Sandia National Laboratories

HyMARC

H2FC Hydrogen and Fuel Cells Program

HyMARC: Sandia's Technical Effort

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Sandia National Laboratories, Livermore, CA, USA

Annual Merit Review Meeting, Arlington, VA – June 7, 2017

Enabling twice the energy density for hydrogen storage

Project ID# ST128

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 09/17/2015

SNL R&D Budget

- FY15 Funding Level: $250K
- FY16 Funds: $925K
- FY17 Funds: $1.175M
- Total DOE Funds: $2.35M

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)

Partners

HyMARC Hydrogen Materials Advanced Research Consortium

Sandia National Laboratories

Lawrence Livermore National Laboratory

BERKELEY LAB Lawrence Berkeley National Laboratory

Relevance and impact

Provide the *foundational understanding of phenomena governing thermodynamics and kinetics of hydrogen release and uptake* in all classes of H_2 storage materials

Energetics	Kinetics	Reversibility	Capacity

(Task 1)	(Task 2)	(Task 3)	(Task 4)	(Task 5)
Thermodynamics	**Diffusion**	**Surfaces**	**Interfaces**	**Additives**
V. Stavila, Lead		R. Kolasinski, Lead		L. Klebanoff, Lead

Sandia's objectives/responsibilities within HyMARC:

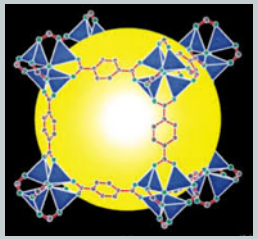
⇒ **Provide leadership for HyMARC** as a whole, and specifically to Tasks 1, 3, and 5
⇒ Investigate what **physical and chemical influences can improve thermodynamics**
⇒ **Determine the importance of hydrogen diffusion** (surface, bulk) on H_2 storage kinetics
⇒ **Elucidate surface/interface phenomena** (structure, composition) that impact H_2 storage
⇒ **Understand intermediate formation** and methods for mitigation to increase capacity
⇒ Determine the underlying **mechanisms for additive increase in kinetics and reversibility**
⇒ **Apply SNL multiscale codes to discover new materials and new mechanisms** of storing hydrogen, provide input for database development

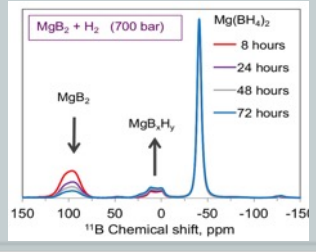
Approach: Mitigate problematic physical phenomena

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

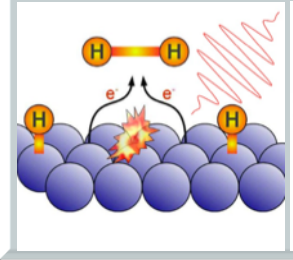


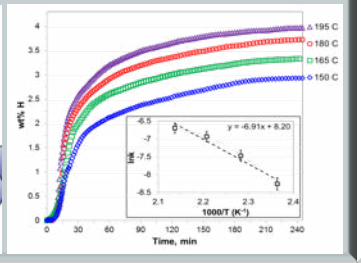


Kinetics

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

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

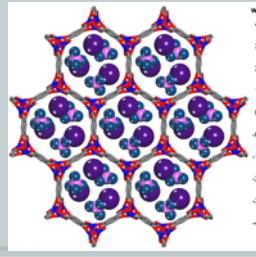


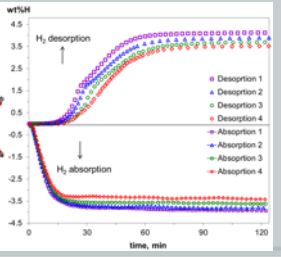


Reversibility

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



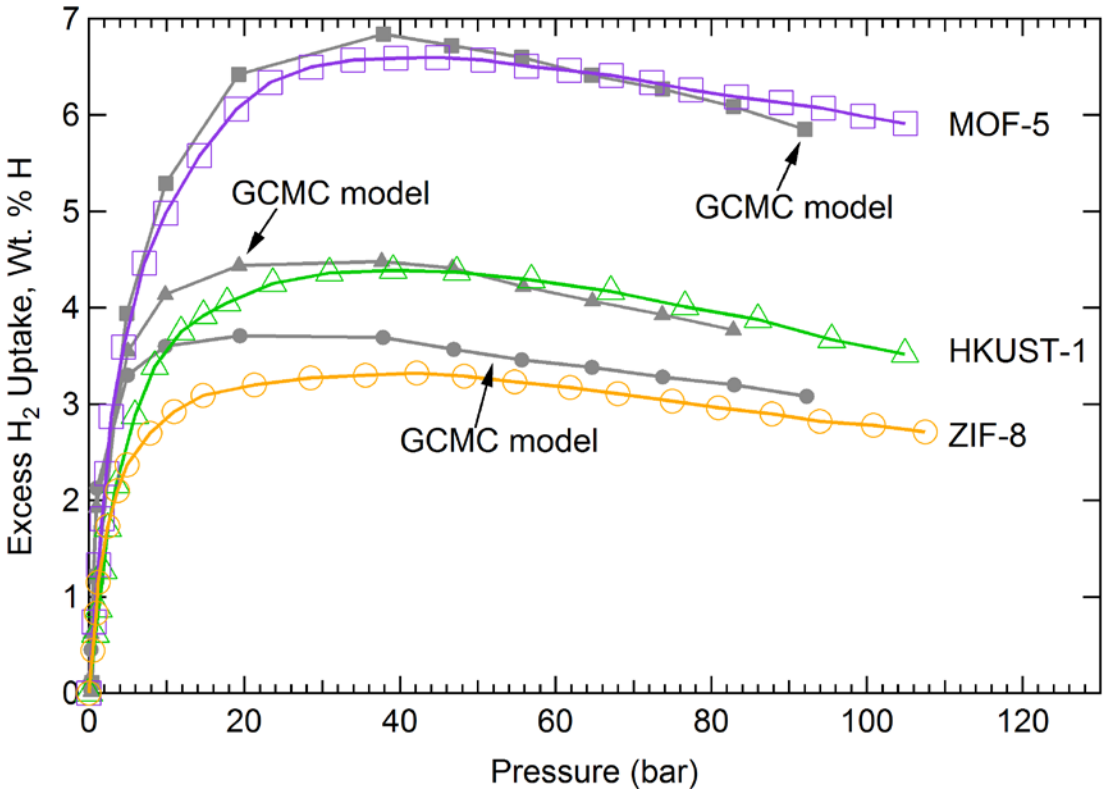


⇒ ***<u>Sorbents:</u> Develop Quantum Monte Carlo (QMC) and Grand Canonical Monte Carlo (GCMC) tools to identify design rules for materials with H_2-sorbent binding energies of 15-20 kJ mol^{-1} H_2***

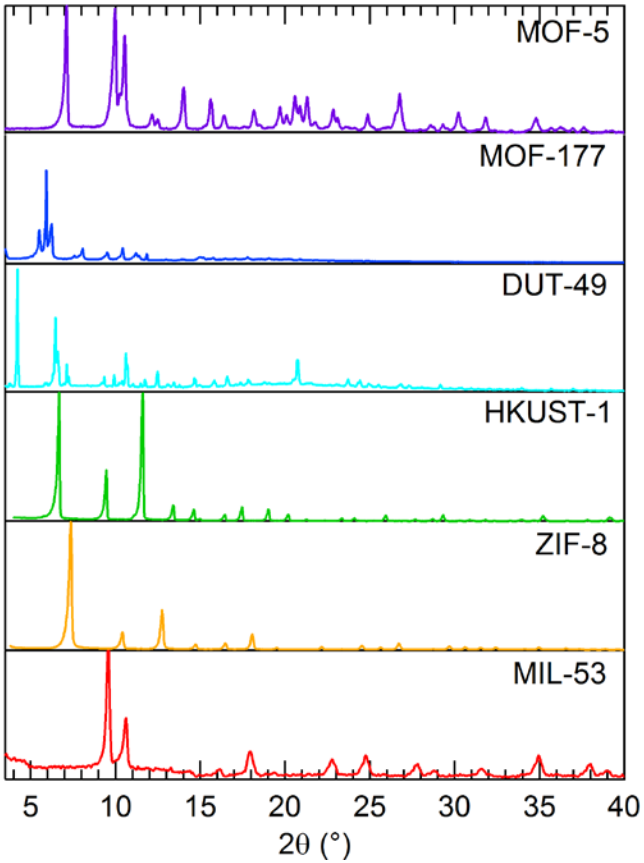
⇒ ***<u>Metal hydrides</u>: Evaluate doping, amorphization, surface modification and nanostructuring as strategies to improve the kinetics and thermodynamics of metal hydrides to achieve reversible hydrogen release and uptake with $\Delta H \approx 27$ kJ mol^{-1} H_2***

Accomplishment (Sorbent thermodynamics): Library of MOFs for QMC and GCMC model validation

H_2 isotherms at 77 K for QMC and GCMC model validation



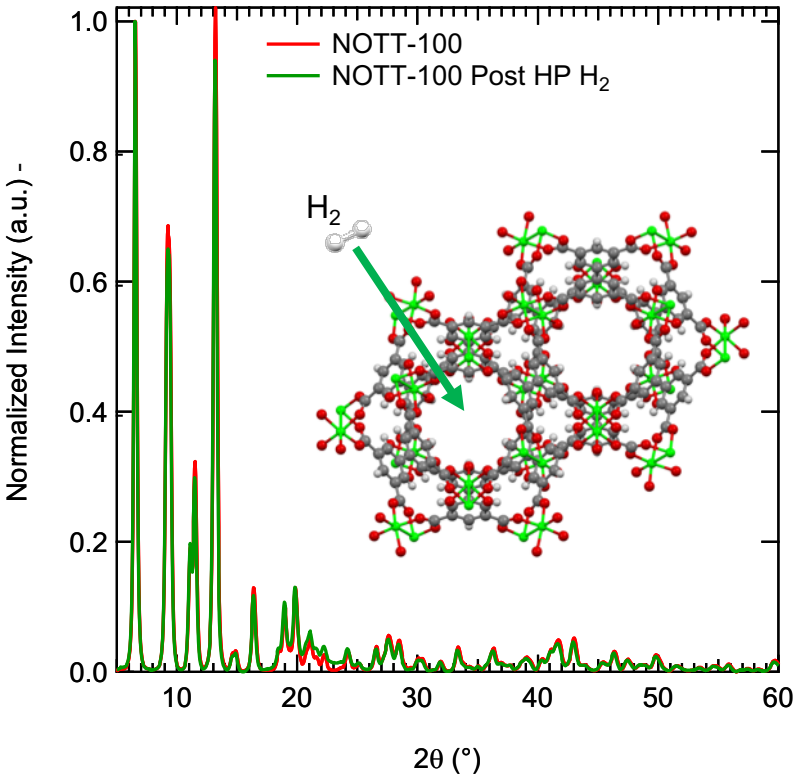
XRD patterns of synthesized MOFs



⇒ ***Developed protocols for reproducible MOF synthesis and activation and measured high-accuracy hydrogen isotherms for QMC and GCMC theory model validation***

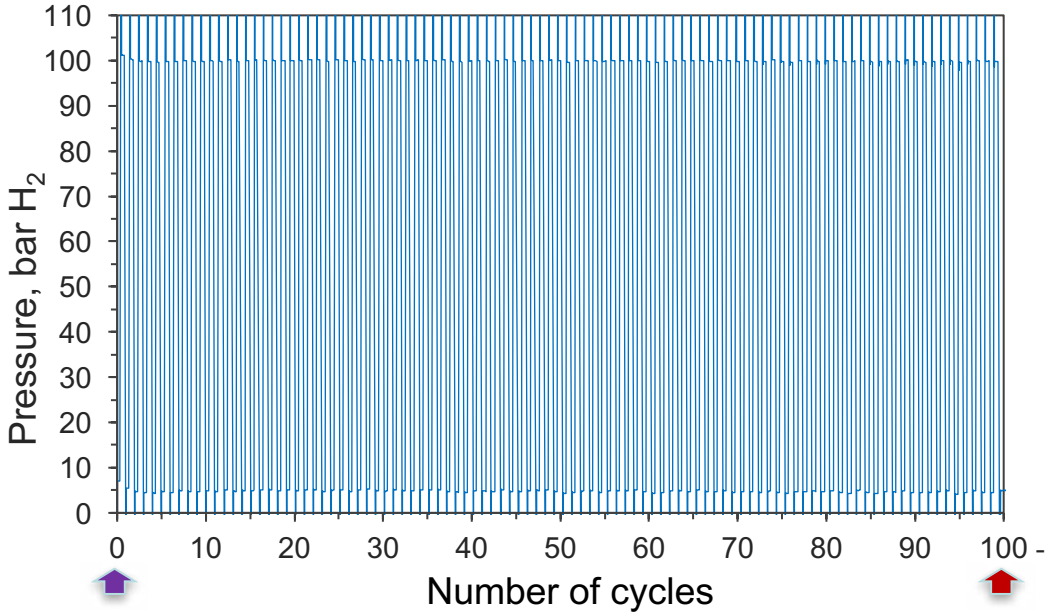
⇒ ***Simulations and experiments are in agreement within a 10-20% "band of uncertainty"***

Accomplishment (Reversibility in sorbents): MOF surface area and capacity degradation observed upon H_2 cycling



