

Hydrogen Storage Materials Advanced Research Consortium: Sandia Effort

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Project ID# ST128

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Overview

Timeline

- Project start date: 09/17/2015
- Project end date: 09/30/2018

SNL R&D Budget

- FY15 Funding Level: \$250K
- FY16 Funds: \$1.175M
- Total DOE Funds: \$1.175M

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)

HyMARC Partners



Relevance

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

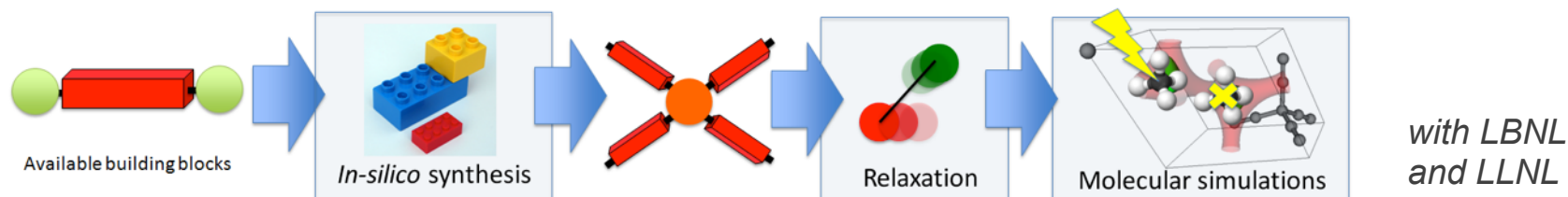
Sandia's objectives/responsibilities within HyMARC:

- ⇒ provide gas sorption and other property data required to **develop and validate thermodynamic models** of sorbents and metal hydrides, including the effects of 350 and 700 bar H₂ delivery pressures
- ⇒ identify the **structure, composition, and reactivity** of gas-surface and solid-solid hydride surfaces contributing to rate-limiting desorption and uptake
- ⇒ synthesize **metal hydrides and sorbents** in a variety of formats (e.g. bulk powders, thin films, nanostructures) and **develop *in situ* techniques** for their characterization
- ⇒ apply SNL **multiscale codes to discover new materials** and new mechanisms of storing hydrogen, provide input for database development

Theory/modeling	Synthesis	Characterization
DFT, Classical MD, database development	MOFs, bulk and nanoscale metal hydrides, high-pressure H ₂ synthesis	LEIS, porosimetry/gas sorption, <i>in situ</i> XRD, FTIR, XPS, soft X-ray synchrotron techniques

Approach: Sorbents

Identify a library of structural motifs for computing interaction potentials and provide hydrogen absorption/desorption isotherm data to develop validated theory models



High accuracy modeling of the effects of:

- *open coordination sites, polarizable groups, acid-base functionality, flexibility, gate-opening phenomena and morphology (particle size, core-shell geometry, etc.)*
 - **Only limited H₂ adsorption data are available in the literature (typically at 77 K)**
 - **Measure reliable H₂ adsorption isotherms at various temperatures (with NREL)**

MOF	Characteristic
MOF-5, MOF-177	High surface area; Zn-carboxylate structure
HKUST-1, PCN-14, NOTT-(100-103)	Open Metal Sites; Cu-carboxylate structure
M-DOBDC (M=Mg, Co, Ni, Zn)	Open Metal Sites; 1-D pores; constant topology
Mn-BTT, ZIF-8	Nitrogen heterocycle linkers

QMC calculations are underway for MOF-5, MOF-505 and NOTT-100

Approach: Metal hydrides

Understand thermodynamic and kinetic limitations of bulk and nanoscale metal hydrides through a combination of multiscale modeling, synthesis and *in situ* characterization.

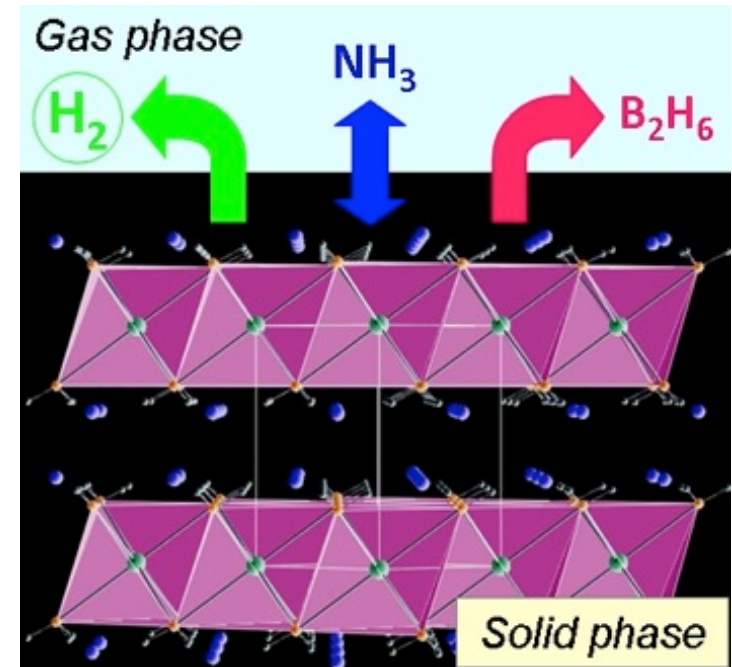
Bulk hydrides:

- ⇒ enable reversibility by suppressing unfavorable reaction pathways or eliminating phase transitions (as in interstitial hydrides)
- ⇒ assess whether reaction entropies could be used to counteract large enthalpic changes via crystalline-to-amorphous transitions

Nanoscale hydrides:

- ⇒ control desorption thermodynamics by eliminating intermediate reaction steps
- ⇒ alter thermodynamics relative to bulk through surfaces and interfaces (particle size/shape, defects, lattice distortions, grain boundaries, solid-state phases)

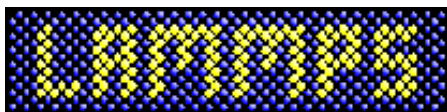
With LLNL, LBNL and ALS



Control: Reversibility, reaction rates, hydrogen purity

Sandia's technical roles within HyMARC

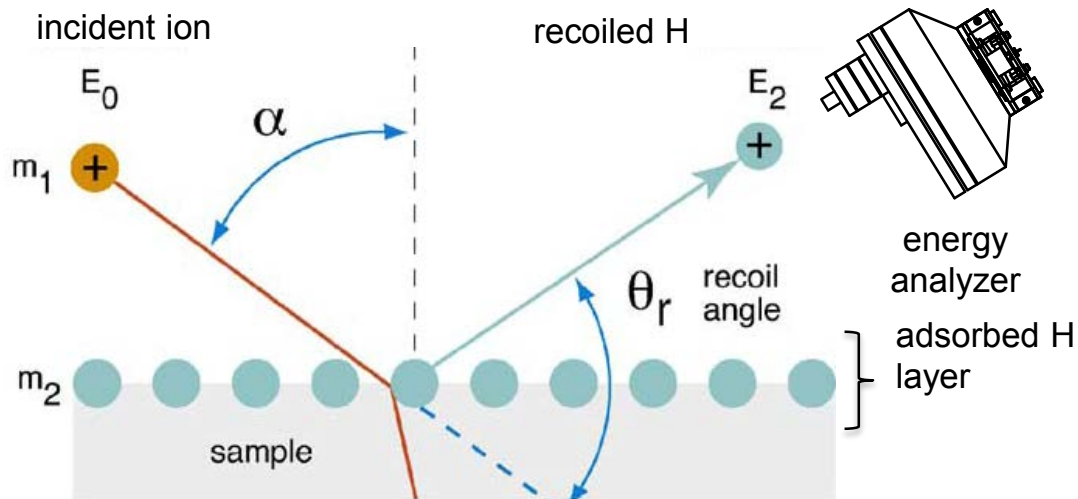
- High-pressure characterization of hydride and sorbent interactions with H_2 (up to 100 MPa H_2)
- Synthesis and characterization of porous Metal-Organic Frameworks and doped carbons
- High-throughput MD calculations to determine diffusion energy barriers using LAMMPS, a code developed at Sandia for large domain parallel computing
- Materials characterization with surface-sensitive techniques such as Low Energy Ion Scattering, X-ray Photoelectron, X-ray Absorption and Auger Spectroscopy
- Spectroscopic and soft X-rays methods to decipher how additives promote H_2 storage reactions



