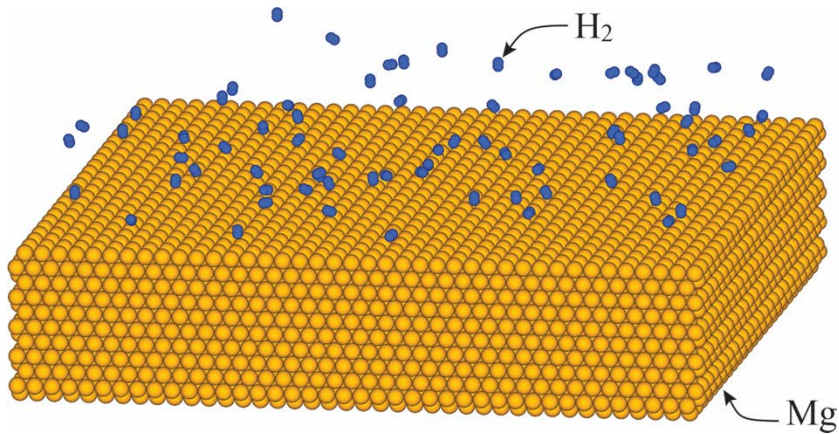
1. A highly-automated fitting code has been developed
2. Preliminary fitting to the DFT values of the  $Mg-B_{12}H_{12}$  interaction is encouraging



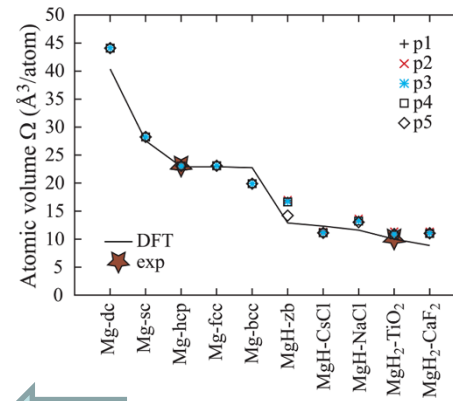


# Accomplishment (Kinetics): Validated models of diffusion

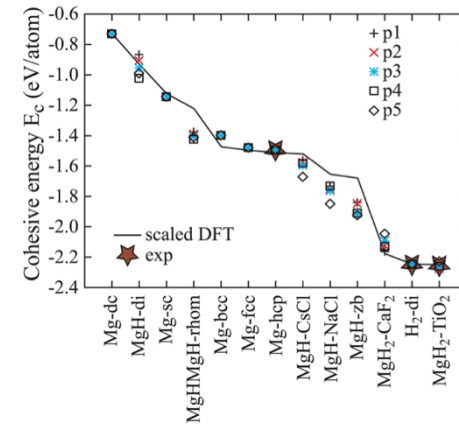
## MD Simulations of (De)Hydrogenation



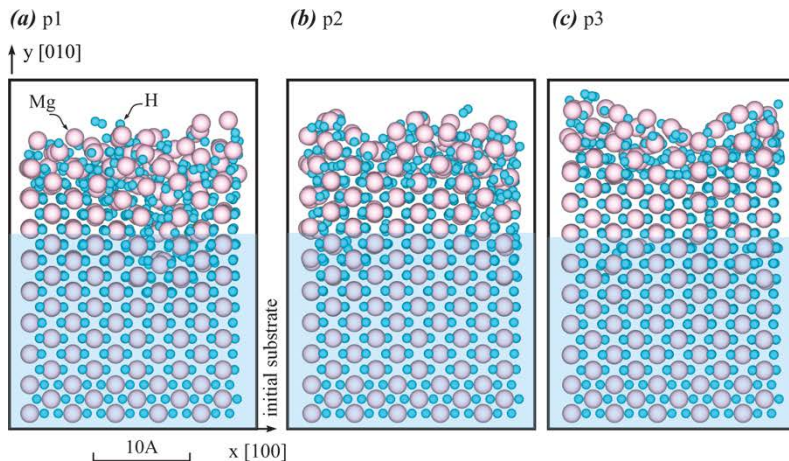
## Energy Trends



## Volume Trends



## Crystalline Growth



1. Our MD enables (de)hydrogenation simulations without assumptions
2. We achieve this by using:
  - A high-fidelity bond order based force-field format
  - Ensure energy and volume trends of different phases
  - Capture crystalline growth of MgH<sub>2</sub>
3. We developed 5 versions of such force-fields, enabling uncertainty quantification due to force-field variations
4. A manuscript entitled “An analytical bond order potential for Mg-H systems” is in preparation