NOTT-100 under 700 bar H_2 for 25 h

Testing reversibility, cycle life, and durability

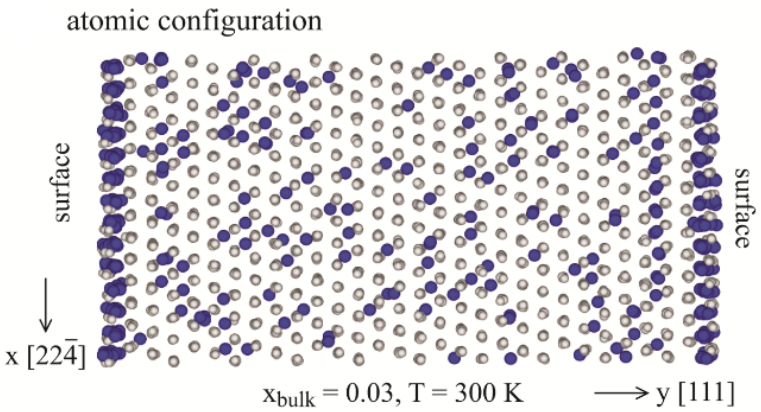


NOTT-100	BET, m^2/g	wt% H (0 °C, 35 bar H_2)
As-synthesized	1130	0.52
After 100 cycles	1060	0.49

- ***NOTT-100 (Cu-paddlewheel): structure stable under H_2, no changes in XRD pattern up to 700 bar H_2***
- ***6.2% decrease in BET surface area and 5.7% decrease in hydrogen uptake (at 0 °C and 35 bar H_2) after 100 charge/discharge cycles; degradation mechanism is under investigation***

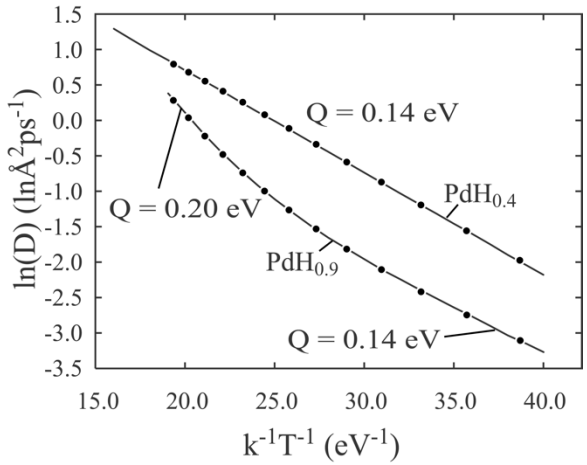
Accomplishment (Kinetics): Validated models of diffusion

MD prediction of H segregation on {111} Pd surface



Model consistent with experiments by Conrad *et al*. showing H segregation on Pd(111) surface, *Surf. Sci.*, **1974**, *41*, 435.

Validated H diffusion in bulk Pd



- Experimental data by Bucur *et al*, Holleck *et al*, Simmons *et al*, Maeda *et al*, Pietrzak *et al*, Hara *et al*, Yoshihara *et al* and Zuchner *et al* validate the predicted single barrier at low compositions.
- Experiments by Aron et al, Cornell et al, Mazzolai et al, Burger et al, Torrey et al validate the predicted two barriers of ~0.1 and ~0.2 eV at high hydrogen content.

📖 *X. W. Zhou, F. El Gabaly, V. Stavila, M. D. Allendorf, JPCC,* **2016**, *120*, 7500.

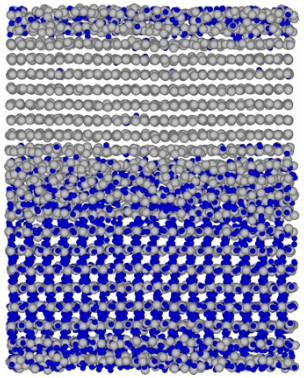
MD models were validated for palladium hydride; next, we are applying this approach to MgH_2

- ⇒ ***Bond-Order Potential (BOP) formalism is analytically derived from quantum mechanical theories***
- ⇒ ***BOP parameters are fitted to bond energy, bond length, and elastic constants of a large number of Mg, H, and Mg-H phases***
- ⇒ ***High-power computing and multiple iterations results in significantly improved BOP over literature potentials***

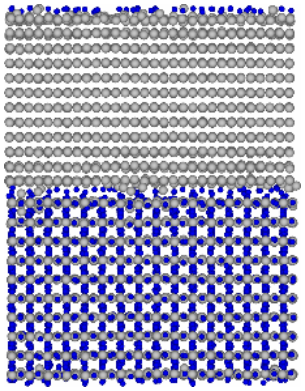
This is an unique Sandia capability as theoretical force field method development is a difficult and time-consuming task

MD simulations of Mg-on-MgH_2 at 300 K

ReaxFF (Adri van Duin et al.), 0.1 ns



Our BOP, 1.0 ns

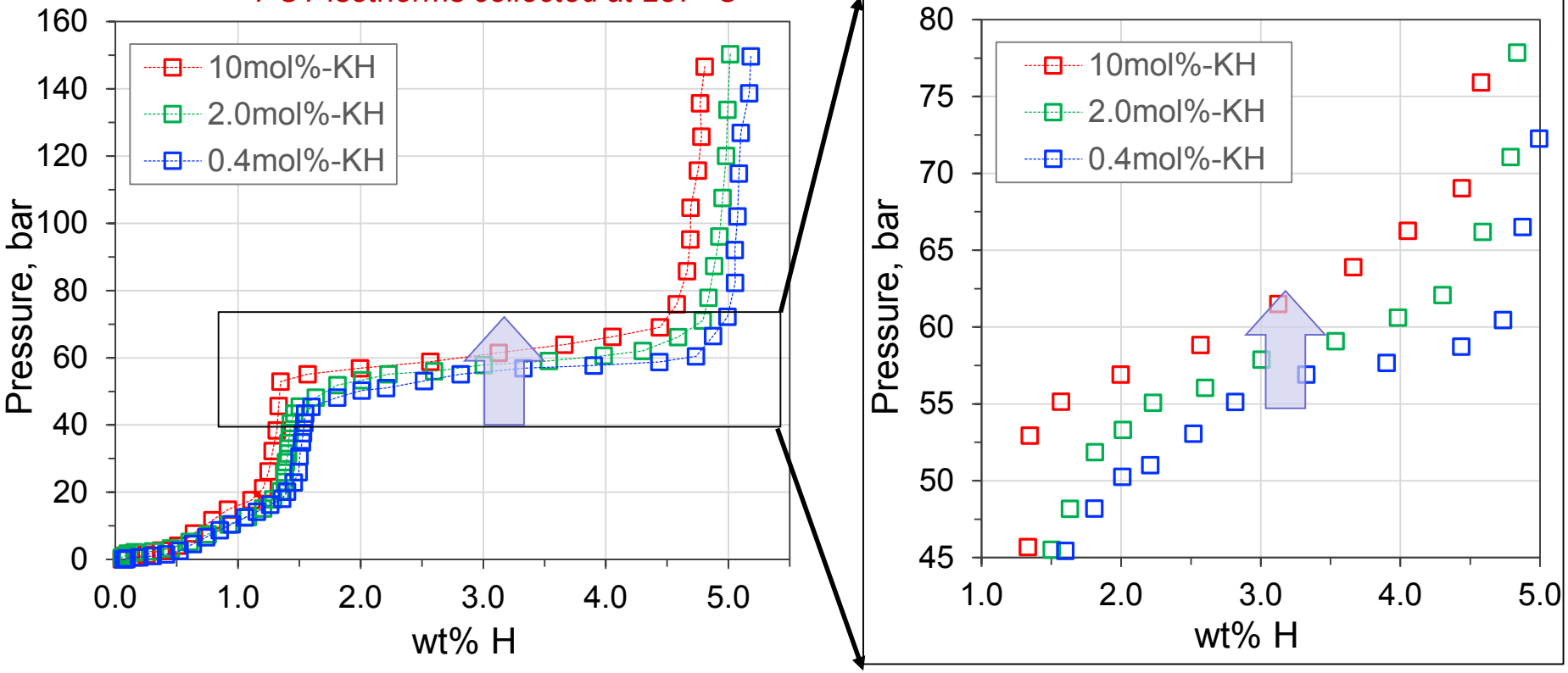


Accomplishment (Thermodynamics): KH doping increases the equilibrium hydrogen pressure of Li-Mg-N-H

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

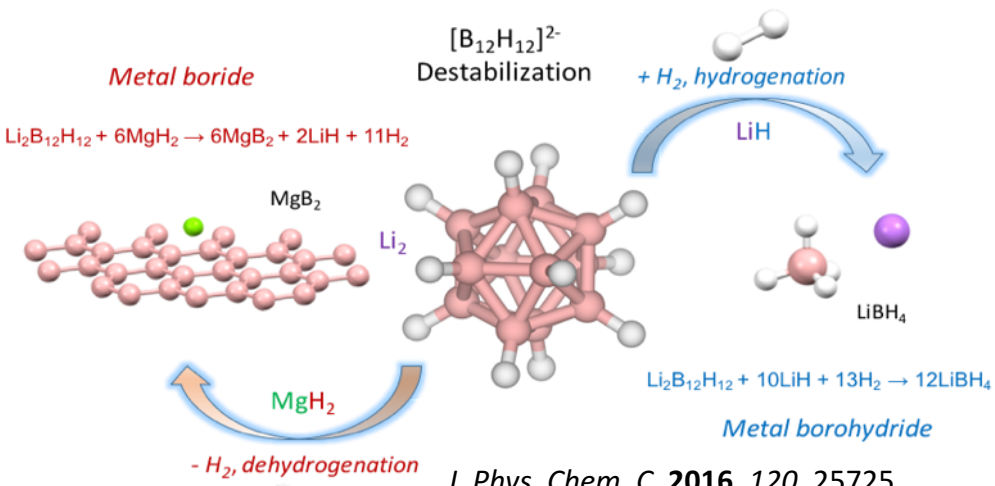
Cheng *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 5828

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***

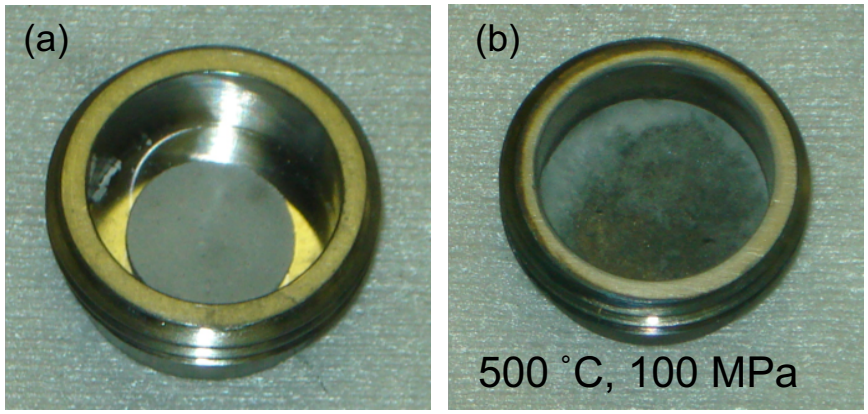
Accomplishment (Reversibility): Established reaction conditions to increase reactivity of $[B_{12}H_{12}]^{2-}$ intermediates



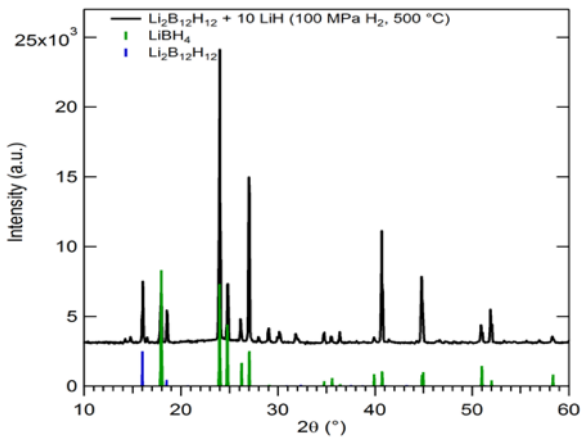
J. Phys. Chem. C, **2016**, *120*, 25725.

