SAND2016-6692C

Hydrogen Storage Materials Advanced Research Consortium: Sandia Effort

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Sandia National Laboratories, Livermore, CA, USA

Annual Merit Review Meeting, Arlington, VA – 8 June, 2016

Project ID# ST128

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

Lawrence Livermore National Laboratory

BERKELEY LAB
Lawrence Berkeley National Laboratory

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 H_2 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 material**s 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, *in situ* XRD, FTIR, XPS, soft X-ray synchrotron techniques**

Slide 3

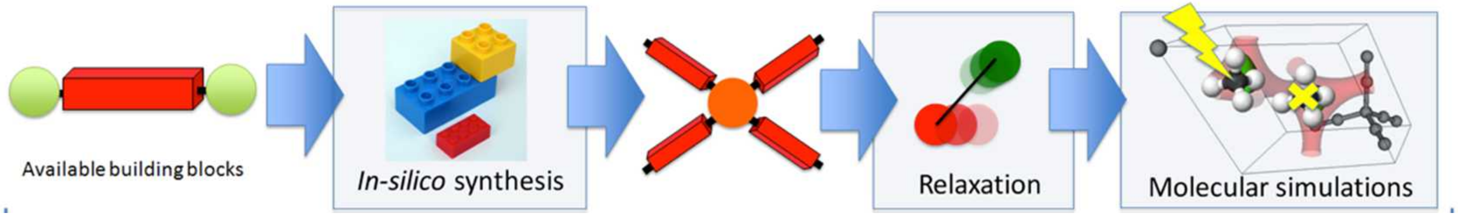
KL2 Klebanoff, Lennie, 4/5/2016

KL1 Hey Vitalie, you don't mention the kinetic problems and the thermodynamic problems, which is really the space we are working in (we are free from the gravimetric and volumetric target restraints in our work).. I would reword this to say: Metal Hydrides and sorbents are attractive candidates for lightweight H2 storage for light duty FC vehicles, but they have undesirable kinetic and thermodynamic properties.

Klebanoff, Lennie, 4/5/2016

Approach: Sorbents

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



with LBNL and LLNL

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 H_2 adsorption data are available in the literature (typically at 77 K)**
  - **Measure reliable H_2 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)

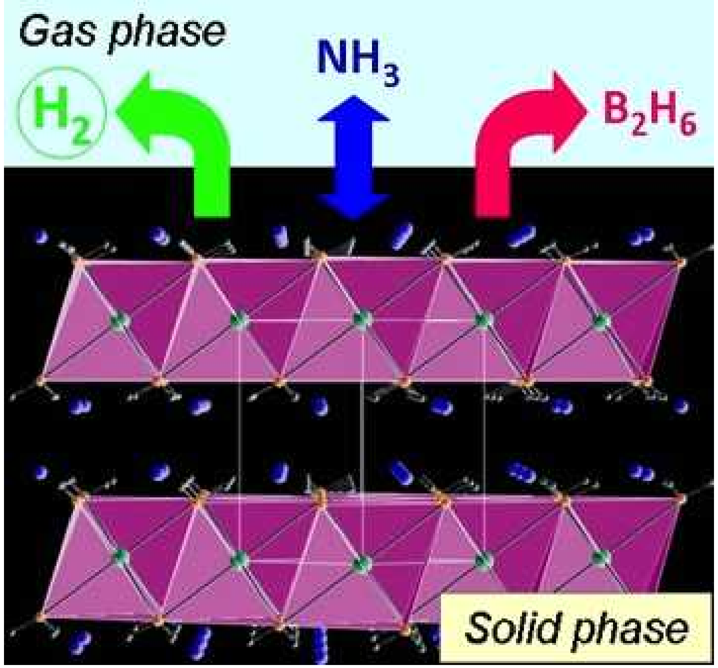
⇒ assess whether reaction entropies could be used to counteract large enthalpic changes via crystalline-to-amorphous transitions

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*

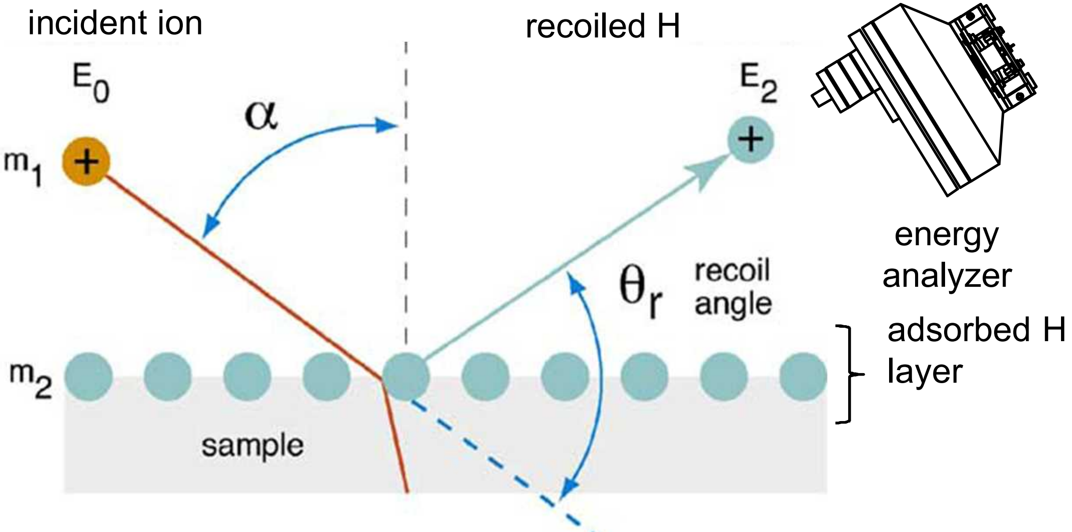
Sandia’s technical roles within HyMARC

- 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

LAMMPS

Large-scale Atomic/Molecular Massively Parallel Simulator

High-pressure H_2 station (up to 1000 bar)