Large-scale Atomic/Molecular Massively Parallel Simulator



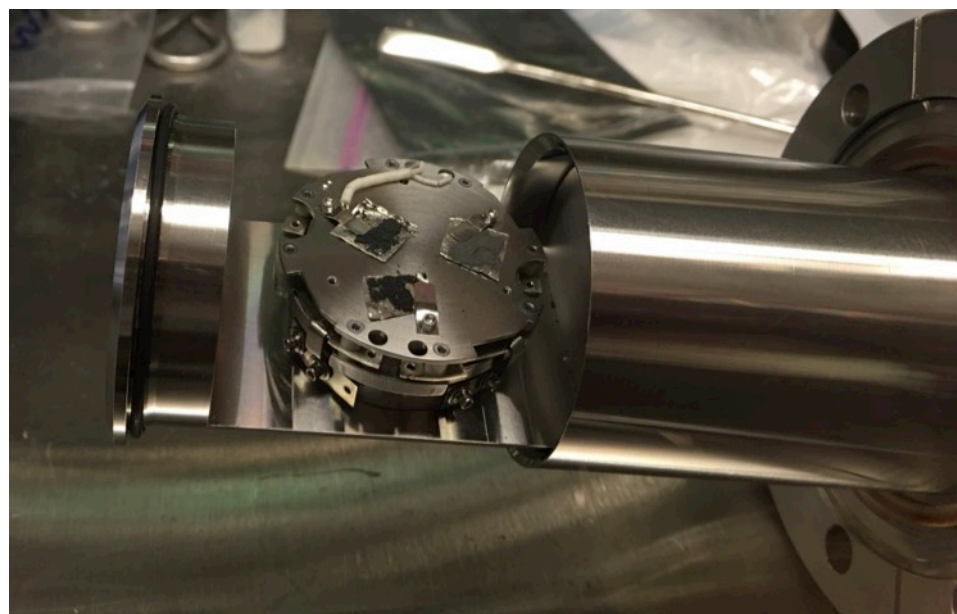
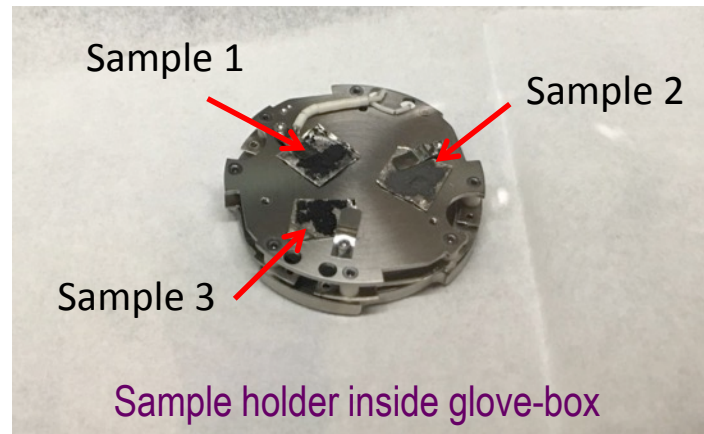
High-pressure H_2 station
(up to 1000 bar)



LEIS: Low Energy Ion Scattering Spectroscopy

Clean transfer system for XPS and LEIS

Designed and built two holders for anaerobic transfer of samples



- Designed and fabricated at SNL
- Transfer of samples under inert atmosphere
- Compatible with XPS systems at SNL and ALS

Thermodynamics (Task 1): Bulk metal hydrides

Understand the factors controlling the enthalpy ΔH° and entropy ΔS° of H_2 adsorption and desorption and to develop validated models for computational materials design.

Effect of doping on thermodynamics

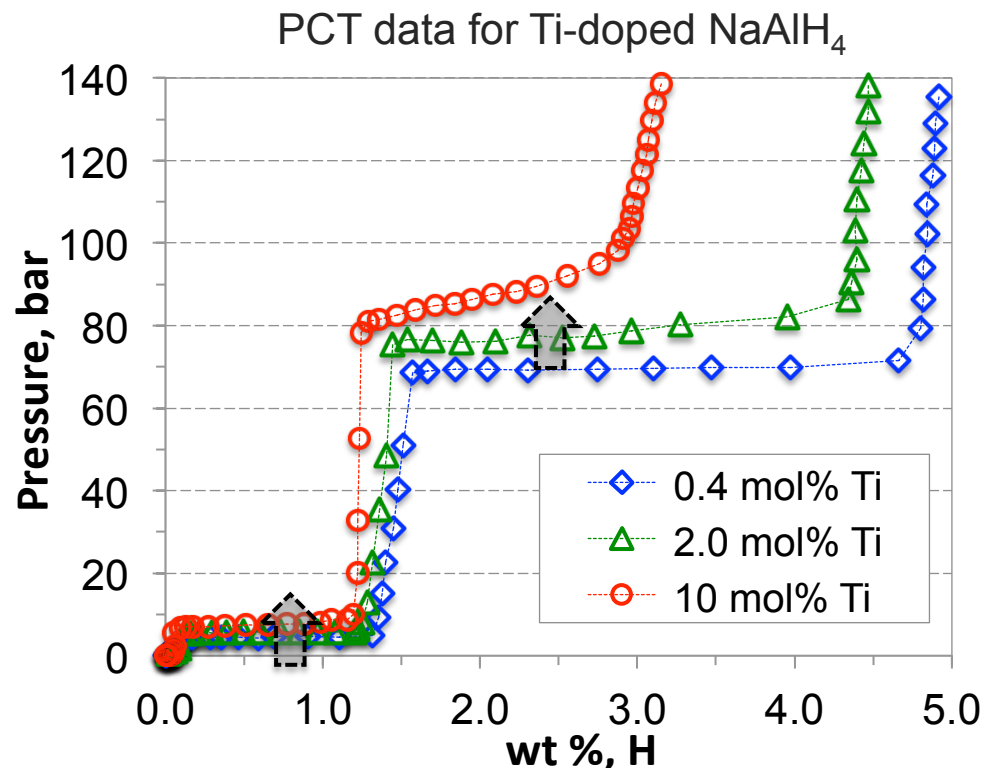
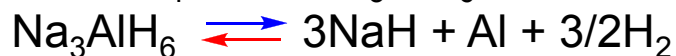
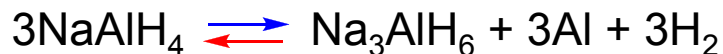
FY16 model system: Ti-doped $NaAlH_4$

⇒ What governs the thermodynamics of H_2 uptake and release in sodium alanate?

⇒ Can entropic effects (bulk, surface, interfacial) alter the overall thermodynamics?

⇒ What is the effect of titanium on the plateau pressure?

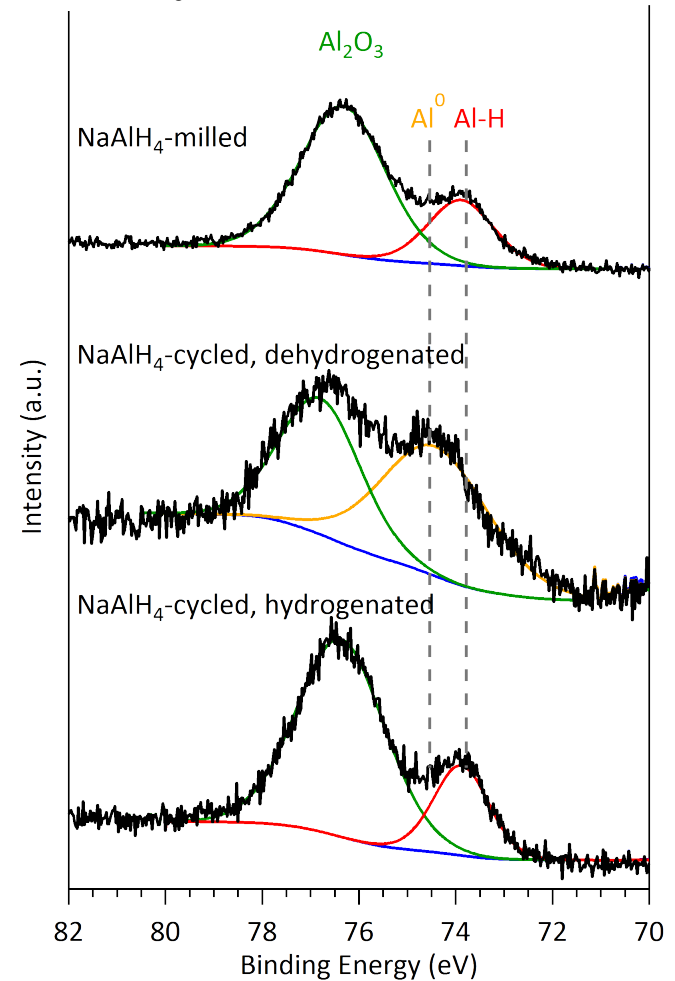
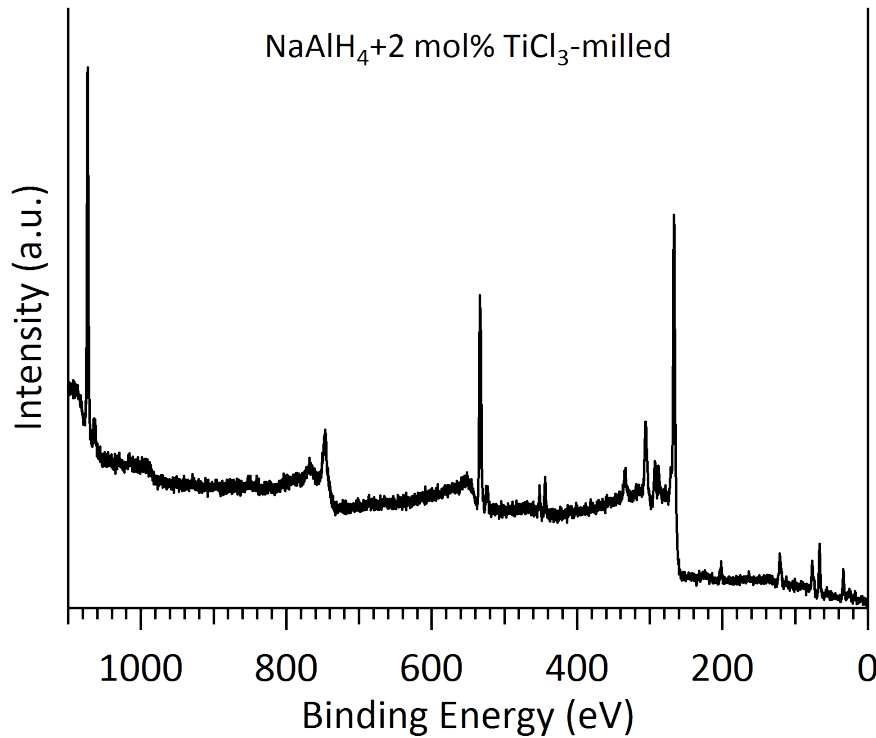
Goal: develop a validated multi-scale theory model of H_2 release and absorption