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

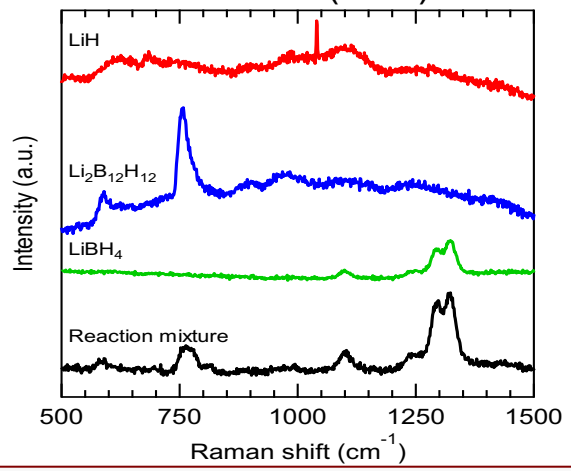
Before reaction *After reaction*



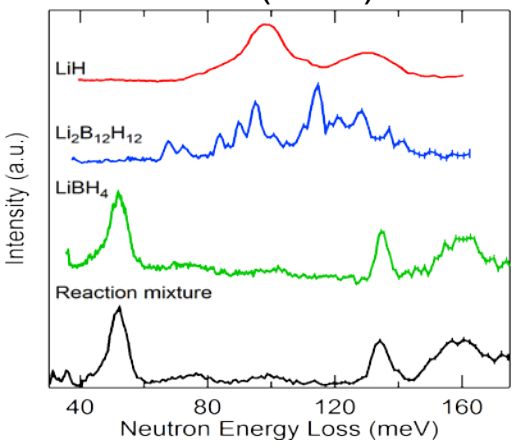
XRD (SNL)



Raman (SNL)



NVS (NIST)

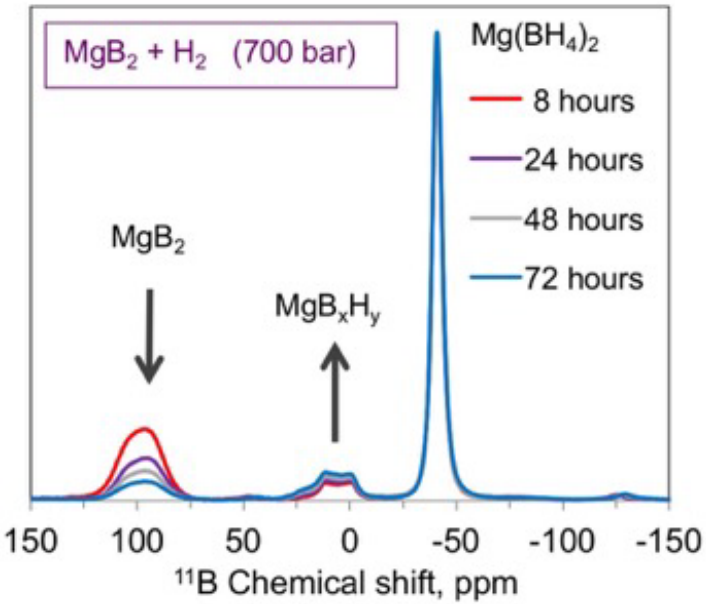


⇒ ***The reactivity of alkali metal $B_{12}H_{12}$-species can be increased either by applying high-pressure H_2 to form borohydrides or through dehydrogenation to form metal borides***

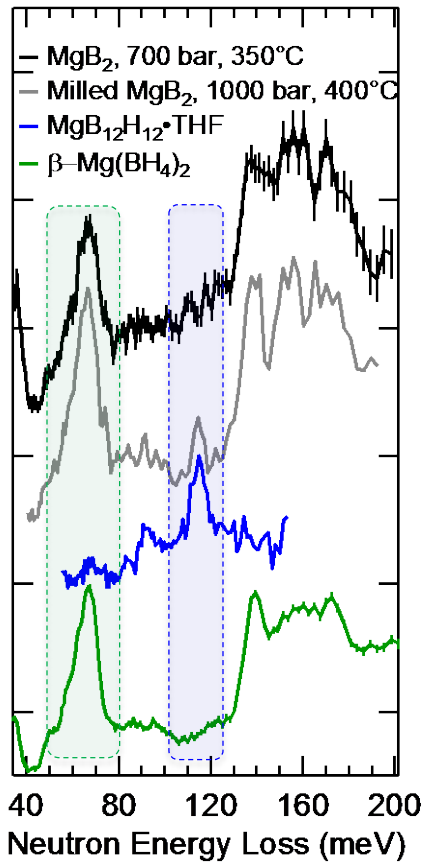
Accomplishment (Reversibility): Revealed reactivity of $Mg(BH_4)_2$ and MgB_2 under high-pressure H_2

with NIST, PNNL (HySCORE) and UH-Manoa (Seedling)

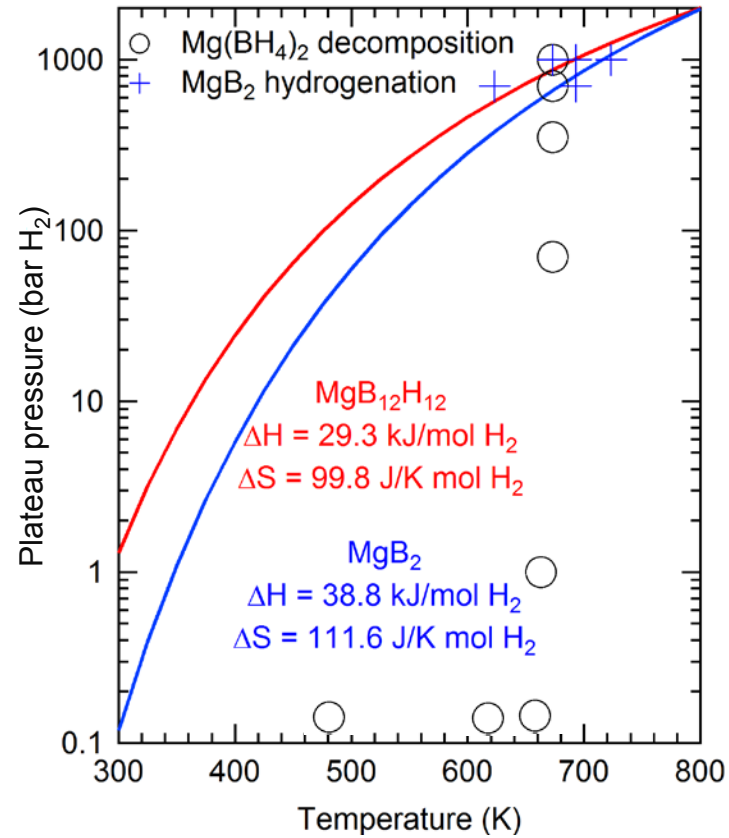
$$MgB_2 + H_2 \rightarrow Mg(BH_4)_2 \rightleftarrows MgB_{12}H_{12} + MgH_2$$



NVS (NIST)



Probing plateau pressure function of T



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

⇒ ***Bulk $Mg(BH_4)_2$ generates Mg-B-H intermediates even at $P(H_2) \geq 350$ bar*** *(see extra slides)*

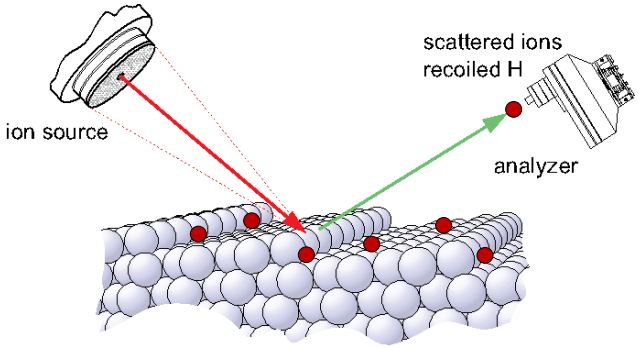
⇒ ***Results used for assembling a reliable Mg-B-H phase diagram and for theory model validation***

Approach (Surfaces): Employ suite of complementary diagnostics to probe phenomena at relevant length-scales

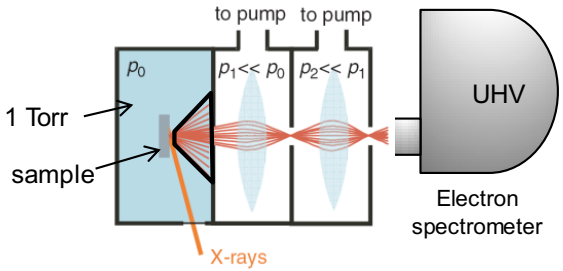
Motivation:

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

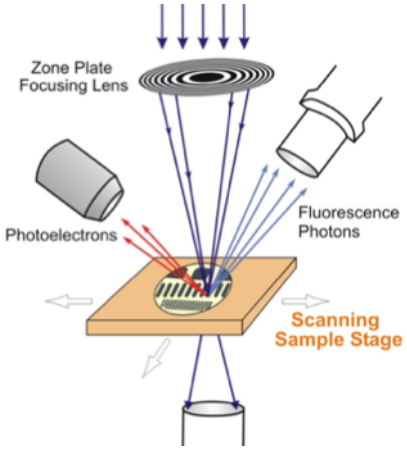
Technical Approach: *In-situ* techniques enable us to probe the surface chemistry for H_2 storage materials



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?***

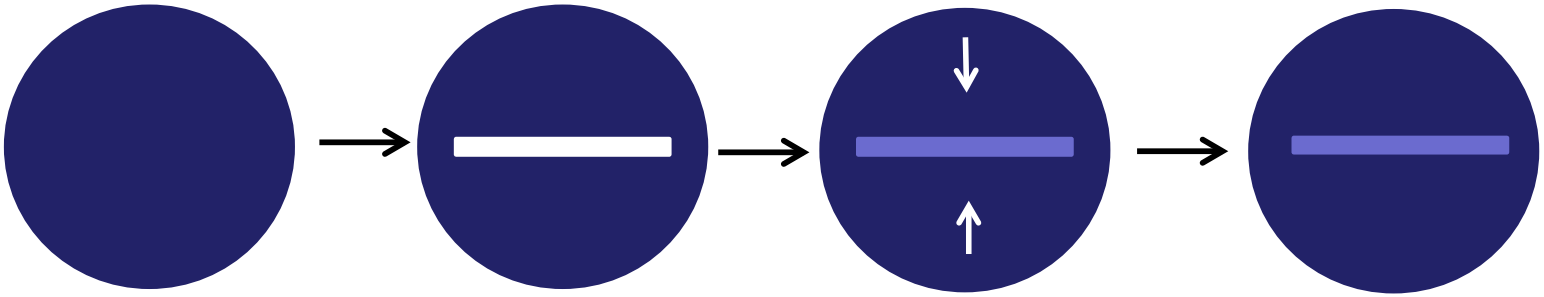
⇒ ***What is the spatial distribution of species of interest?***

⇒ ***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)

Accomplishment (Surfaces): Developed a method to accurately measure surface diffusion using LEIS

Methodology: *Use ion beam to clear the surface area of H, and then use ion scattering to monitor diffusion from periphery. The approach avoids thermal damage to sensitive samples.*



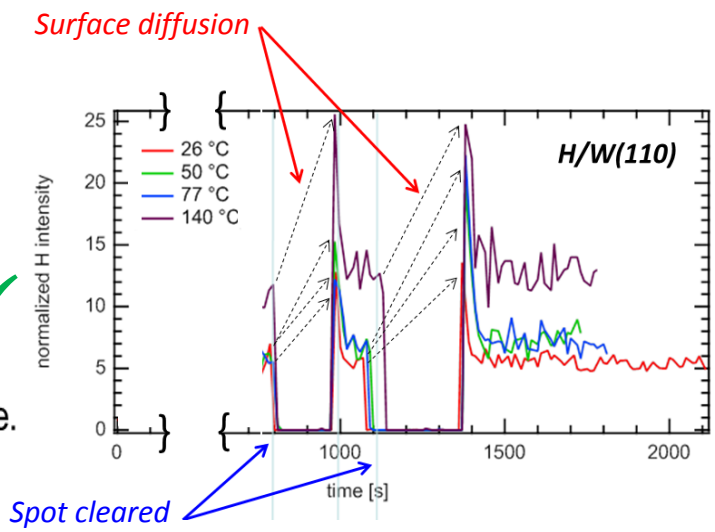
H-covered Surface → Grazing-incidence ion beam sputters H from a line on the surface → H Diffusion Refills the Cleared Line → Ion Scattering Detects Refilling H

Robert Kolasinski
Leonard Klebanoff
(LEIS)

Tae-Wook Heo
(modeling)

Qualifying the capability involves demonstrating:

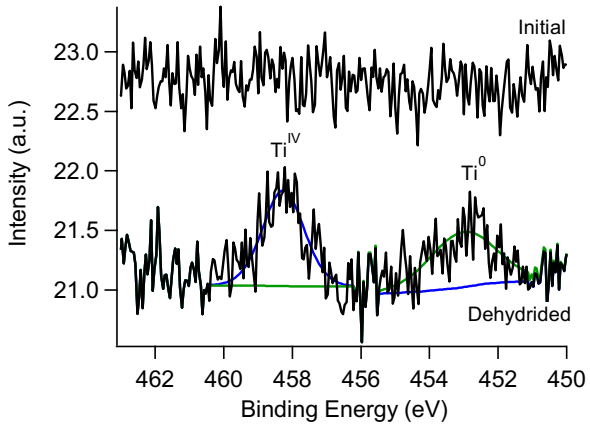
1. H can be detected at ~ 0.1 monolayer levels. ✓
2. We are not damaging the substrate by the ion-induced H removal. ✓
3. H can be removed quickly compared to diffusion timescales (minutes). ✓
4. The refilling H can be quickly detected (seconds). ✓
5. The H is due to surface diffusion and not simple adsorption from the gas phase.
6. Sensible temperature-dependent diffusion can be seen. *(in progress)*



Accomplishment (Kinetics): Analysis of surface and bulk Ti-doped $NaAlH_4$ reveals Ti role in H_2 desorption

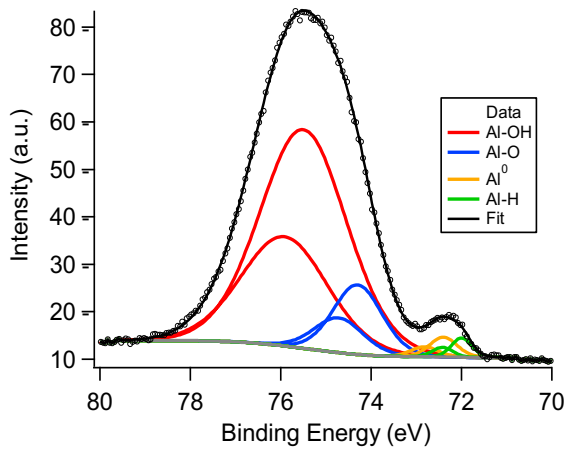
Model system for method development: Ti-doped $NaAlH_4$