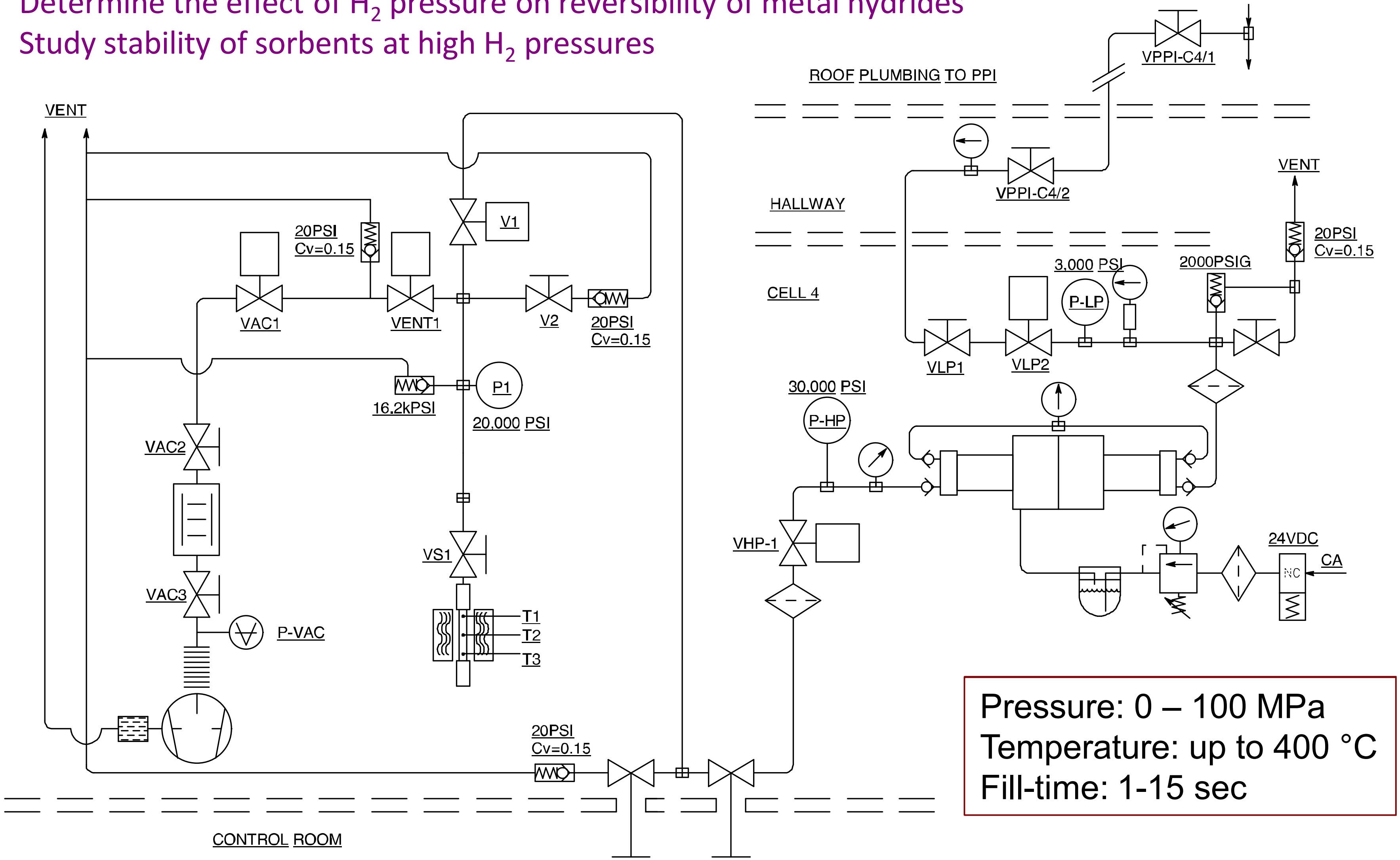


LEIS: Low Energy Ion Scattering Spectroscopy

Sandia high-pressure station

Redesigned and upgraded the high-pressure hydrogen station (up to 100 MPa H_2)

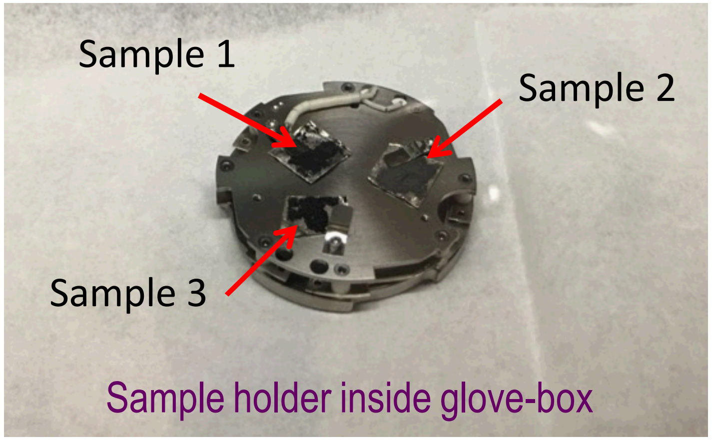
- Determine the effect of H_2 pressure on reversibility of metal hydrides
- Study stability of sorbents at high H_2 pressures