The role of titanium in sodium alanate is still poorly understood. Ti not only enables reversibility and accelerates kinetics, but it also affects the equilibrium pressure of H_2 .

Tasks 1, 3 and 4: XPS of TiCl_3 -doped NaAlH_4

XPS data obtained using the HyMARC-developed clean transfer system



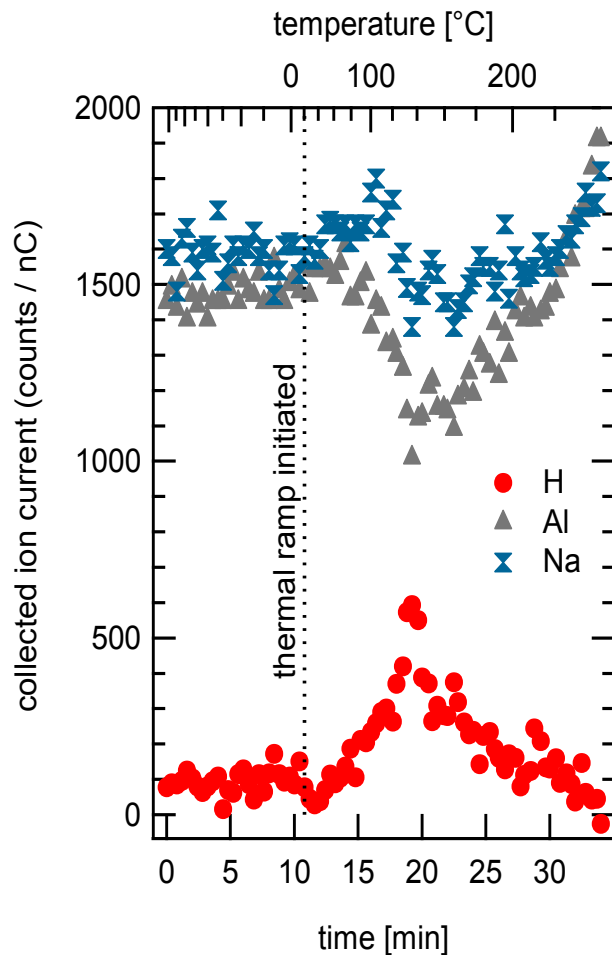
Surface
Composition

	Milled	Cycled, Hydrogenated
Na	24%	30%
Al	30%	16%
O	45%	47%

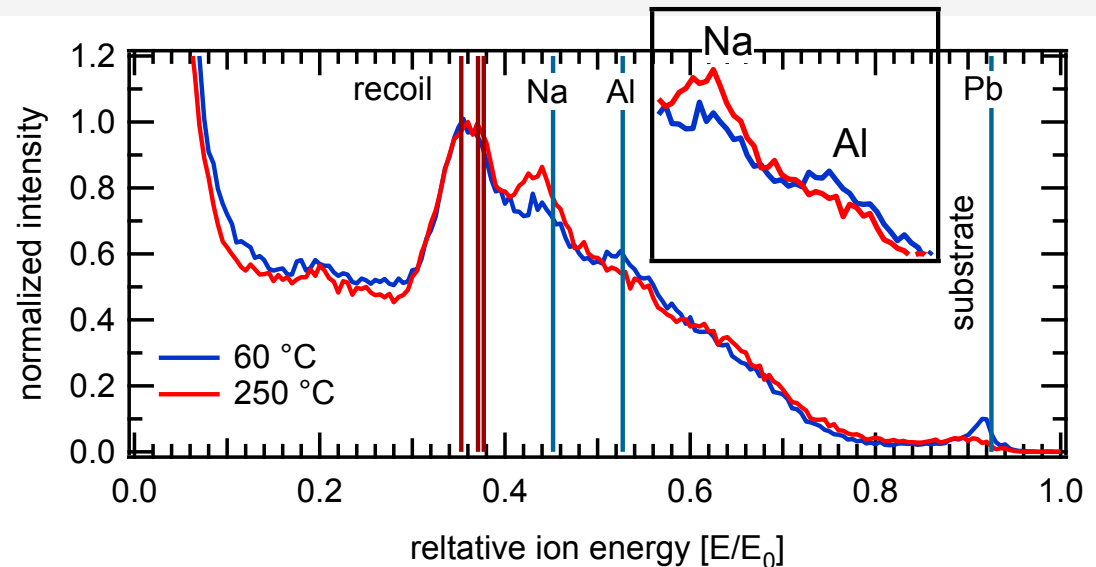
- ⇒ The XPS data confirms the surface of TiCl_3 -doped sodium alanate is oxygen-rich
- ⇒ Al 2p region shows oxide, hydride, and metal; dehydrogenated material is Al⁰-rich

Tasks 1,3 and 4: *In situ* LEIS experiments demonstrate capability to track surface composition of Ti-doped NaAlH_4

Approach: We pressed a NaAlH_4 powder (doped with 2mol% TiCl_3) into a Pb-alloy foil and monitored the surface composition during thermal desorption using LEIS.



With LEIS, we directly observe H segregation to the surface at $\approx 150^\circ\text{C}$ as the hydride begins to rapidly desorb H_2 . The surface becomes enriched with Na during the heating. This is confirmed by the surface composition revealed by the ion energy spectra below at 60 and 250 °C.



Task 2: Mass transport

MD simulations of hydrogen diffusion in aluminum

Conventional Atom Jump Methods

- Huge number of jumps (different chemistry, numbers of neighbors, locations with respect to defects, etc.)

e.g., jumping atom can have different neighboring species (circles of different color.)