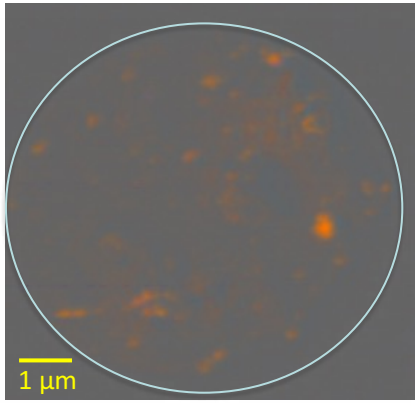
- Incorporates many challenging features within a well-studied material (experiment and theory)
- *Sample format: designed to emulate realistic materials*



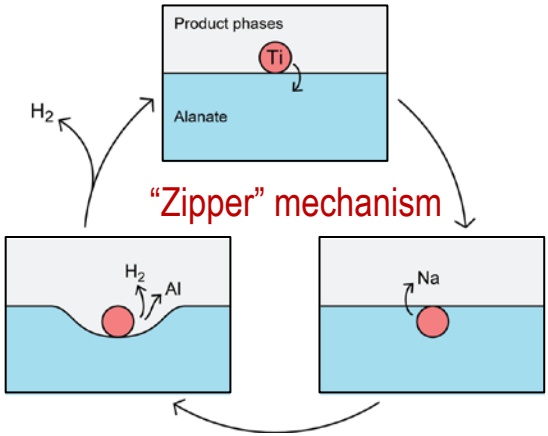
No evidence of surface Ti (Ti, Ti_2O_3, or $TiCl_x$) before or during desorption (AP-XPS, LEIS, and Auger spectroscopy).

Four Al species detected by AP-XPS during dehydrogenation





STXM of doped particle Ti^0 in orange



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

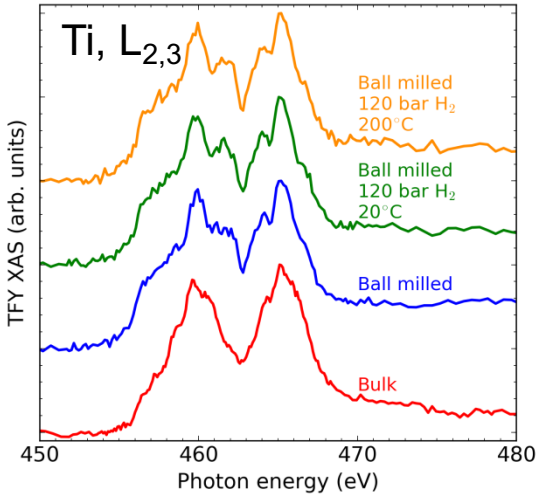
⇒ *manuscript in progress*

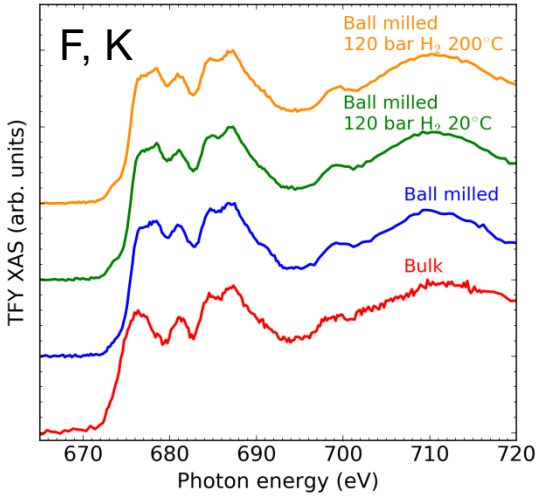
⇒ ***New things learned even with well-studied material: lack of Ti on the surface or near-surface (0 – 10 nm) during H_2 desorption disproves models invoking surface Ti during dehydrogenation***

⇒ ***Accurate assignments of XPS and XAS spectral features highlight importance of computational spectroscopy***

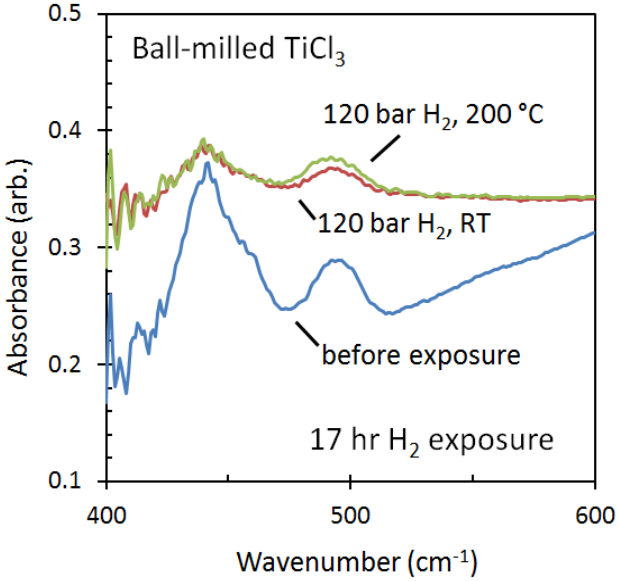
Accomplishments (Additives): Detailed analysis shows that pure TiF_3, $TiCl_3$ do not promote H_2 dissociation

XAS study of Ti and F species



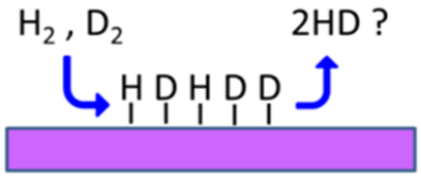


FTIR probe of Ti-Cl bonding



- *-XAS shows that bulk and ball-milled TiF_3 and $TiCl_3$ are not affected by H_2 even at 120 bar.*
- *-IR and XRD analysis also indicate that bulk and ball-milled TiF_3 and $TiCl_3$ are unreactive towards hydrogen.*

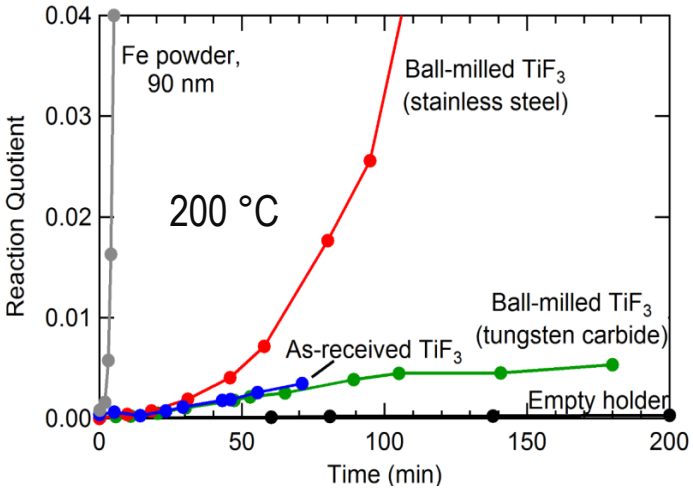
H-D exchange studies



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

~ 4.0 at equilibrium

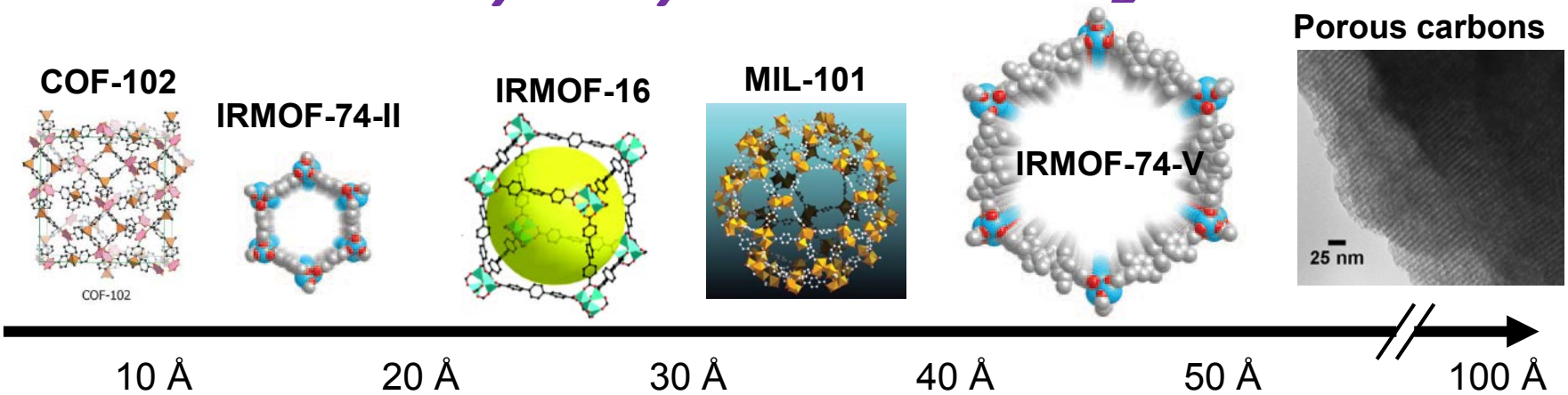
- *Only small amounts of HD formed, indicating no catalysis of H-H bond scission by TiF_3 (bulk or milled)*



⇒ ***Experiments show definitively that pure TiF_3 and $TiCl_3$ cannot influence H_2 storage reactions***

Approach (Reversibility and Kinetics): Nanostructured metal hydrides for hydrogen storage

Why study nanostructuring?

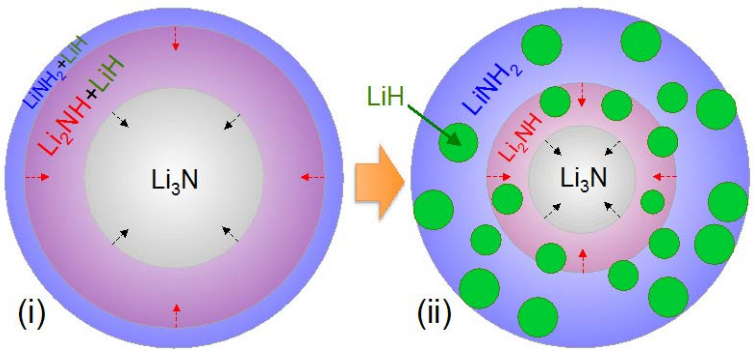


Host (MOFs, porous carbons, graphene aerogels) pore size and functionality can be systematically varied

We want to determine whether reducing metal hydride particle size and functionality:

- ⇒ ***Improves thermodynamics***
- ⇒ ***Increases reaction rates***
- ⇒ ***Enables reversible H_2 uptake and release***
- ⇒ ***Avoids un-wanted intermediates and byproducts***

$$Li_3N + 2H_2 \rightleftharpoons LiNH_2 + 2LiH$$



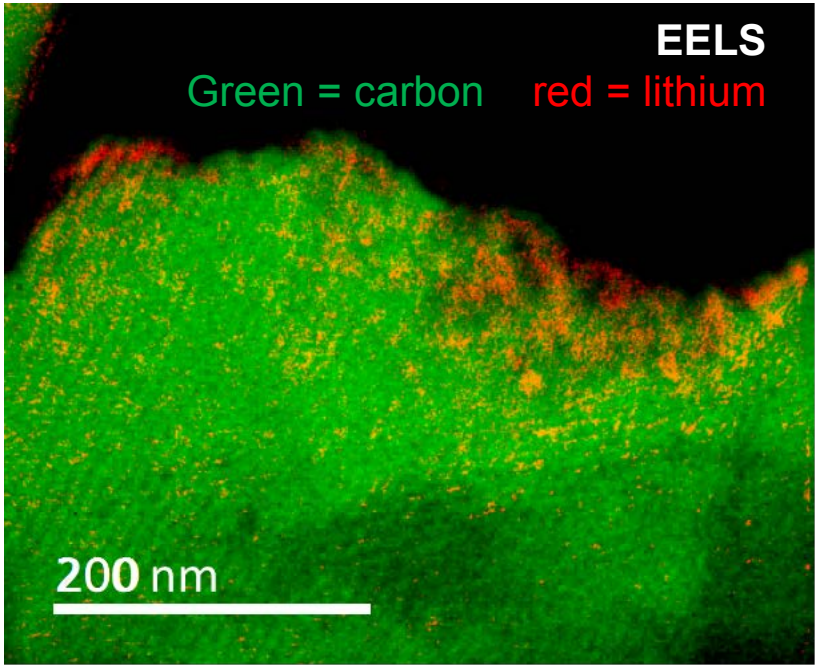
B. Wood et al. Adv. Mater. Interfaces **2017**, *4*, 1600803

Accomplishment: Demonstrated improved kinetics and intermediate suppression at nanoscale