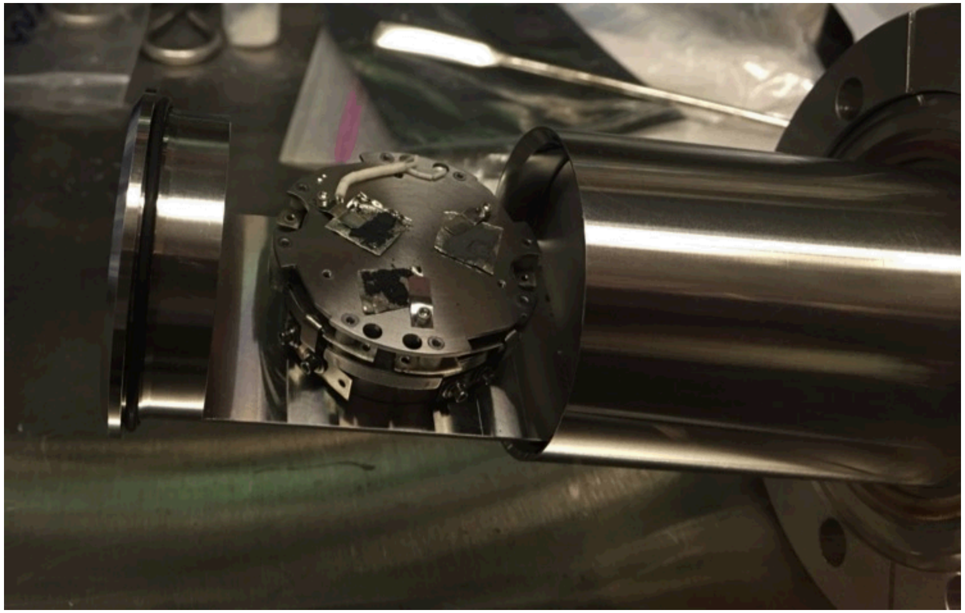
Pressure: 0 – 100 MPa
Temperature: up to 400 °C
Fill-time: 1-15 sec

Clean transfer system for XPS and LEIS

Designed and built two holders for anaerobic transfer of samples



Sample holder inside glove-box



- 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 $\Delta H°$ and entropy $\Delta S°$ 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?

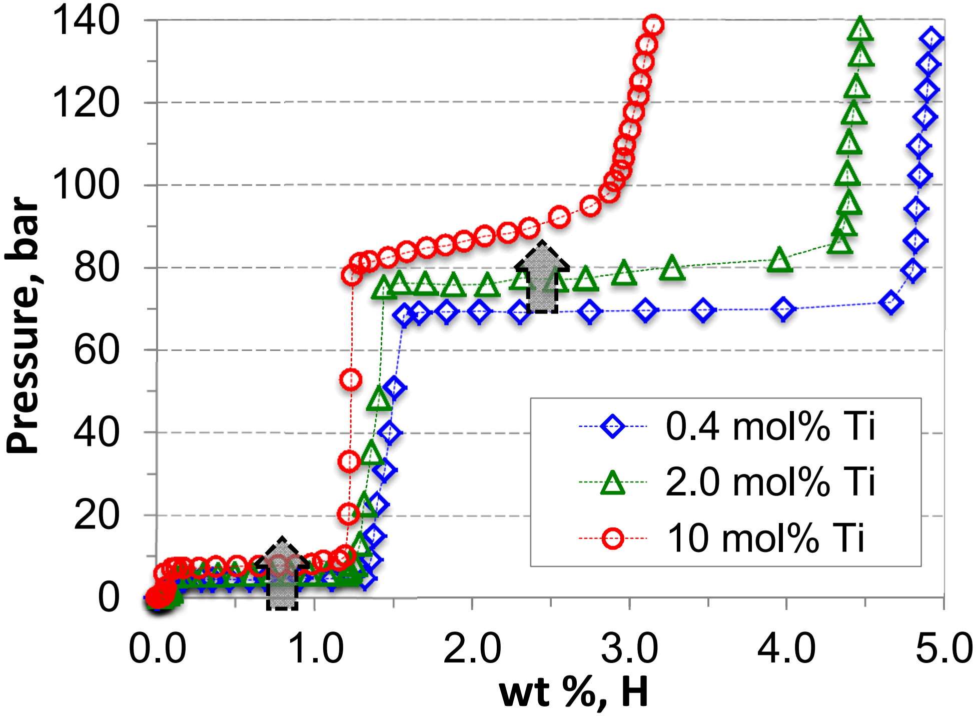
⇒ What is the effect of titanium on the plateau pressure?