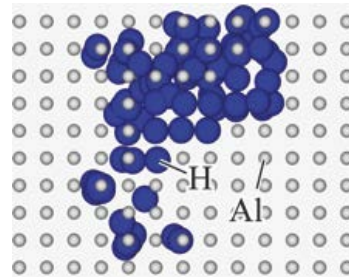



- Unclear how hundreds of thousands of diffusion paths (barriers) relate to an overall experimental diffusion behavior
- Dynamic evolution of structures not allowed

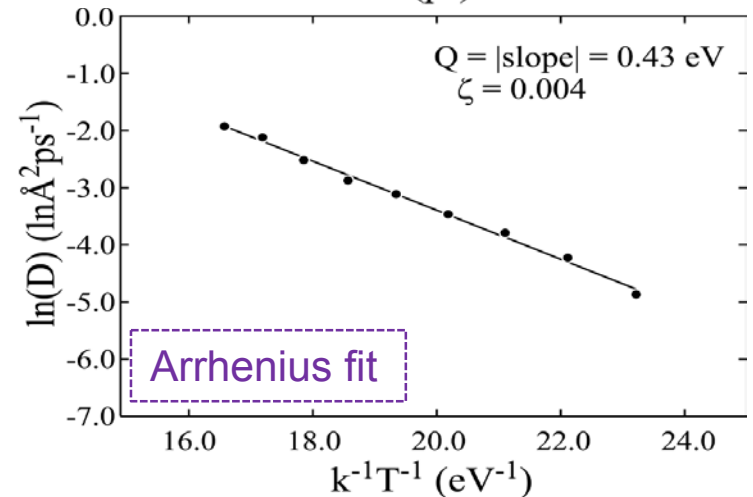
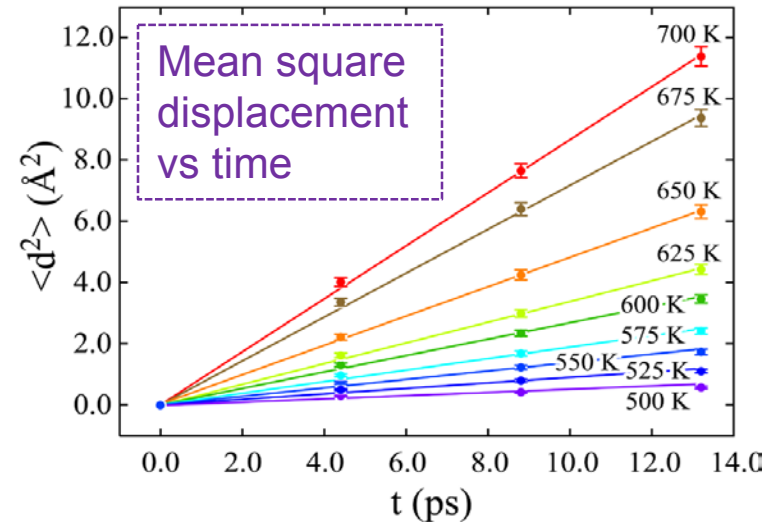
Advantages of MD Methods

- History of mean square displacement
- Sufficient for constructing the Arrhenius equation

MD allows diffusion atoms to be tracked



 X. W. Zhou, F. El Gabaly, V. Stavila, M. D. Allendorf, *J. Phys. Chem. C*, **2016**, v. 120, p. 7500.



⇒ Developed MD methods to accurately predict hydrogen diffusion barriers in aluminum

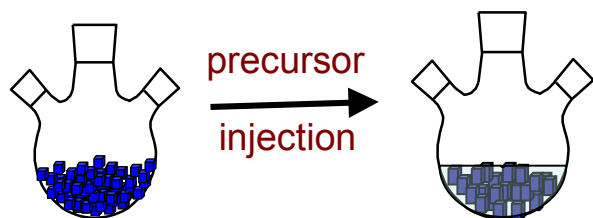
Tasks 1 and 4: Nanoscale effects in metal hydrides

Use nanostructuring to improve kinetics, alter the reaction pathways, and elucidate the effects of particle size/shape, defects and nanointerfaces



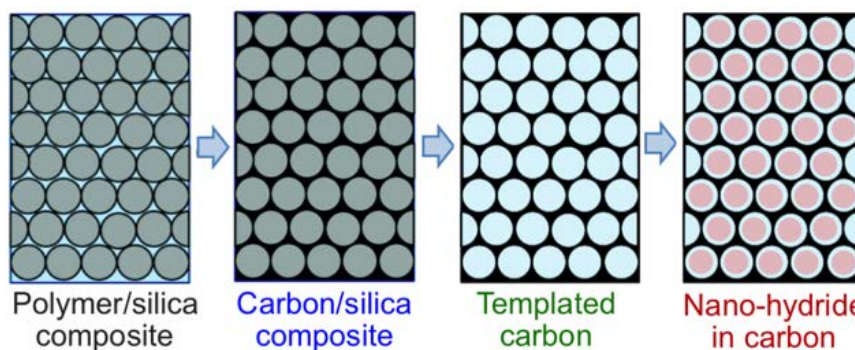
- ⇒ Can the thermodynamics of H_2 uptake and release be altered through nanostructuring?
- ⇒ What is more important: particle size or interactions with porous hosts?
- ⇒ What is the effect of nanointerfaces?

Metal hydride infiltration

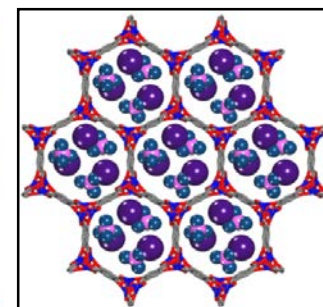


With E. Majzoub (U. of Missouri)

Templated carbons



MOFs

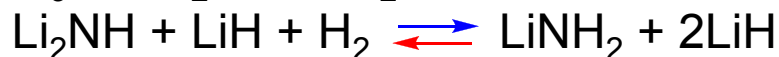


hydride@MOF-74

- ⇒ Developed infiltration approaches for metal hydride nanoparticles into lightweight porous carbons and metal-organic frameworks (MOFs)
- ⇒ Achieved stable Li_3N and LiNH_2 nanoparticles inside mesoporous carbons (pores of 3-12 nm) and microporous MOFs (e.g. 1.2 nm pores of MOF-74(Mg))

Task 4: Nanointerface engineering

Bulk:



(work of P. Chen, D. Chandra, B. David, et al.)

Nano (Li_3N in 3-10 nm nanoporous C):

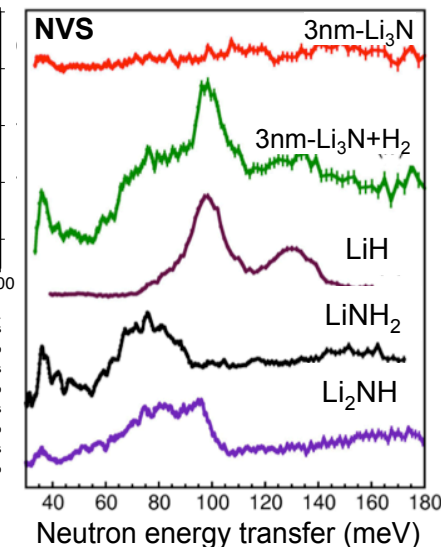
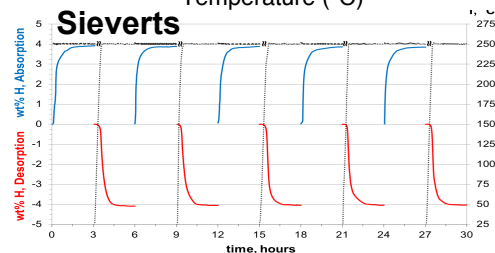
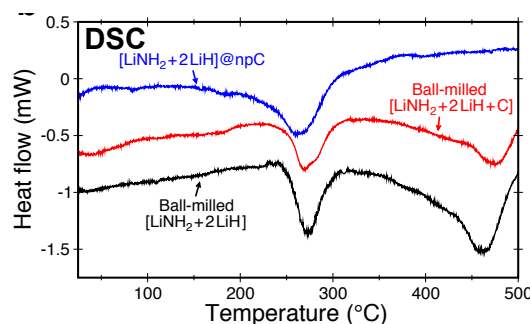
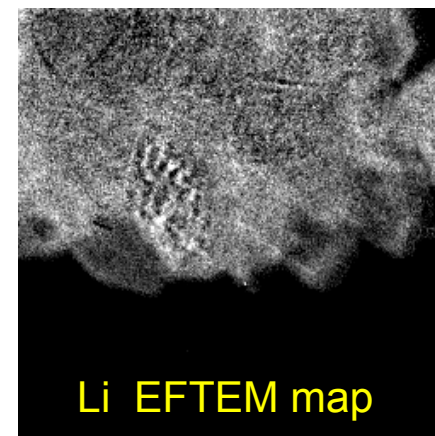
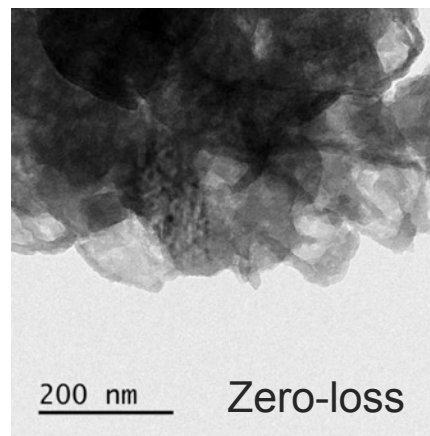


⇒ The $\text{Li}_3\text{N}@C$ nanocomposite displays a reversible H_2 capacity of 4 wt% H.