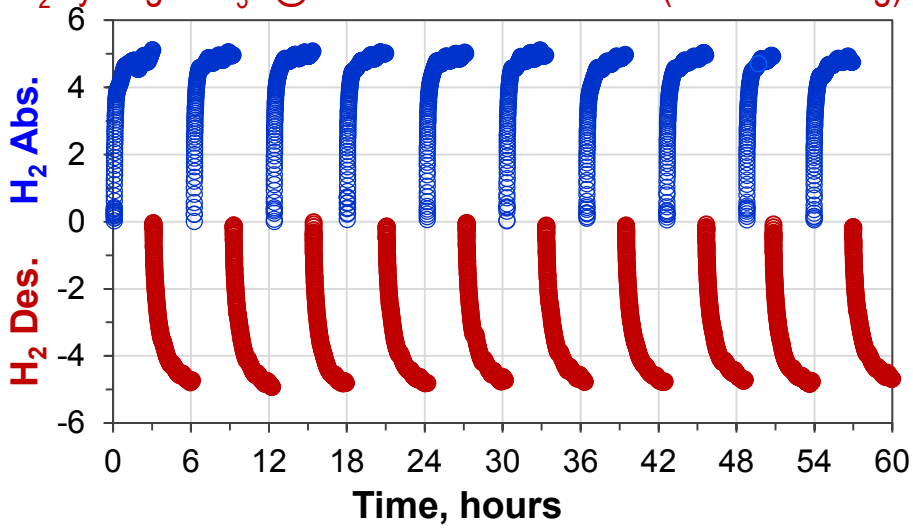
Bulk (2-step reaction pathway)

$$Li_3N + 2H_2 \rightleftharpoons Li_2NH + LiH + H_2 \rightleftharpoons LiNH_2 + 2LiH$$

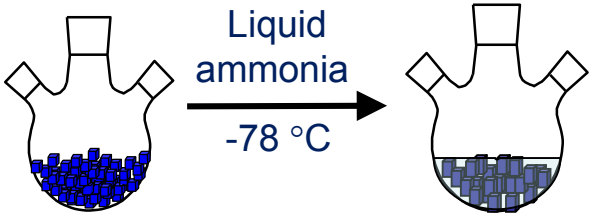
Nano(<12 nm, 1-step reaction pathway)

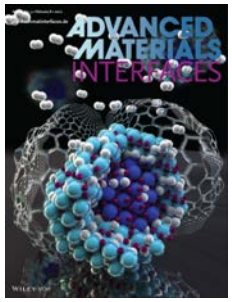


H_2 cycling in Li_3N@6nm-Carbon at 250 °C (52wt% loading)



US Patent Application # 62/235,930





Adv. Mater. Interfaces **2017**, *4*, 1600803

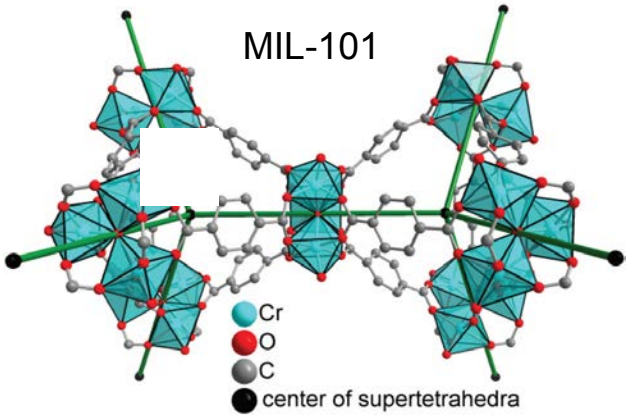
(*Journal Cover*)

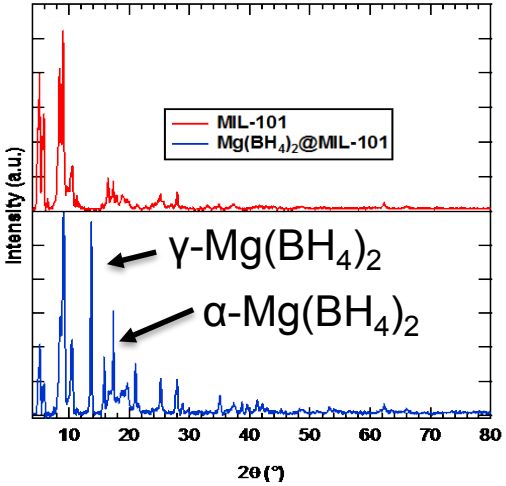
- ***Liquid NH_3 infiltration approach enables high loadings (>50% by weight) of Li_3N in porous carbons***
- ***Demonstrated 5wt% reversible H_2 cycling and Li_2NH species suppression in Li_3N@6nm-Carbon***

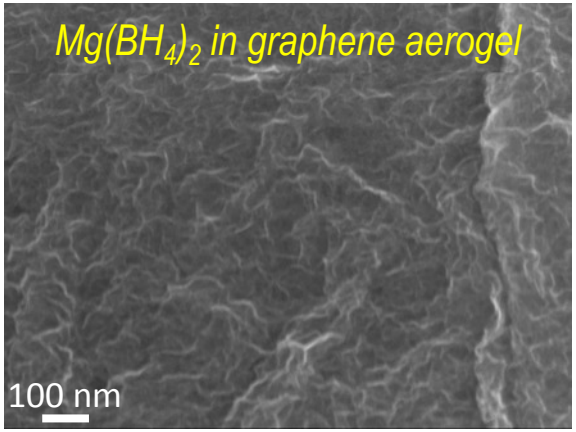
Accomplishment: In-pore synthesis of nanoscale $Mg(BH_4)_2$ inside MOFs and graphene aerogels

$$Mg(nBu)_2 + BH_3{\bullet}S(Me)_2 \rightarrow Mg(BH_4)_2{\bullet}2S(Me)_2$$

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

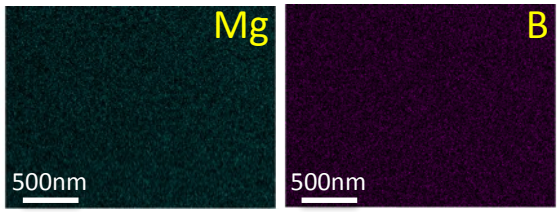




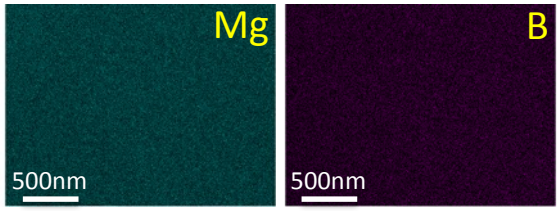


MIL-101	BET Surface Area (m^2/g)	Pore Volume (cc/g)
Uninfiltrated	1628	0.80
Infiltrated	288	0.16

EDS maps, as-synthesized



EDS maps, after desorption



- ***SEM and EDS mapping shows Mg and B are evenly distributed within the sample, confirming $Mg(BH_4)_2$ is inside the pores***
- ***The new synthetic method allows efficient infiltration of high-capacity metal borohydrides to minimize the weight penalty***

Accomplishment (Thermodynamics): Sandia 1000 bar high-pressure hydrogen station fully operational

Sandia high-pressure H_2 station

HyMARC-HySCORE-Seedling projects collaboration

- Up to 1000 bar H_2 and 400 ˚C
- Holds up to 4 different samples at once
- Employed for:
  - Synthesis of metal hydrides that cannot be synthesized in another way
  - Destabilization of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ compounds
  - Hydrogenation of metal borides, *e.g.* MgB_2, MgB_2-etherates
  - Stability of hydrides and sorbents under high-pressure H_2

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Milestones

Milestone (revised)	Description	Status*
Q3 FY16	Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating *Developed surface hydride characterization tools using Ti-$NaAlH_4$ model system*	100%
Q4 FY16	Identify hydride mobile species and diffusion pathways *Validated theory models for accurate prediction of surface and bulk H-diffusion*	100%
Q4 FY16	Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, >10 nm for one prototype hydride *Synthesized nanostructured (1-20 nm) MgH_2, $Mg(BH_4)_2$ and $LiNH_2$/2LiH samples*	100%
12/31/17	Use QMC, DFT, and force fields to compute H_2 binding and select appropriate levels of theory for MOFs	50%
9/30/17	Sensitivity analysis of local binding and second-sphere effects *Measured low- and high-pressure hydrogen adsorption isotherms for sorbents*	20%
3/31/17 **Go/No-go**	Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing $\Delta H°$ *Identified a library of sorbents with open metal sites and Lewis acid/base sites*	100%
6/30/17	Modify LEIS instrument to enable surface diffusion measurements *Established a reliable low-energy ion-beam method to measure H-diffusion*	100%
9/30/17	Evaluate additive/composite strategies for improving effective ΔE *Revealed the effect of potassium on H_2 plateau pressure in Li-Mg-N-H*	20%
9/30/17	Prototype hydride surface and interface chemistry kinetic models *Provided experimental kinetic H_2 uptake/release data for Li_3N model validation*	100%

Summary of progress

Modeling

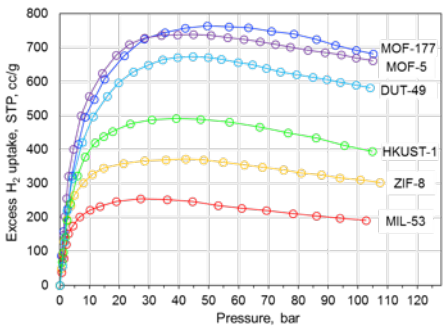
- A molecular dynamics modeling framework was established to accurately predict the diffusion kinetic barriers; proof-of-concept demonstrated for H-diffusion in Al, Mg, and Pd.

Synthesis

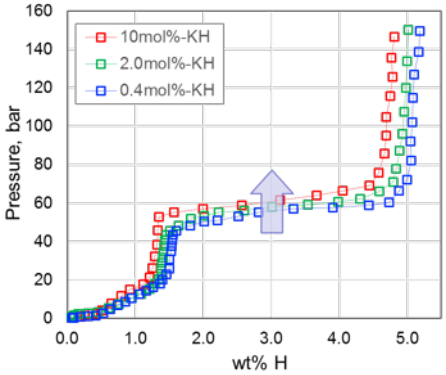
- Used Sandia high-pressure (up to 1000 bar) system to reveal the effects of high-pressure hydrogen on stability and reaction pathways of metal borohydrides
- Measured >100 low- and high-pressure H_2 adsorption isotherms for various carbons, polymers and MOFs to validate the GCMC and QMC calculations and to build a comprehensive library of structural motifs for computing interaction potentials
- Elucidated the reactivity of various additives with hydrogen and metal hydrides
- Revealed the role of nanointerfaces in ≤ 10 nm particles of $LiNH_2$+2LiH confined in nanoporous carbons

Characterization

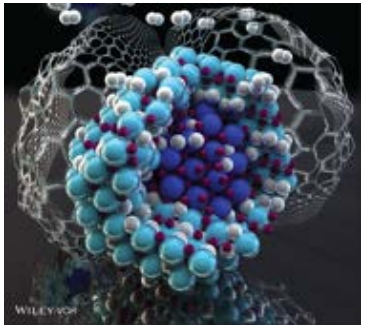
- Demonstrated that LEIS can measure surface diffusion
- Established capabilities to elucidate the effect of surfaces on hydrogen diffusion using XAS, AP-XPS, STXM, and LEIS studies



Sorbents



Bulk: $2LiNH_2 + MgH_2$



Nano: $Li_3N+2H_2 \Leftrightarrow LiNH_2+2LiH$

Future work

Modeling

- Apply newly-established Mg-H bond order potentials to reveal H-transport mechanisms in magnesium based metal hydrides

Synthesis

- Optimize synthetic approaches to microporous sorbents with a high density of open metal sites and/or Lewis acid-base sites
- Synthesize amorphous materials to test the thermodynamics theory framework
- Develop new encapsulation approaches to improve metal hydride loading inside mesoporous hosts and improve 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 diffusion in magnesium and magnesium borohydride
- Collect reliable temperature-dependent hydrogen desorption and absorption isotherms for both metal hydride and sorbent theory model validation
- Apply XAS, AP-XPS and neutron diffraction (with HySCORE) to gain insights into the degradation mechanisms of MOFs extensively cycled under hydrogen

Collaborations: Interactions with seedling projects

Prof. Eric Majzoub

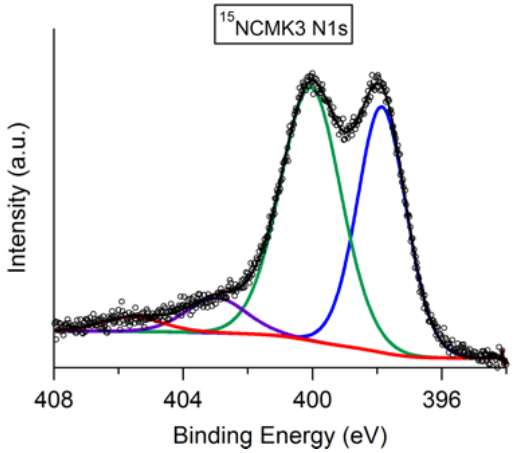
Dr. Godwin Severa -
Prof. Craig Jensen -