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

$$3NaAlH_4 \rightleftarrows Na_3AlH_6 + 3Al + 3H_2$$

$$Na_3AlH_6 \rightleftarrows 3NaH + Al + 3/2H_2$$

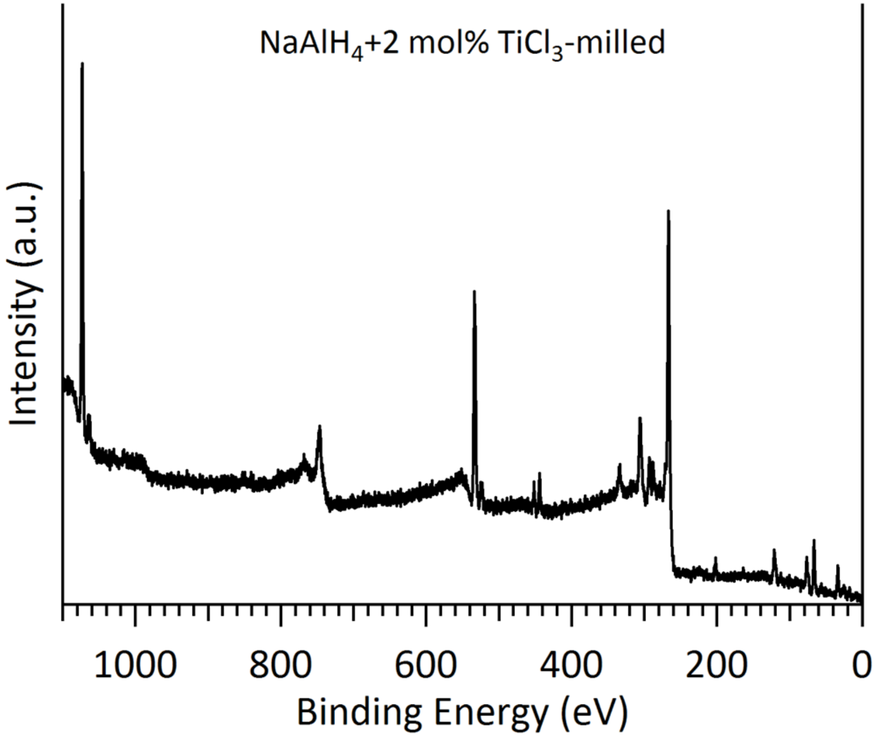
PCT data for Ti-doped $NaAlH_4$

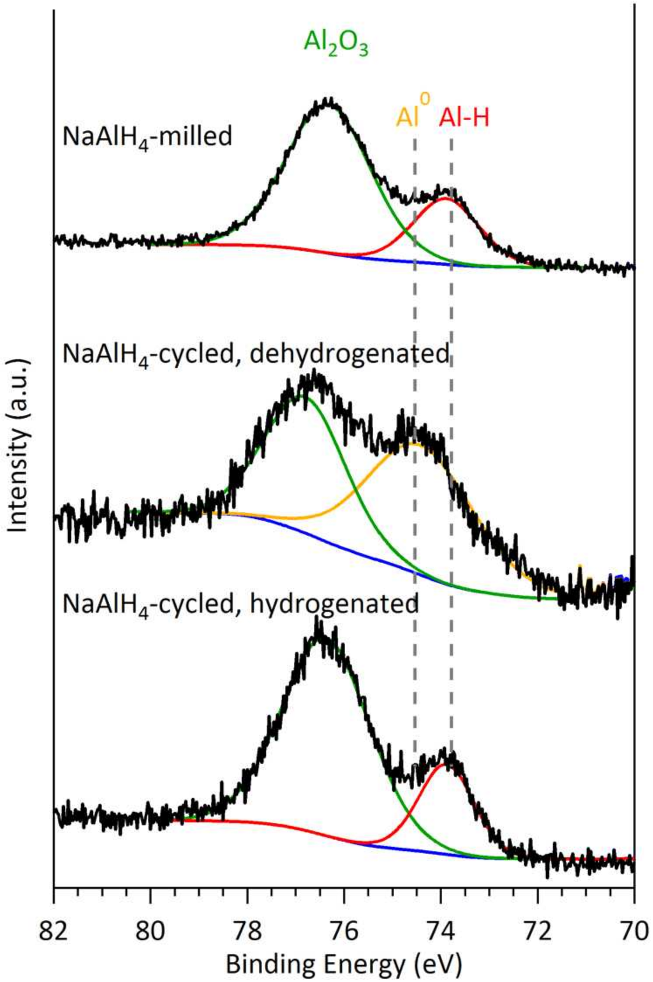


The role of titanium in sodium alanate is still poorly understood. Ti not only enables reversibility and accelerates kinetics, but it also affects the equilibrium pressure of H_2.

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

XPS data obtained using the HyMARC-developed clean transfer system





Surface Composition

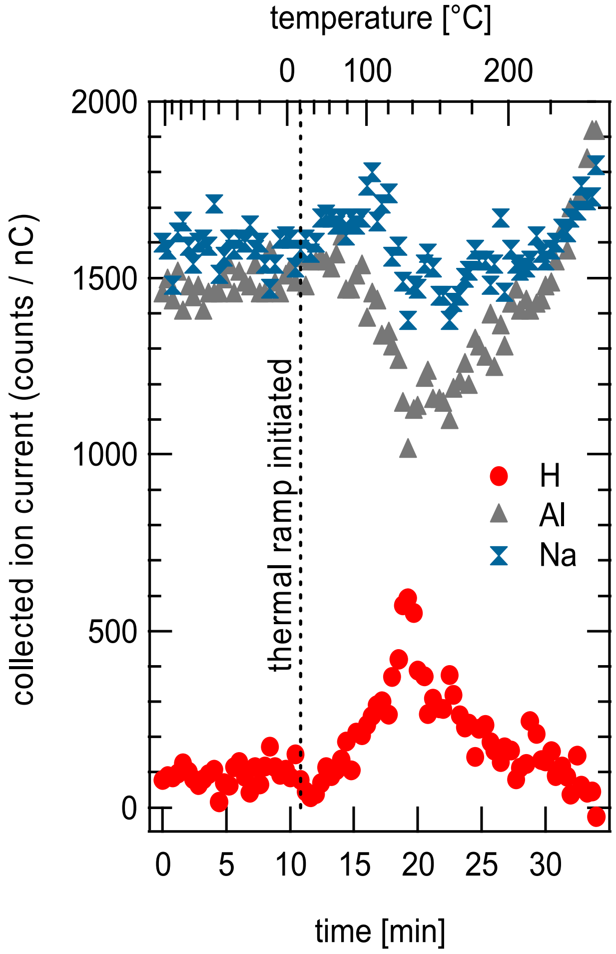
	Milled	Cycled, Hydrogenated
Na	24%	30%
Al	30%	16%
O	45%	47%

⇒ The XPS data confirms the surface of $TiCl_3$-doped sodium alanate is oxygen-rich