⇒ The full cycling capacity in the $\text{Li}_3\text{N}/[\text{LiNH}_2 + 2\text{LiH}]$ system is realized at 250 °C, which is 180 °C lower compared to bulk.

Multiscale modeling (B. Wood et al, LLNL) revealed that nanoconfinement of the high-capacity $\text{Li}_3\text{N}/[\text{LiNH}_2 + 2\text{LiH}]$ system fundamentally alters the reaction pathways as a direct consequence of solid-solid nanointerfaces within the material.

Q2 FY16 milestone



In collaboration with Mahidol University, LLNL, LBNL, NIST (T. Udovic)

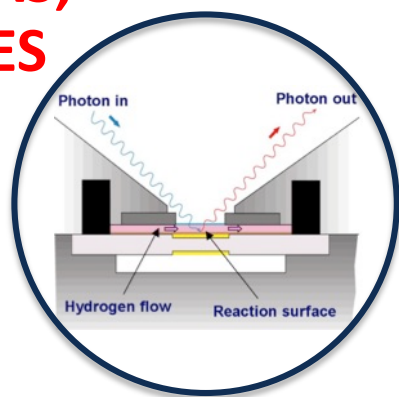
Submitted for publication

Task 3: Multi-technique approach provides comprehensive picture of storage material surface chemistry

Problem: Adsorption at the surface is an initial (potentially rate-limiting) step for hydrogen-uptake by storage materials. The present understanding of surface chemistry is inadequate for predicting hydrogen uptake and release.

Technical Approach: We apply advanced surface characterization tools to practical storage materials. This work guides more detailed experiments and modeling to reveal underlying surface processes (e.g. chemisorption, surface diffusion).

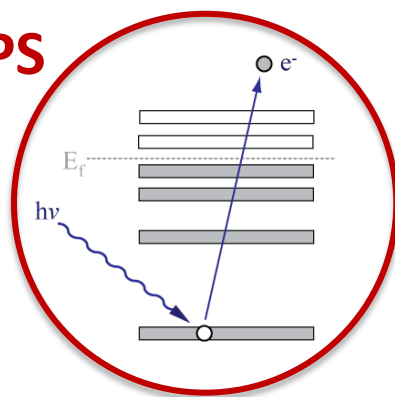
**XAS,
XES**



X-ray Absorption and Emission Spectroscopy

Probe surface and near-surface electronic states

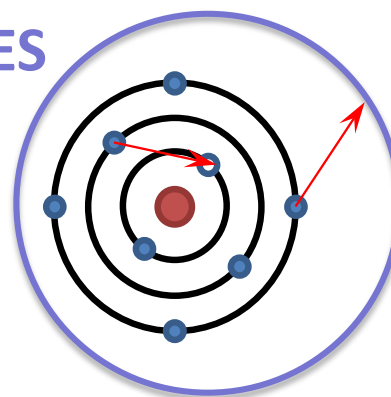
XPS



X-ray Photoelectron Spectroscopy

Binding information / oxidation states

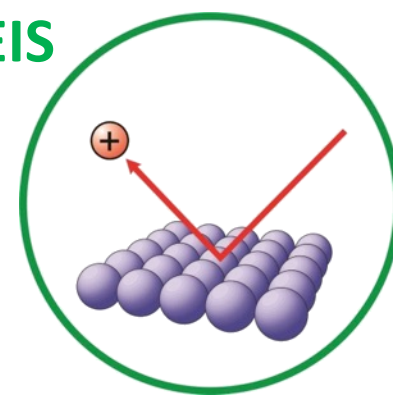
AES



Auger Electron Spectroscopy

Surface composition

LEIS



Low Energy Ion Scattering

Directly detect adsorbed H

Task 3: LEIS measurements of H₂ diffusion

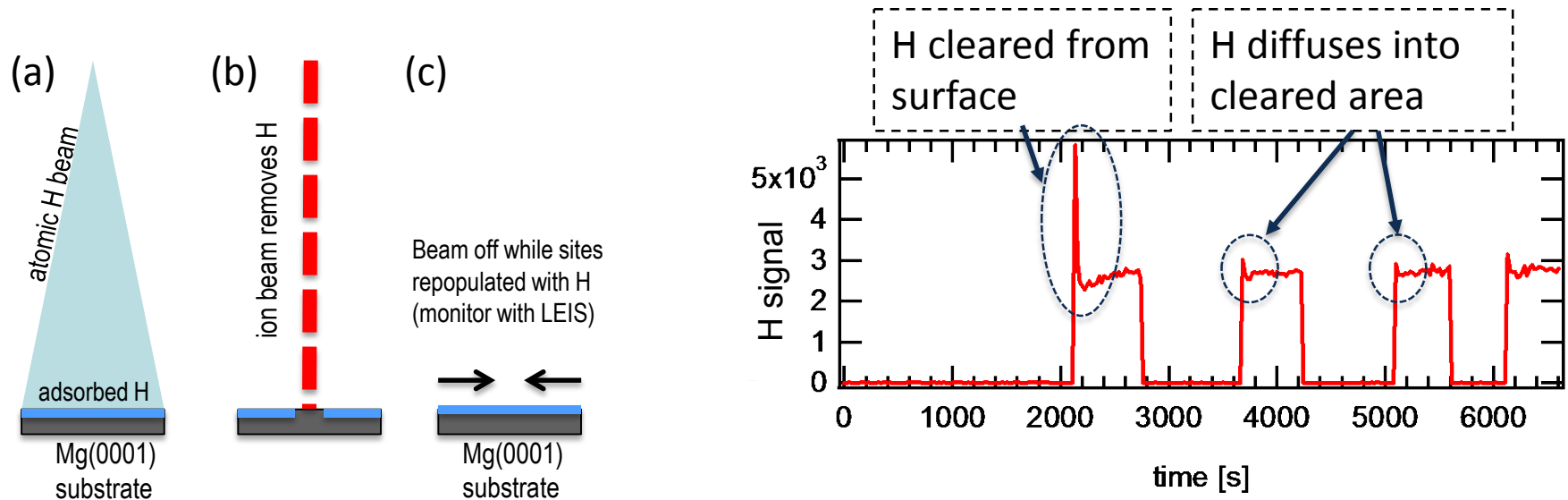
We seek to answer:

- How does surface diffusion contribute to recombination / surface-bulk transport?

Prevailing technique can't be used: Laser-induced thermal desorption (LIDT) involves rapid laser heating to ~1200 °C, compatible with high melting materials (e.g. Ru, W.). Hydrogen storage materials are low-melting: e.g., Mg sublimates at 450 °C.

Our Approach: Explore potential for making surface diffusion studies without sample heating with ion-based techniques:

- (a) Dose surface with atomic hydrogen. (b) Clear a well-defined region using Ne⁺ beam. (c) Monitor H diffusion into region with LEIS. LEIS can measure surface diffusion. ✓



Task 5: Catalytic additives

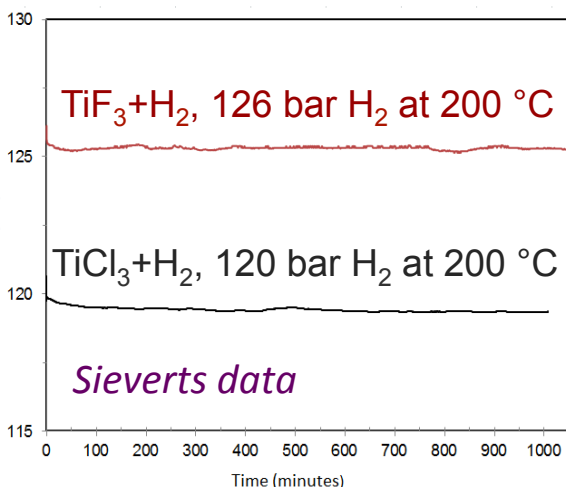
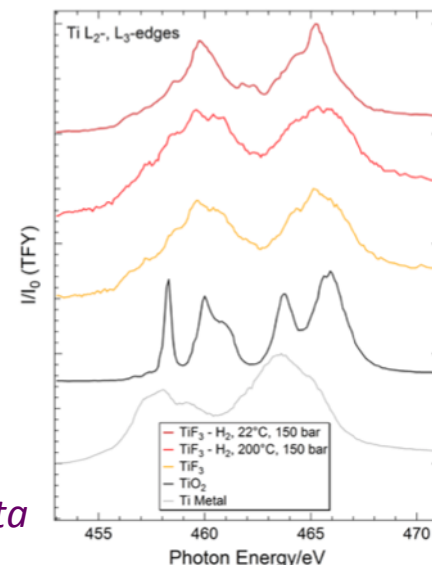
Philosophy: *The current situation with the role of catalytic additives is complicated. Consequently, we must begin with simple systems that allow definitive conclusions to be made and enable multiscale theory model validation*

⇒ Assess first how additives themselves in bulk form react with H₂
⇒ Examine the known catalytic additives TiF₃ and TiCl₃ for reaction with hydrogen at 200 °C, 120 bar for ≈17 hours with Sieverts H₂ uptake, X-ray absorption spectroscopy and FTIR

-- negligible change in TiF₃ vibrational structure with FTIR, negligible H₂ uptake seen with Sieverts.