Prof. Mike Chung -

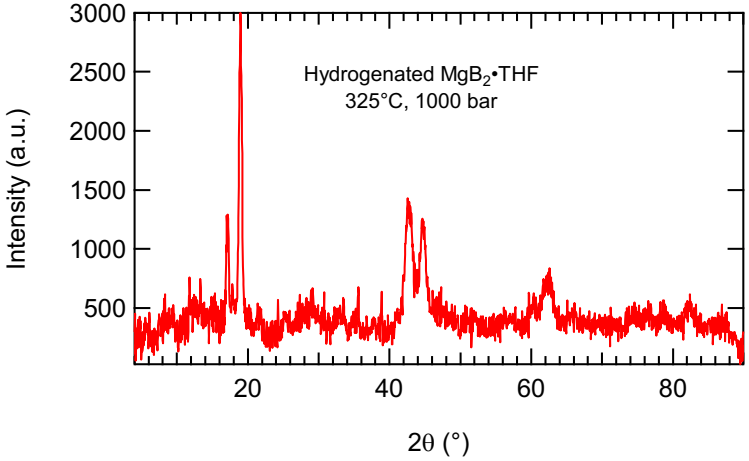
Prof. Channing Ahn
Dr. John Vajo

Dr. Di-Jia Liu

- *Hosted researchers from three seedling projects*
- *Porosimetry (low and high P), high pressure hydrogenation, XPS, LEIS, XRD, and IR experiments performed at Sandia*
- *Technical discussions and planning with all five projects*



James White
Vitalie Stavila
Farid El Gabaly
Annabelle Benin
Rob Kolasinski
Mark Allendorf



HyMARC external collaborations and funding

- T. Udovic and C. Brown (HySCORE, NIST): Neutron diffraction/spectroscopy
  - *Exchanged >15 samples for neutron diffraction and NVS studies*
- T. Autrey and M. Bowden (HySCORE, PNNL): NMR and TEM of metal borohydrides
  - *Exchanged samples, site visits in October 2016*
- M. Head-Gordon (HySCORE, LBNL): DFT computations of H_2 physisorption sites in MOFs
- Timmy Ramirez (ORNL): small angle neutron scattering, neutron diffraction
- Viktor Balema, Vitalij Pecharskij (AMES): metal hydrides, mechanochemistry
- T. Jensen (Aarchus University, Denmark): nanoscale effects in metal hydrides
- P. Chen (Dalian University, China): Synthesis and characterization of ternary metal amides
- P. Pakawatpanurut (Mahidol University, Thailand): synthesis of nanoscale metal amides
- S. Kaskel (Technische Universität Dresden, Germany): High-surface area MOFs
  - *Exchange visit by Sandia researcher to TU Dresden for 1 month in July 2016*

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We gratefully acknowledge EERE/FCTO for financial support!

Technical Back-Up Slides

Approach (Kinetics): Develop foundational knowledge of additive function for catalytic additives

Philosophy: ***The current situation with the role of catalytic additives is complicated. We start with the conceptually simplest systems, and advance to the more complex realistic systems.***

Starting point: $TiCl_3$ and TiF_3. Although TiF_3, $TiCl_3$ promote kinetics in a wide range of materials, the active species and enhancement mechanisms remain

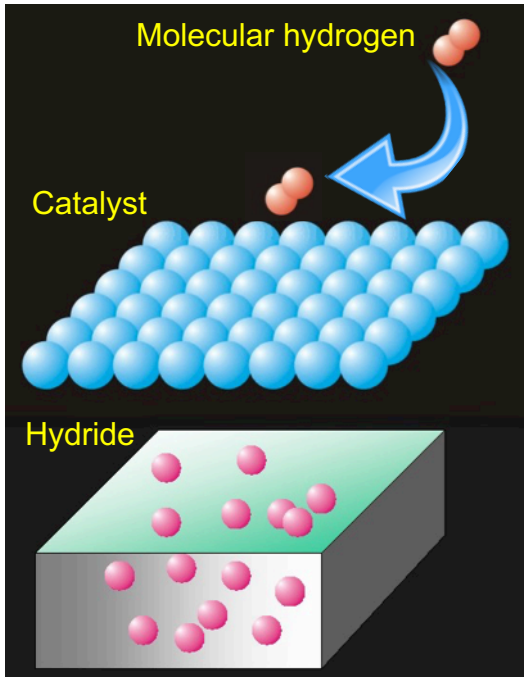
Material Class	Speculated Active Species
Mg-based	MgF_2, TiH_2
Al-based	Ti_2Al_5, $TiAl_3$, TiAl, general alloys indicated $Ti_{(1+x)}Al_{(1-x)}$, LiCl, NaCl, zero-valent Ti metal, zero valent Ti "at the Al surface," TiH_2, increase in H vacancies, "point defect hexahydrides" and grain-refinement retention in the Al-based materials
B-based	LiF, TiB_2 and TiH_2
N-based	LiCl and TiN

- ***Investigate the reactivity of bulk and ball-milled TiF_3 and $TiCl_3$ towards H_2 at the T's and P's for which enhancement is observed.***
- ***Assess additive role in H_2 dissociation.***
- ***Entry point for additive theory development.***
- ***Advance to model system.***

Sandia National Laboratories: *Lennie Klebanoff, Vitalie Stavila, Don Cowgill*

Berkeley Lab: *Yi-Sheng Liu, Jinghua Guo*

Lawrence Livermore National Laboratory: *ShinYoung Kang, Brandon Wood, Alex Baker, Keith Ray, Jon Lee, Tae Wook Heo*



Accomplishment: Surface chemistry of Ti-doped $NaAlH_4$

Initial condition of the surface:

- $NaAlH_4$ recrystallized from THF; XRD and XAS show high purity
- Clean transfer approaches reveal surface oxide present even under ppb levels of O_2 and H_2O before and after milling with $TiCl_3$
- STXM shows only Ti^0 in bulk, so oxide is limited to surface

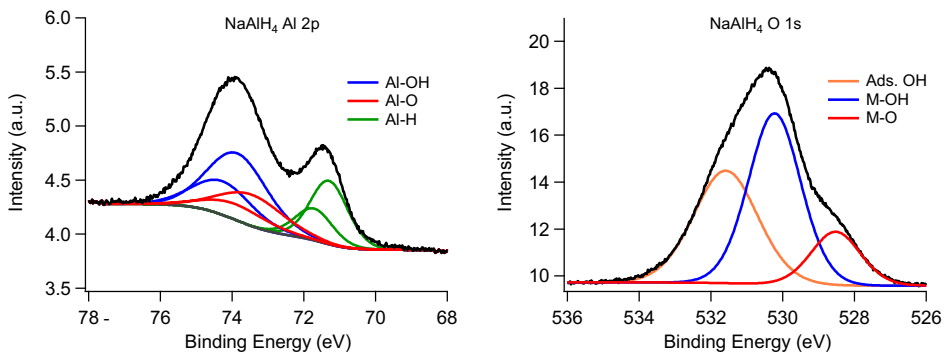
***In situ* experiments: sample material heated to 200 °C**

- Oxygen changes from Al-O to Al-OH and ads. OH over the course of desorption

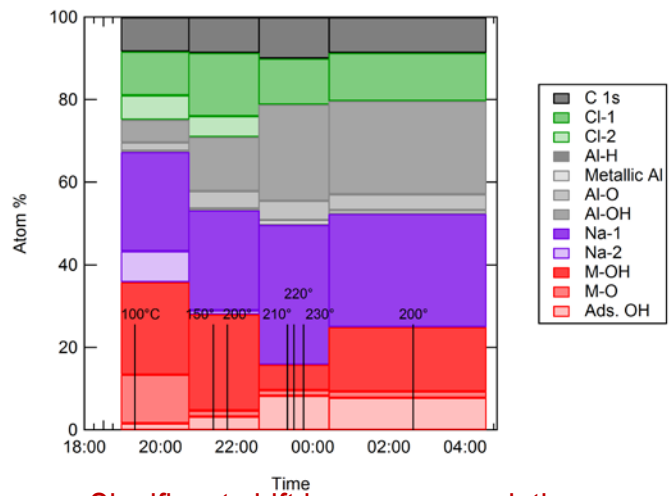
James White (AP-XPS, STXM)
Farid El Gabaly (AP-XPS, STXM)
Robert Kolasinski (LEIS)
Vitalie Stavila (synthesis)

Jonathan Lee (STXM)
Alexander Baker (STXM)
Brandon Wood (theory)

Yi-Sheng Liu (XAS and XES)
Jinghua Guo (XAS and XES)
David Prendergast (theory)



Significant oxidation of Al is detected at surface after recrystallization, though hydride is still present

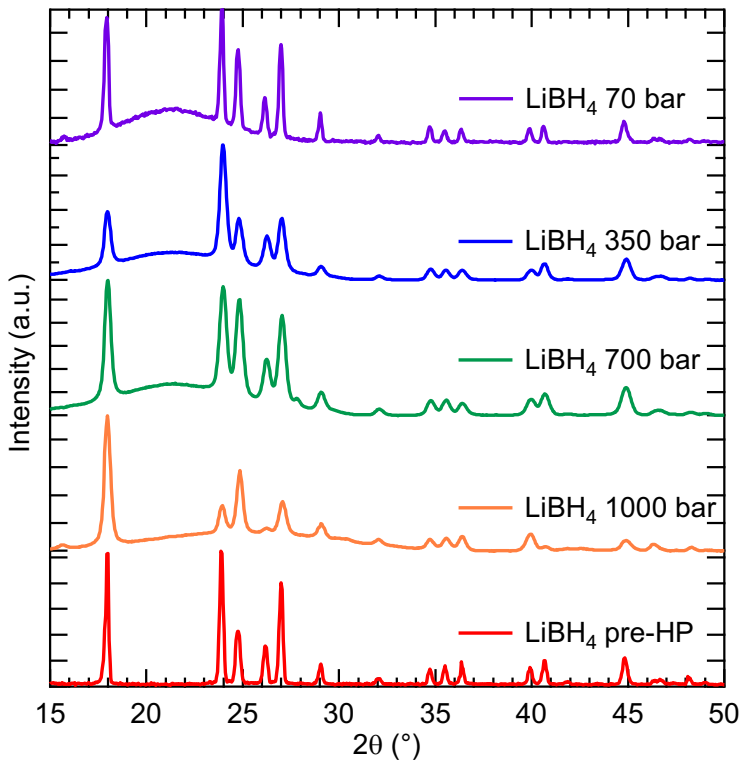


Significant shift in oxygen speciation over time

⇒ ***Sodium alanate surface is initially oxidized, even after being recrystallized from THF***

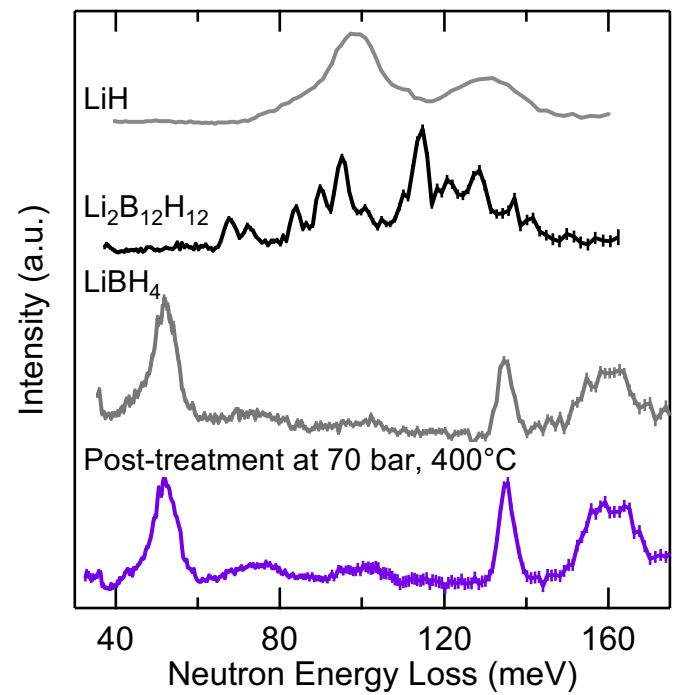
⇒ ***Amount and kinds of oxygen present change during cycling from oxide to hydroxide species and vice versa as hydrogen goes through active and non-passivating layer***

Accomplishment (Thermodynamics): Effect of high-pressure H_2 on bulk MBH_4 (M = Li, Na, K)



$LiBH_4$

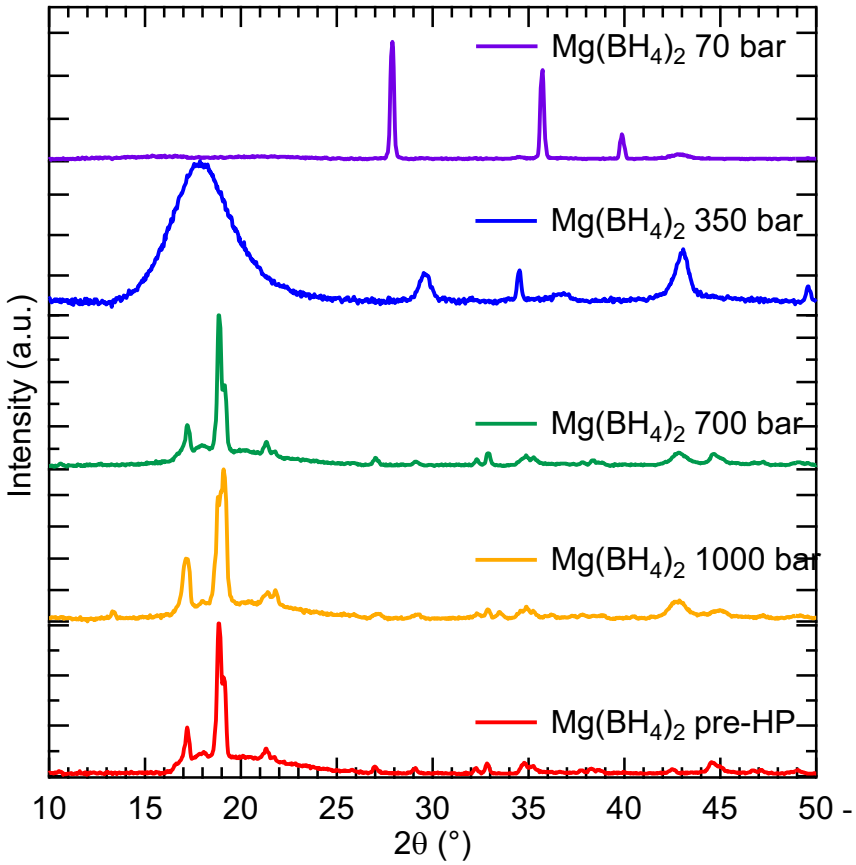
Melted upon heating to 400 °C, increasing amorphous character