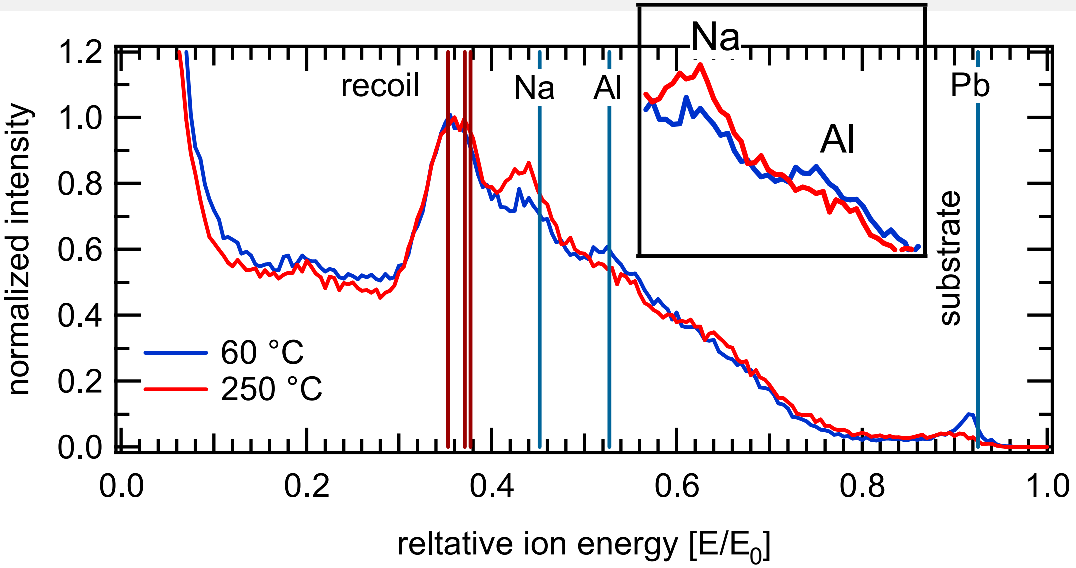
⇒ Al 2p region shows oxide, hydride, and metal; dehydrogenated material is Al^0-rich

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 ≈150 °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.)

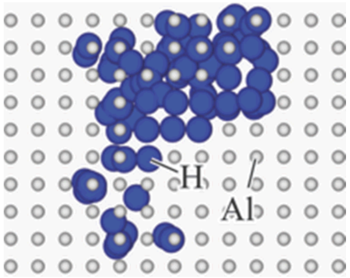
e.g., jumping atom can have different neighboring species (circles of different color.)

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

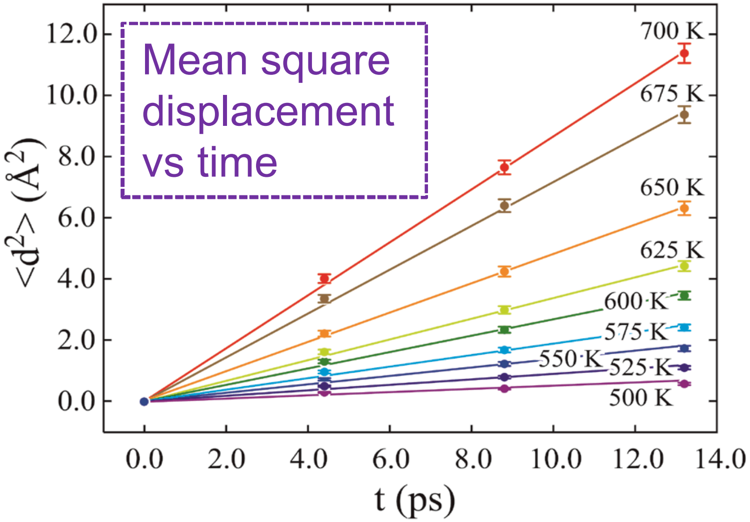
Advantages of MD Methods

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

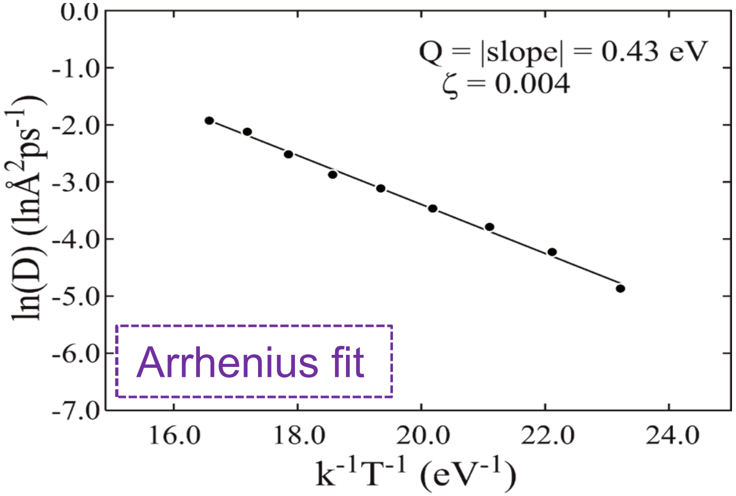
MD allows diffusion atoms to be tracked



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



Mean square displacement vs time



Arrhenius fit

⇒ 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

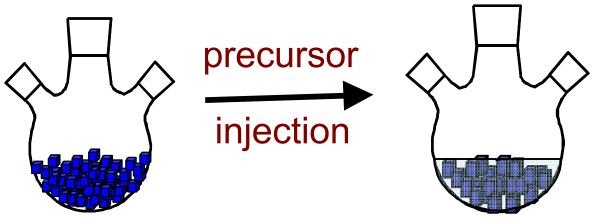
FY16 model system: $LiNH_2 + 2LiH \rightleftharpoons Li_3N + 2H_2$

⇒ Can the thermodynamics of H_2 uptake and release be altered through nanostructuring?

⇒ What is more important: particle size or interactions with porous hosts?

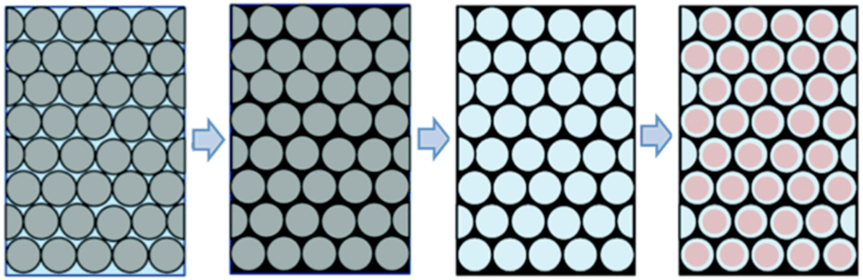
⇒ What is the effect of nanointerfaces?