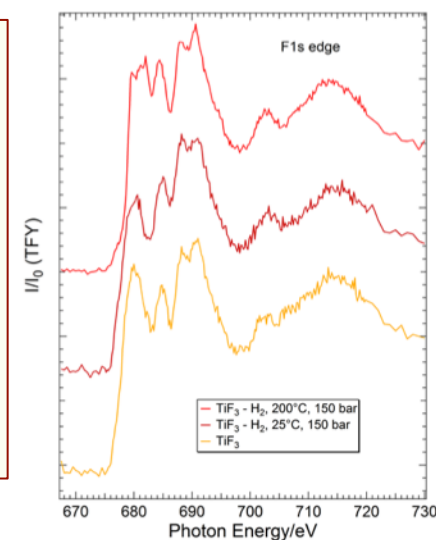
-- negligible change in Ti electronic structure with XAS in fluorescence yield mode, No evidence of Ti metal or oxide

XAS data



Results: Bulk TiF₃ was found to be unreactive to H₂ at the temperatures and pressures for which it acts “catalytically” as an additive (e.g. in NaAlH₄). Same result is also seen for TiCl₃.
Next Single Step: Examine H₂ reactivity of ball-milled TiF₃ and TiCl₃ with and without metal hydrides

With LLNL, LBNL and ALS



Milestones and future work

Milestone	Description	Status/Proposed completion
1	Synthesize library of bulk-phase model storage systems for use in Tasks 1-5	Q1 FY16 (100% complete)
2	Size control method for one prototype complex hydride nanostructure	Q2 FY16 (100% complete)
3	Demonstrate <i>in-situ</i> soft X-ray AP-XPS, XAS, XES tools, with sample heating	Q3 FY16 (50% complete)
4	Characterization+Theory: Identify hydride mobile species and diffusion pathways	Q4 FY16 (50% complete)
5	Synthesis+Characterization: Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, >10 nm for one prototype hydride	Q4 FY16 (75% complete)

Summary: Progress and accomplishments

Modeling

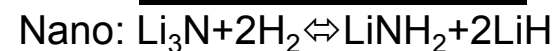
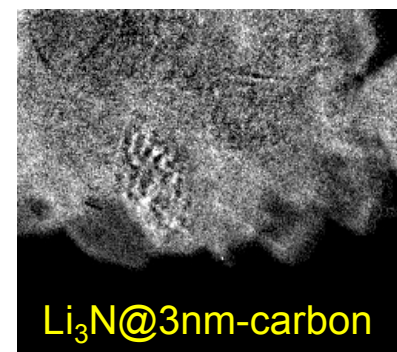
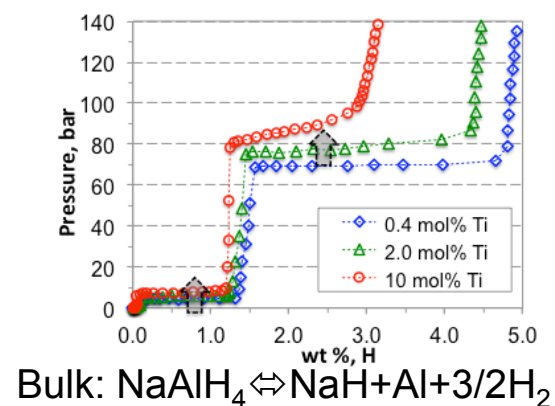
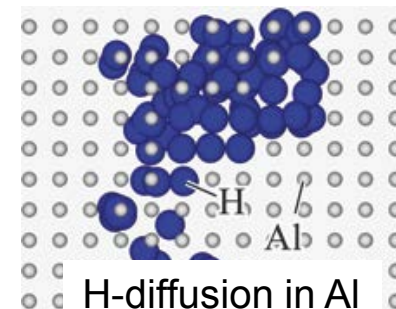
- A molecular dynamics modeling framework was established to accurately predict the diffusion kinetic barriers; proof-of-concept demonstrated for H-diffusion in Pd and Al.

Synthesis

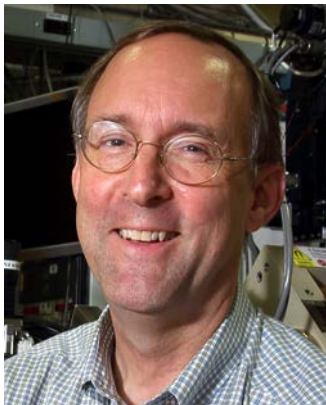
- Sandia high-pressure (up to 1000 bar) system was upgraded
- Identified model MOFs for GCMC and QMC studies to calculate interaction potentials and predict H₂ isotherms
- Initiated a comprehensive study of titanium role in sodium alanate and determined the effect of Ti-doping levels on hydrogen plateau pressure
- Elucidated the H₂ reactivity of TiCl₃ and TiF₃ additives by themselves (no hydride present)
- Developed synthetic protocols for synthesizing ≤ 10 nm particles of LiNH₂/2LiH in nanoporous carbons and MOFs

Characterization

- Demonstrated that LEIS can measure surface diffusion
- Developed clean anaerobic techniques for sample transfer for XPS, Auger, XAS and LEIS *in situ* studies



Sandia team and responsibilities



Mark Allendorf
(MOFs, hydrides)



Vitalie Stavila
(Sorbents, hydrides)



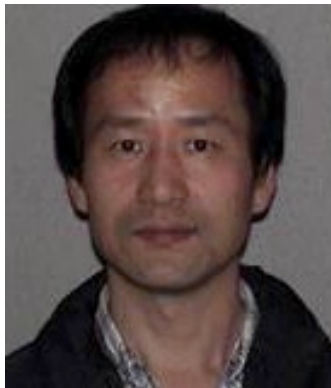
Rob Kolasinski
(LEIS techniques)



Lennie Klebanoff
(catalysis, surfaces)



Farid El Gabaly
(Soft X-ray techniques)



Xiaowang Zhou
(MD simulations)



James White
(TEM, SEM, XPS)



Jon Zimmerman
(interface and defect modeling)

External collaborations

- T. Udovic and C. Brown (NIST): Neutron diffraction/spectroscopy on sorbents and hydrides
 - *exchanged >12 samples for neutron diffraction and NVS studies*
- T. Autrey and M. Bowden (PNNL): NMR and TEM of metal borohydrides
 - *Exchanged samples, site visits in November 2015 and April 2016*
- M. Head-Gordon and J. Long (LBNL): H₂ physisorption sites in MOFs
- T. Gennett and K. Hurst (NREL): accurate hydrogen isotherm measurements
- Viktor Balema (Sigma-Aldrich/Merck): synthesis of metal hydrides, mechanochemistry
- E. Majzoub (UMSL): PEGS, nanoscale effects in metal hydrides
- J.J. Vajo (HRL): Synthesis and characterization of ternary borides and borohydrides
- P. Pakawatpanurut (Mahidol University, Thailand): synthesis of nanoscale metal amides
- S. Kaskel (Technische Universität Dresden, Germany): High-surface area MOFs
 - *a student from Prof. Kaskel's group visited Sandia for 6 weeks to develop new sorbents*

HyMARC collaboration and funding partners



Thank you for your attention!

*We gratefully acknowledge EERE/
FCTO for financial support!*

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Renewable Energy



Technical Back-Up Slides

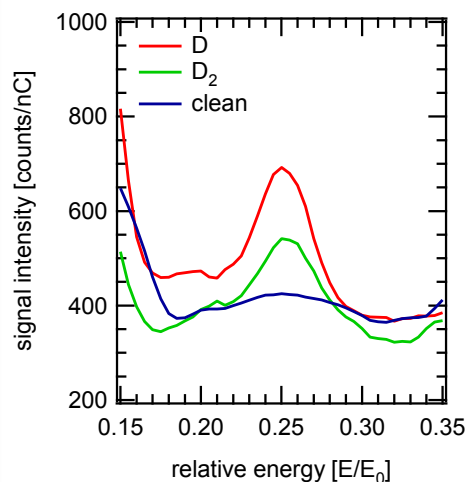
Surface characterization of Ni-doped MgH₂

We seek to answer:

- What are the surface composition & oxidation states of as-prepared hydrides? Are they different from bulk? What happens when the material is cycled?
- How do additives affect dissociation / chemisorption of H?