- ⇒ ***$LiBH_4$ stable at elevated temperature under H_2 pressures from 70-1000 bar as shown by XRD and NVS (collaboration with HySCORE)***
- ⇒ ***$NaBH_4$, KBH_4 remain unchanged under high-pressure hydrogen (70 bar H_2 and above)***

Accomplishment (Thermodynamics): Effect of high-pressure hydrogen on bulk $Mg(BH_4)_2$

Powder XRD data (*ex situ*)



- 70 bar H_2 is not sufficient to suppress decomposition of $Mg(BH_4)_2$ at 400 ºC
- 350 bar experiment has MgB_2 peaks and several other, unidentified (amorphous) species

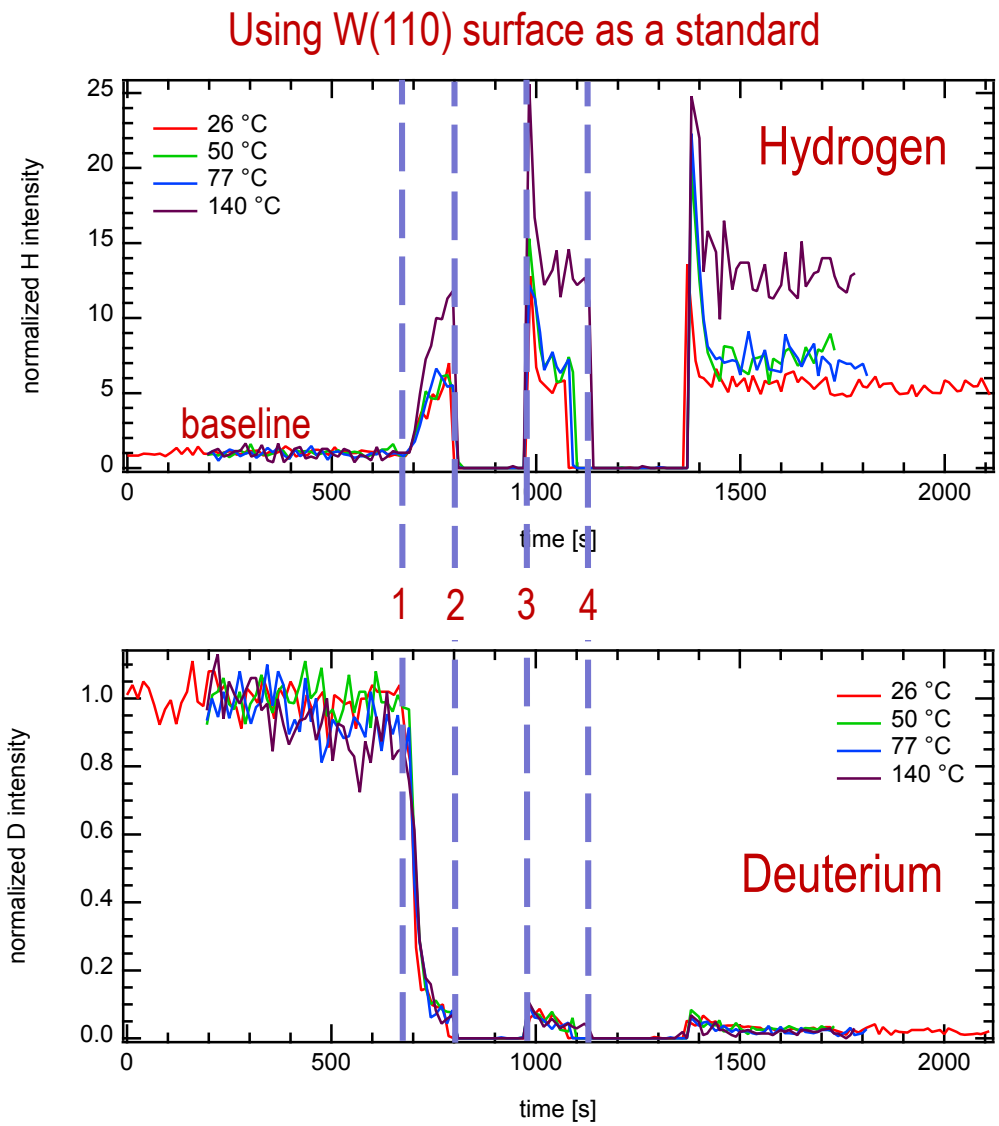
	α-$Mg(BH_4)_2$	β-$Mg(BH_4)_2$	MgB_2	MgH_2
Pre-HP	3%	72%	25%	/
1000 bar	2%	84%	14%	/
700 bar	2%	82%	16%	/
350 bar	66%		34%	/
70 bar	/	/	10%	90%

⇒ *manuscript in progress*

⇒ ***Magnesium borohydride decomposes even under high H_2 pressure***

⇒ ***XRD diffraction reveals MgH_2 and MgB_2 are among decomposition products***

New capabilities: Demonstrated reliable hydrogen surface diffusion measurements using LEIS



Procedure:

1. Ion beam clears a spot
2. Beam deflected off of sample to allow for surface diffusion
3. Beam back on sample to measure diffusion into cleared area.
4. Repeat for second measurement

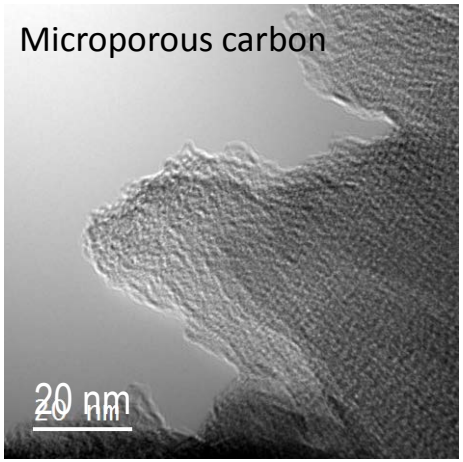
Observations:

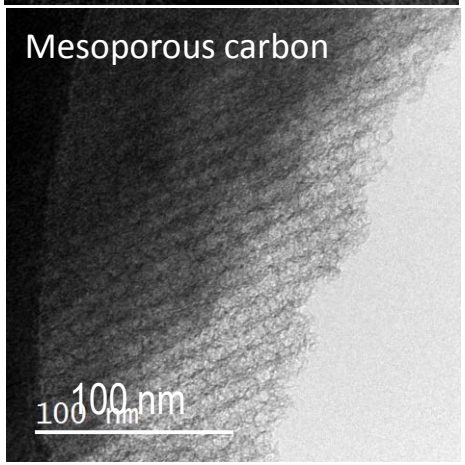
- Observed D refilling, no T dependence.
- D adsorption excluded, but H_2 adsorption possible.
- The H measurements did show proper temperature dependence; need to deconvolve hydrogen adsorption.

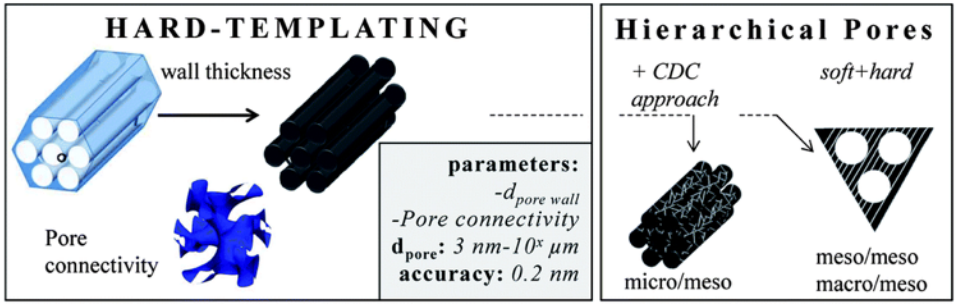
Progress:

- **Results to date demonstrate most aspects of our approach; final steps are to resolve gas-phase adsorption and observe T dependence.**

Accomplishment: Library of promising micro- and mesoporous carbon hosts identified and synthesized







L. Borchardt, S. Kaskel, et al., *Mater. Horiz*, **2014**, *1*, 157-168.

Source	Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Avg. Pore Radius (nm)
UMSL (Eric Majzoub)	NPC	1556	1.817	2.34
	NNPC	1330	1.233	1.85
LLNL (Ted Baumann)	GA1050	1338	4.170	6.24
	GA2000	660	2.688	8.15
DUT (Lars Borchardt)	CMK-3	1263	1.491	2.36
	MC-SiO_2-18	971	1.778	3.66
	TiC-CDC-1000	1545	0.745	0.95
Sandia	JV103C	1125	0.531	0.94
	JV1758	979	0.903	1.84

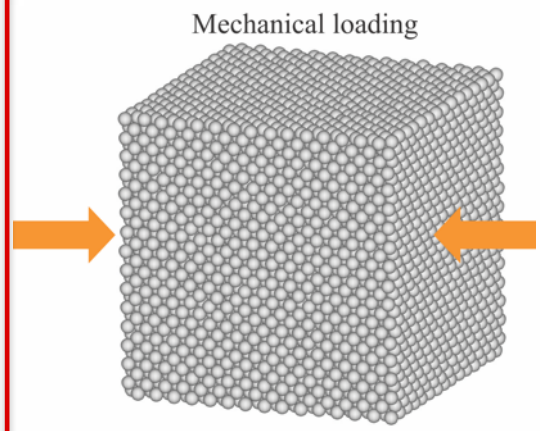
Sandia National Laboratories · Lawrence Livermore National Laboratory · Berkeley Lab · UMSL · Technische Universität Dresden

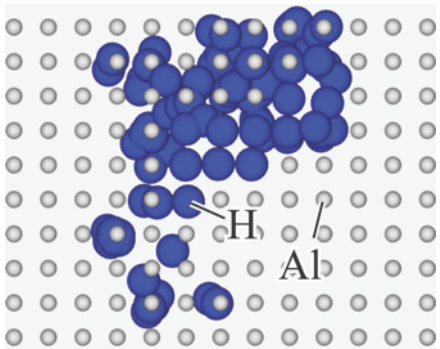
⇒ ***Suite of carbons with various pore volumes, sizes, geometries, and functionalizations available***

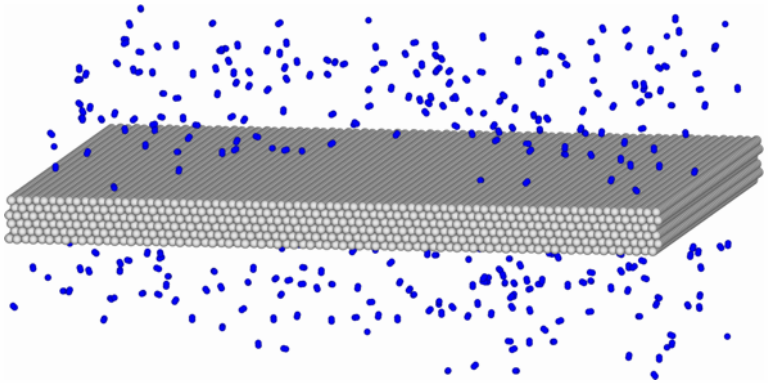
⇒ ***Selected mesoporous carbon hosts display a theoretical weight penalty of less than 20%***

Approach: Molecular dynamics simulations of diffusion rates and mechanisms

Technical approach: MD enables us to derive properties important to hydrogen storage transformation







Mechanical Testing
Determine elastic constants, etc.

Diffusion Simulations
Determine diffusivities, etc.

H_2 – Surface Simulations
Predict hydrogen adsorption/desorption mechanisms, etc.

LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator

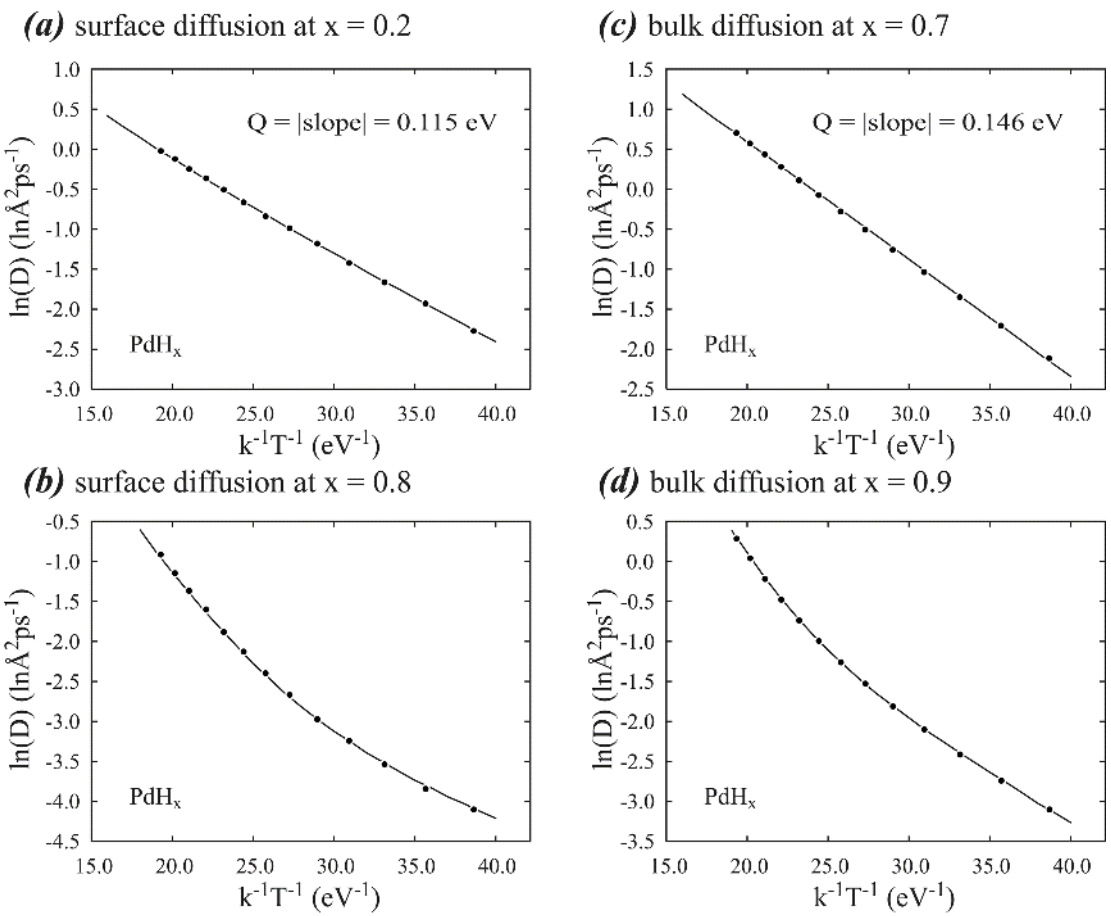
What we hope to learn:

⇒ ***How Gibbs free energy, lattice constants, and elastic constants in the entire composition and temperature space determine the driving forces for the hydrogen storage phase transformation.***

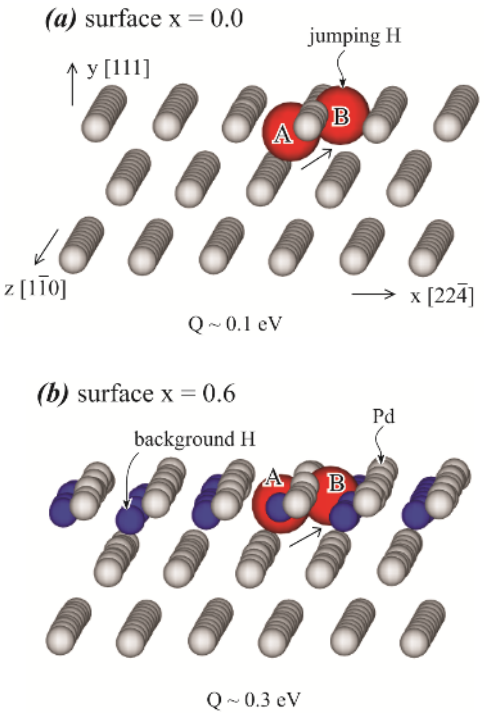
⇒ ***How hydrogen diffusivities in the entire composition and temperature space determine the kinetics of the hydrogen storage phase transformation processes.***

Accomplishment (Surfaces): Surface diffusion in PdH_x

Comparison of predicted surface and bulk diffusivities



Nudged elastic band calculations



MD promotes new understanding

- Well converged MD results on diffusivities were achieved

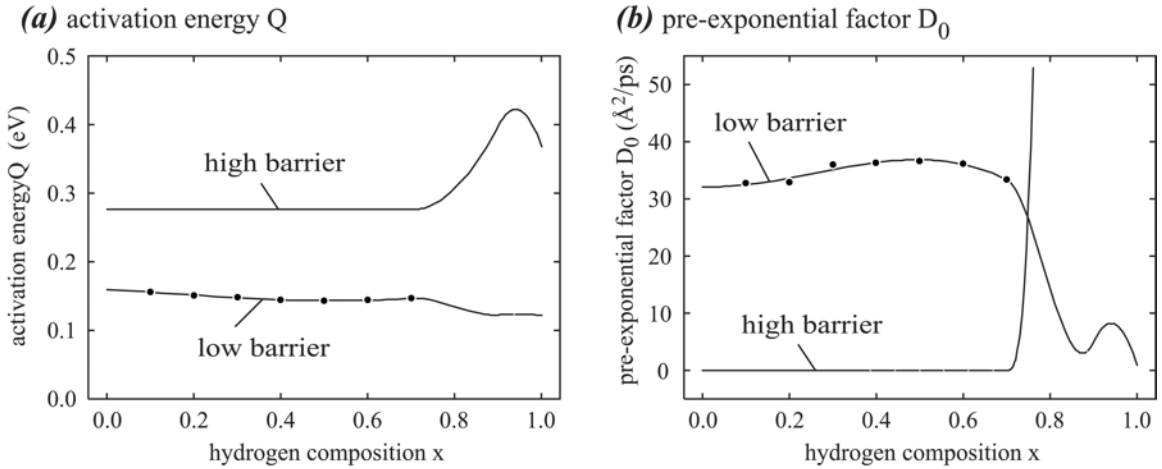
⇒ ***Diffusivities on surfaces are noticeably lower than in bulk, consistent with experimental observations***

⇒ ***Like in bulk, there is only one barrier at low H-composition, but two barriers at high H-composition***

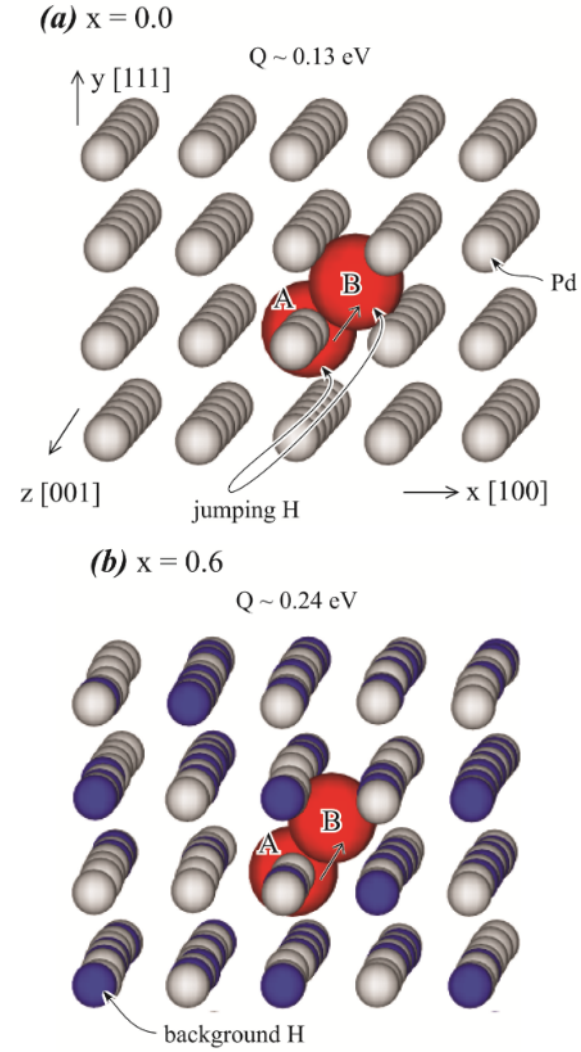
⇒ ***Nudged elastic band studies confirm that the two barriers origin from variations of local H-compositions***

Accomplishment (Kinetics): Molecular dynamics simulations of diffusion rates and mechanisms in PdH_x

$$D = D_{0,1} \cdot \exp\left(-\frac{Q_{0,1}}{kT}\right) + D_{0,2} \cdot \exp\left(-\frac{Q_{0,2}}{kT}\right)$$



Nudged elastic band calculations

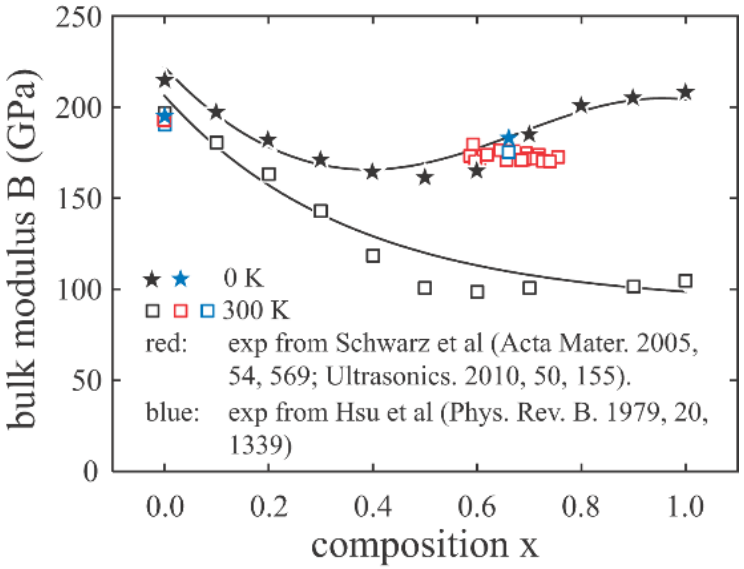


MD simulation approach to revealing diffusion mechanisms:

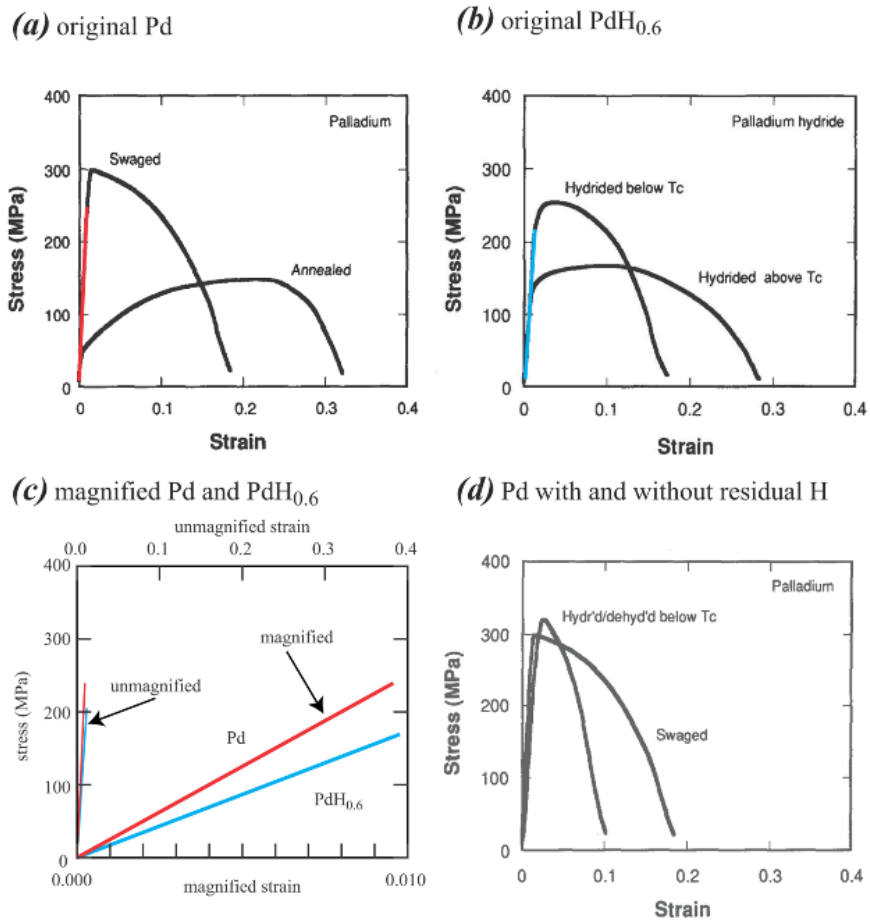
- ⇒ ***Low H-composition has a single diffusion barrier because it is a dilute solution***
- ⇒ ***High H-composition has two diffusion barriers because the local H-composition varies***
- ⇒ ***The results are consistent with nudged elastic band calculations***

Accomplishment: Predicting elastic constants in PdH_x

Predicted vs. dynamically measured bulk modulus



Statically measured Young's modulus



exp from Goods et al (Scripta Metall. Mater. 1992, 26, 561)

MD simulations of mechanical and thermodynamic properties of H_2 storage materials:

- ⇒ ***MD predicts significant decrease of PdH_x elastic constant when H-composition increases***
- ⇒ ***This contradicts supersonic measurements, but is supported by mechanical measurements***
- ⇒ ***Simulations enable properties to be derived as a function of uniform composition, enabling calculations of phase separation driving forces that cannot or are difficult to obtain experimentally***

H diffusion is the root cause for differences in static and dynamical elastic constants!