Metal hydride infiltration



With E. Majzoub (U. of Missouri)

Templated carbons



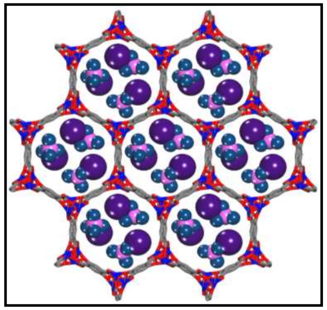
Polymer/silica composite

Carbon/silica composite

Templated carbon

Nano-hydride in carbon

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:

$Li_3N + H_2 \rightleftharpoons Li_2NH + LiH$

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

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

Nano (Li$_3$N in 3-10 nm nanoporous C):

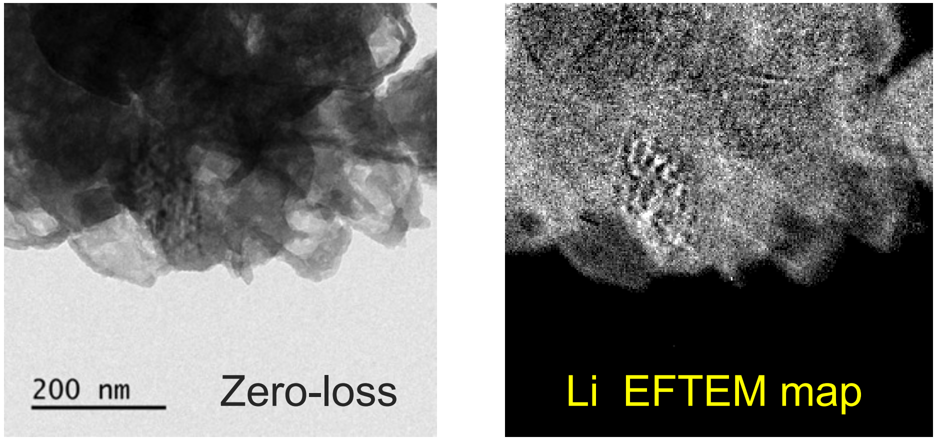
$Li_3N + 2H_2 \rightleftharpoons LiNH_2 + 2LiH$

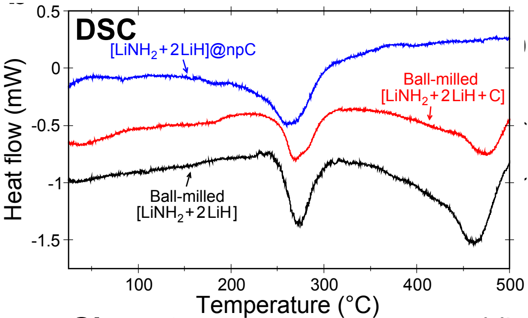
⇒The Li$_3$N@C nanocomposite displays a reversible H$_2$ capacity of 4 wt% H.

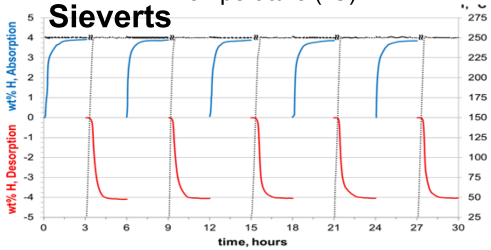
⇒The full cycling capacity in the Li$_3$N/[LiNH$_2$ + 2LiH] system is realized at 250 °C, which is 180 °C lower compared to bulk.

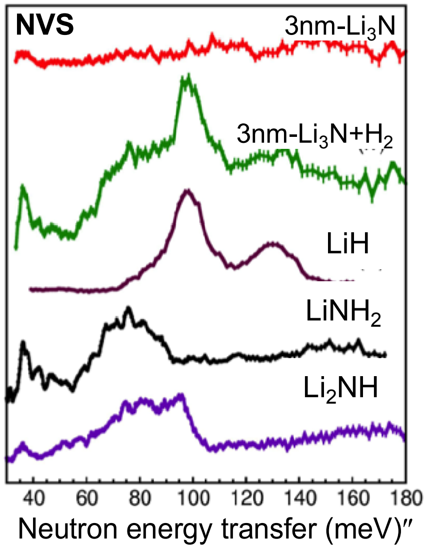
Multiscale modeling (B. Wood et al, LLNL) revealed that nanoconfinement of the high-capacity Li$_3$N/[LiNH$_2$ + 2LiH] system fundamentally alters the reaction pathways as a direct consequence of solid-solid nanointerfaces within the material.

Q2 FY16 milestone









Submitted for publication

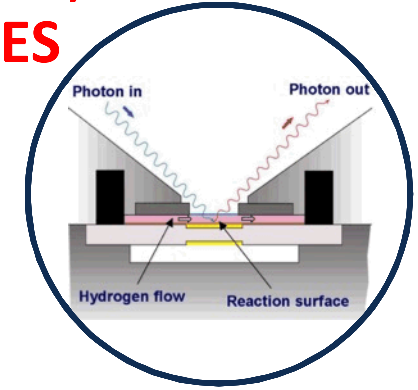
In collaboration with Mahidol University, LLNL, LBNL, NIST (T. Udovic)

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).