Approach: Powders pressed into metal foil in glove box, analyzed **without air exposure** using **clean sample transfer**.

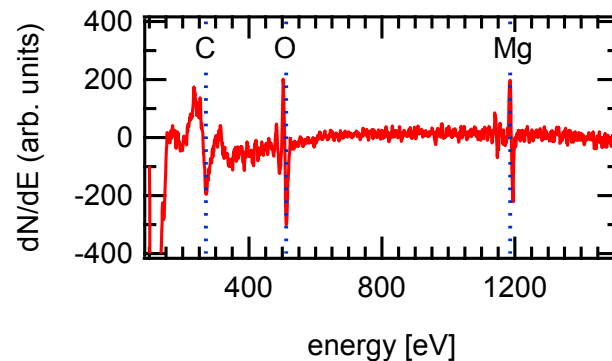
Material: Ni-doped Mg powder (pressed into In foil)



Ion energy spectrum reveals both D₂ and D adsorb on the surface. This suggests the Ni dopant promotes D₂ dissociation.

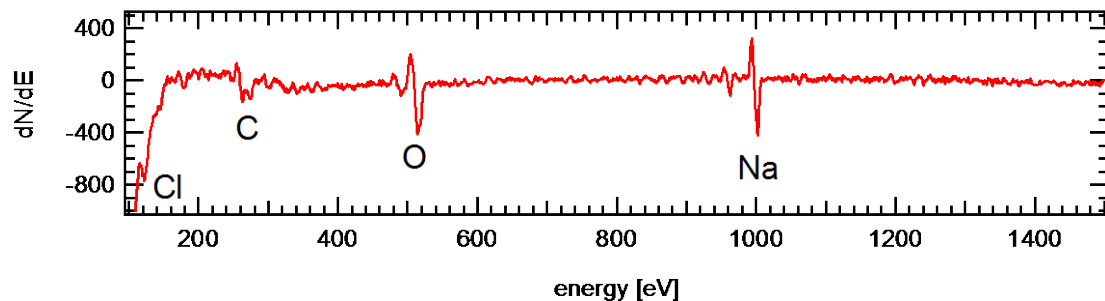
LEIS is the only element-specific way to detect adsorbed hydrogen.

AES reveals composition within first ~ 10 nm of the surface, including adsorbed impurities (O,C)

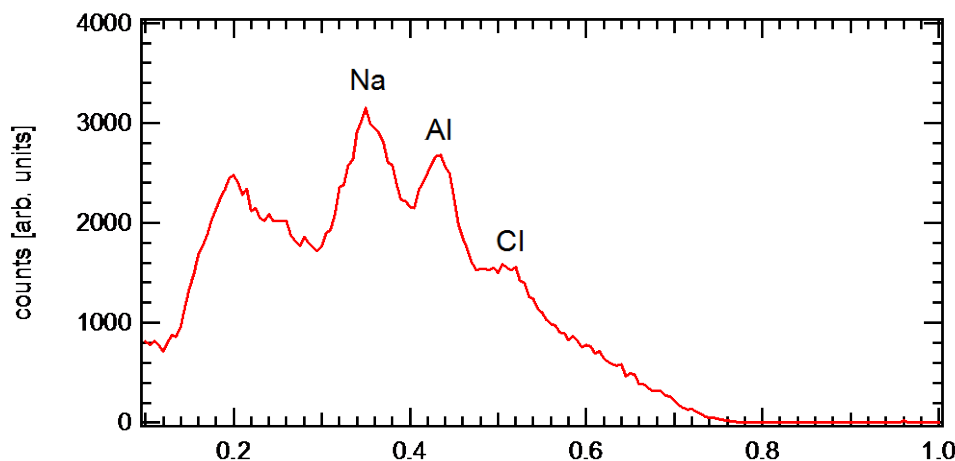


LEIS spectra of TiCl_3 -doped NaAlH_4

Surface composition measured using AES and LEIS



An initial AES survey of the surface revealed the presence of chemisorbed O and C. The surface appeared to be enriched in Na; we also detected the presence of chlorine.



We were able to sputter through the oxide layer using a Ne^+ ion beam. An LEIS spectrum of the cleaned surface reveals the presence of Na, Al, and Cl.

The surface of ball-milled TiCl_3 -doped sodium alanate (2mol% Ti) is rich in sodium and seems to be oxygen terminated.

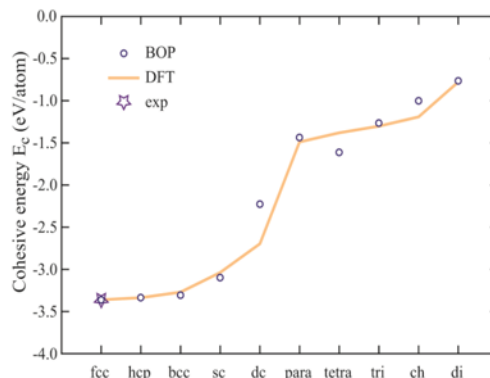
High-accuracy Al-H bond order interatomic potentials

Significant improvement over known potentials:

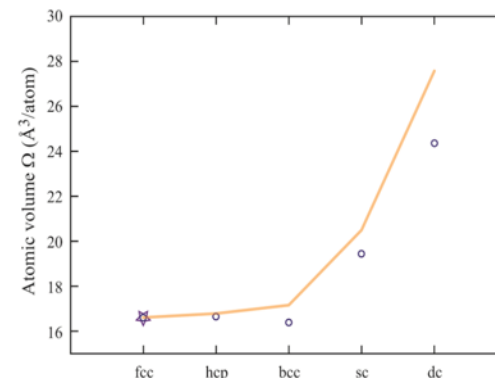
- Captures the high stacking fault energy of aluminum (many literature potentials fail).
- Captures energy and volume trends of many aluminum phases.
- Captures energy and volume trends of many Al-H phases.

Aluminum Phases

(a) Cohesive energy E_c

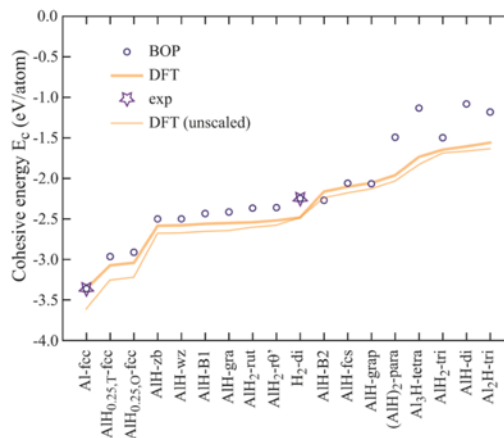


(b) Atomic volume Ω

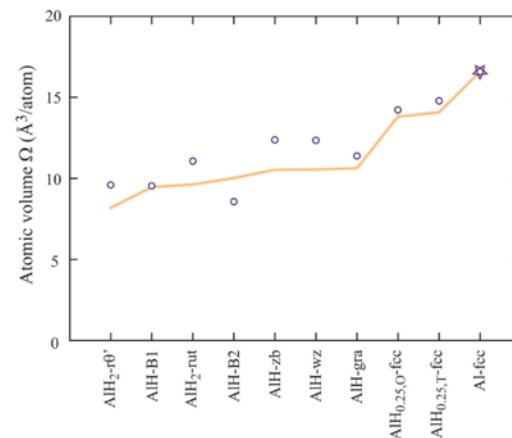


Al-H Phases

(a) Cohesive energy E_c



(b) Atomic volume Ω



X.W. Zhou, D.K. Ward, M. Foster, J.A. Zimmerman, J. Mater. Sci., **2015**, vol. 50, p. 2859.