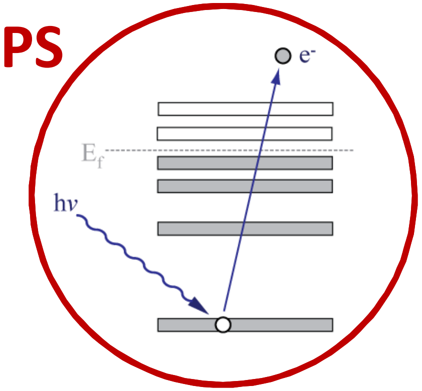
XAS, XES



X-ray Absorption and Emission Spectroscopy

Probe surface and near-surface electronic states

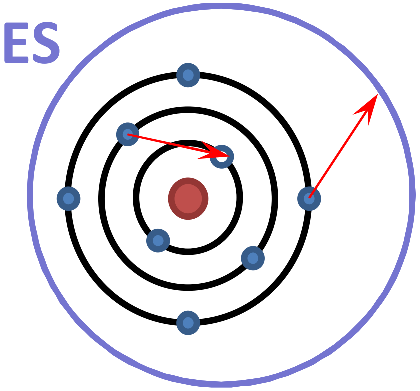
XPS



X-ray Photoelectron Spectroscopy

Binding information / oxidation states

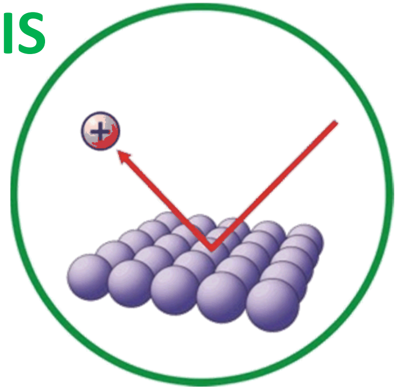
AES



Auger Electron Spectroscopy

Surface composition

LEIS



Low Energy Ion Scattering

Directly detect adsorbed H

Task 3: LEIS measurements of H_2 diffusion

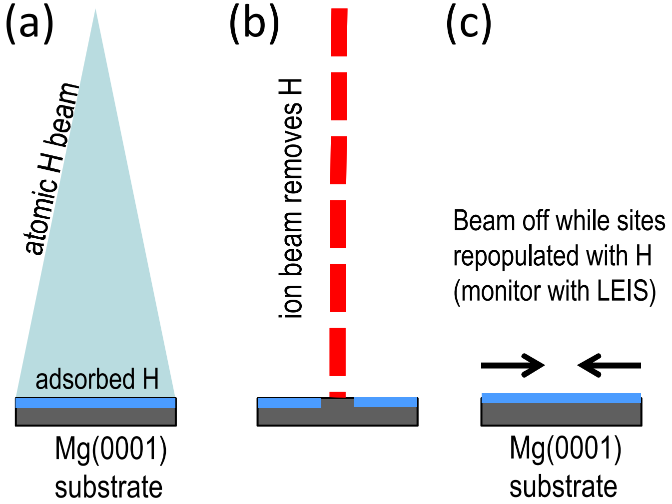
We seek to answer:

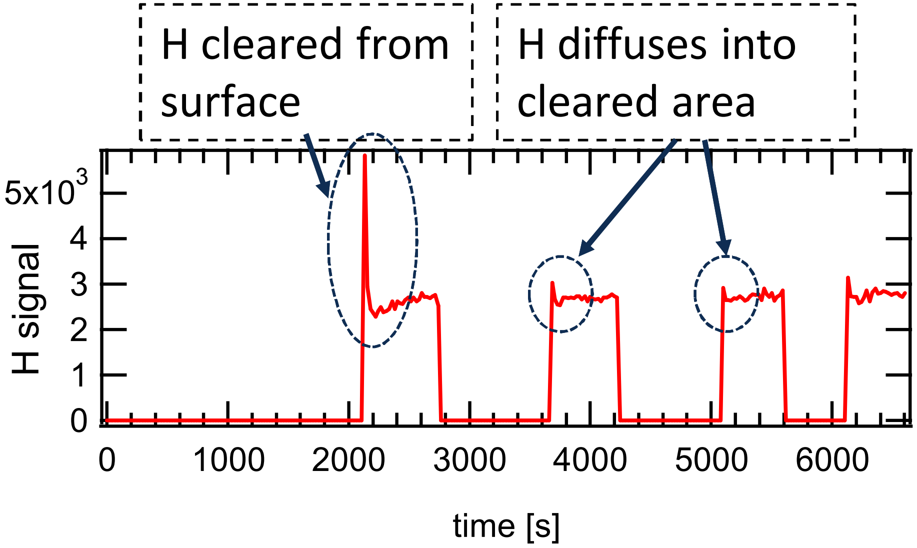
- How does surface diffusion contribute to recombination / surface-bulk transport?

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 sublimes 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. ✓




H cleared from surface

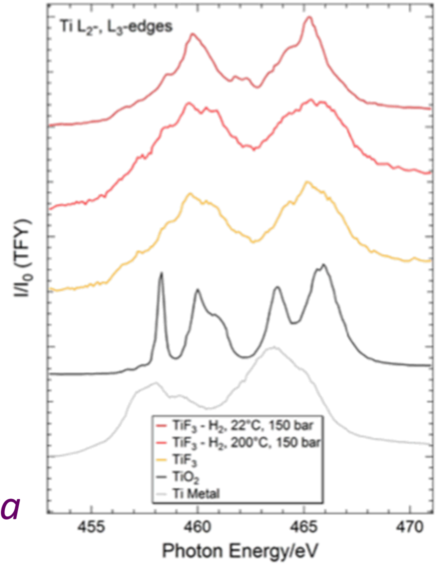
H diffuses into cleared area

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 H_2

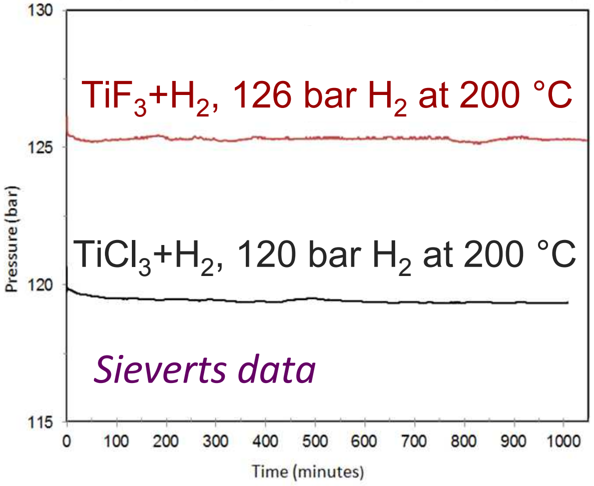
⇒ Examine the known catalytic additives TiF_3 and $TiCl_3$ for reaction with hydrogen at 200 °C, 120 bar for ≈17 hours with Sieverts H_2 uptake, X-ray absorption spectroscopy and FTIR