MD simulations of evolving structures

Impact of MD methods on the diffusion problems in solid-state hydrogen storage materials

- Experimental measurement of diffusion barriers in constantly changing structures is challenging
- Our MD methods accurately determine diffusion barriers for evolving structures
- As an example, we show that the linear “Arrhenius” behavior does not persist during PdH_x hydriding (i.e., when composition x is increasing)

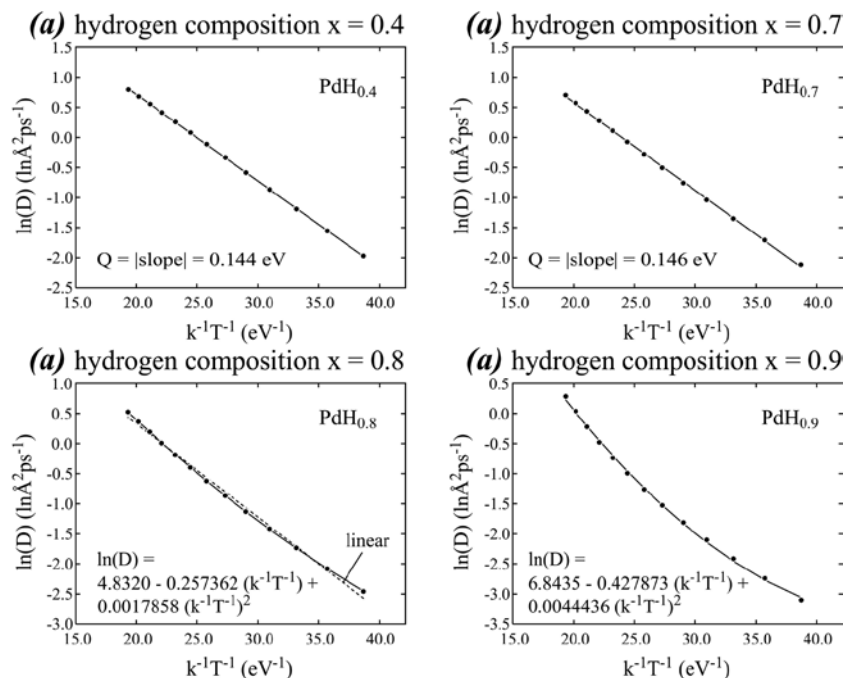
Arrhenius vs. non-Arrhenius type behavior

- Curved Arrhenius plots indicate simultaneous occurrence of multiple diffusion event
- The MD diffusion data can be successfully fitted to a two-mechanism model (solid lines in Arrhenius plots):

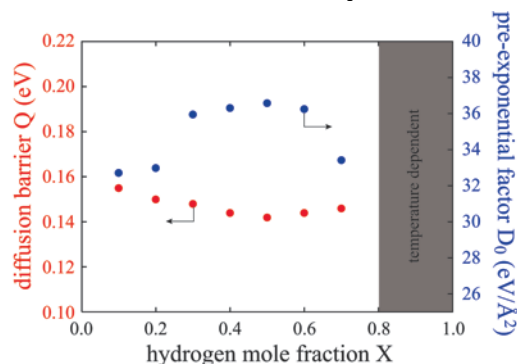
$$D = D_{0,1} \cdot \exp\left(-\frac{Q_{0,1}}{kT}\right) + D_{0,2} \cdot \exp\left(-\frac{Q_{0,2}}{kT}\right)$$

With LLNL, LBNL and ALS

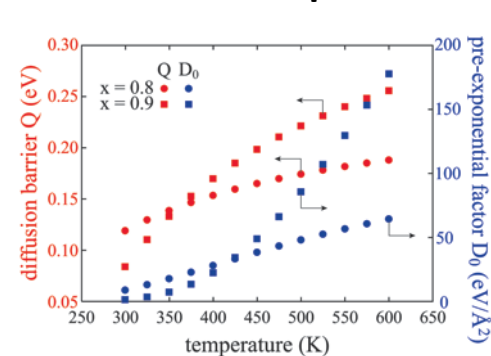
Arrhenius Plots



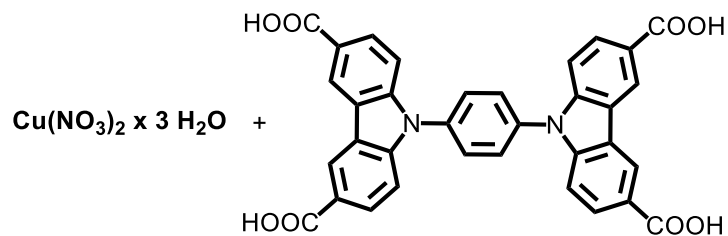
Barrier vs. Composition



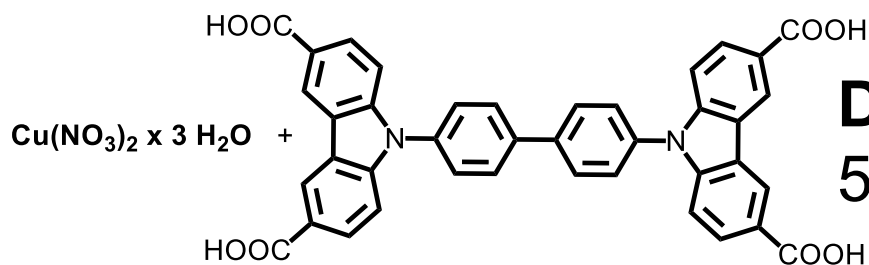
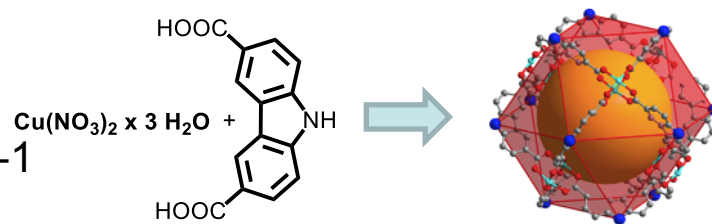
Barrier vs. Temperature



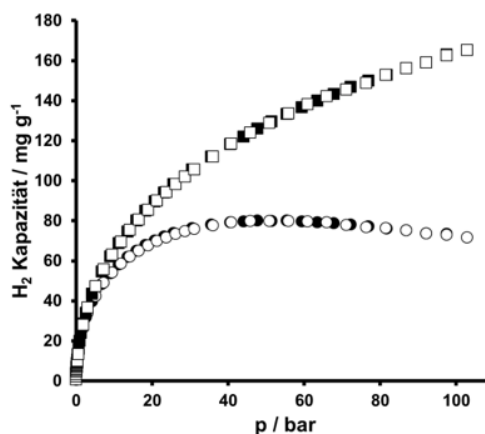
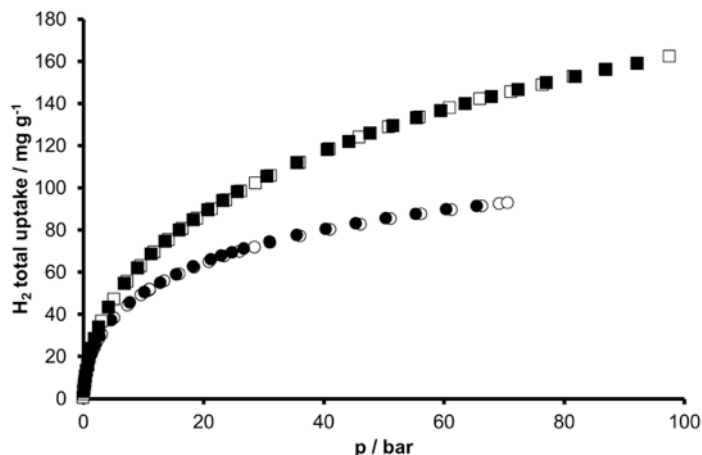
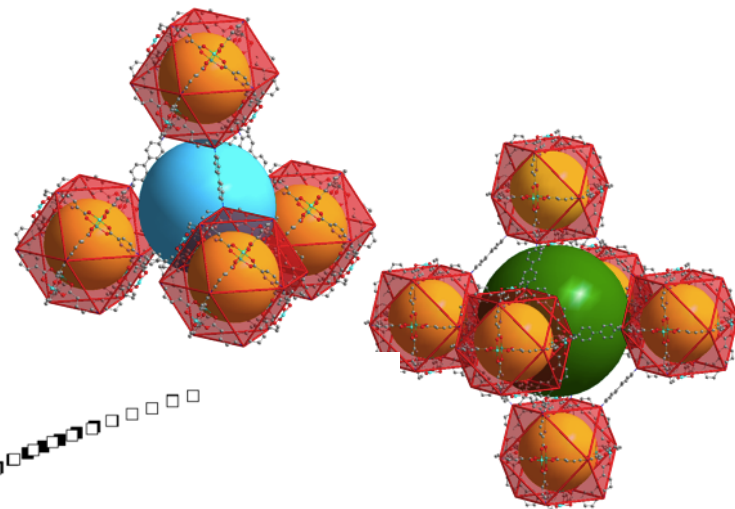
High-surface area MOFs



DUT-48
4898 $\text{m}^2 \text{g}^{-1}$



DUT-49
5476 $\text{m}^2 \text{g}^{-1}$



Collaboration with TU Dresden (Prof. S. Kaskel)

A graduate student from Kaskel's group visited Sandia in February-March 2016 to develop hybrid MOF materials for hydrogen storage