XAS data

-- negligible change in TiF_3 vibrational structure with FTIR, negligible H_2 uptake seen with Sieverts.

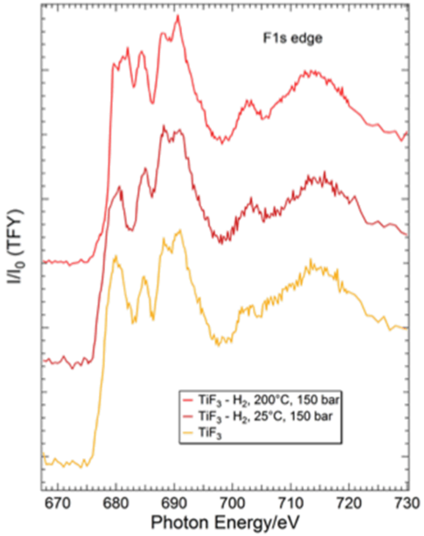
-- negligible change in Ti electronic structure with XAS in fluorescence yield mode, No evidence of Ti metal or oxide



<u>Results</u>: Bulk TiF_3 was found to be unreactive to H_2 at the temperatures and pressures for which it acts "catalytically" as an additive (e.g. in $NaAlH_4$). Same result is also seen for $TiCl_3$.

<u>Next Single Step</u>: Examine H_2 reactivity of ball-milled TiF_3 and $TiCl_3$ 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 *in-situ* 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

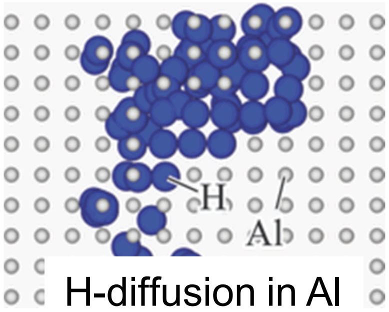
- A molecular dynamics modeling framework was established to accurately predict the diffusion kinetic barriers; proof-of-concept demonstrated for H-diffusion in Pd and Al.

Synthesis

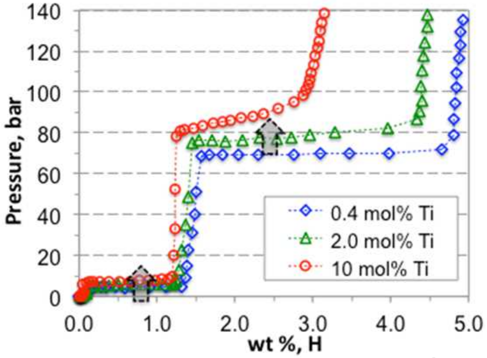
- Sandia high-pressure (up to 1000 bar) system was upgraded
- Identified model MOFs for GCMC and QMC studies to calculate interaction potentials and predict H_2 isotherms
- Initiated a comprehensive study of titanium role in sodium alanate and determined the effect of Ti-doping levels on hydrogen plateau pressure
- Elucidated the H_2 reactivity of $TiCl_3$ and TiF_3 additives by themselves (no hydride present)
- Developed synthetic protocols for synthesizing ≤ 10 nm particles of $LiNH_2/2LiH$ in nanoporous carbons and MOFs

Characterization

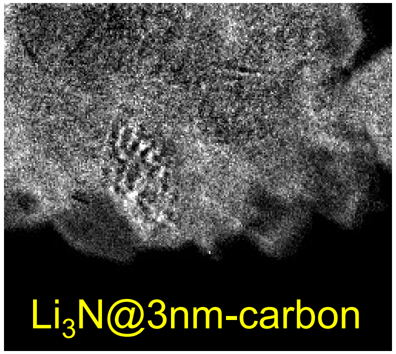
- Demonstrated that LEIS can measure surface diffusion
- Developed clean anaerobic techniques for sample transfer for XPS, Auger, XAS and LEIS *in situ* studies



H-diffusion in Al



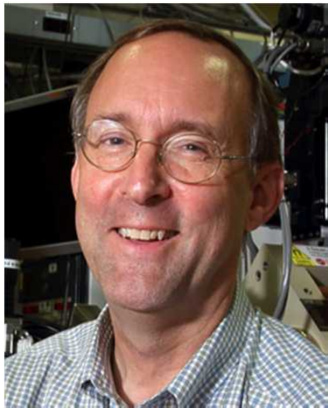
Bulk: $NaAlH_4 \Leftrightarrow NaH+Al+3/2H_2$



Li_3N@3nm-carbon

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

Sandia team and responsibilities

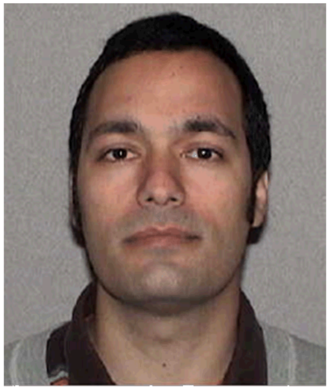


Mark Allendorf
(MOFs, hydrides)

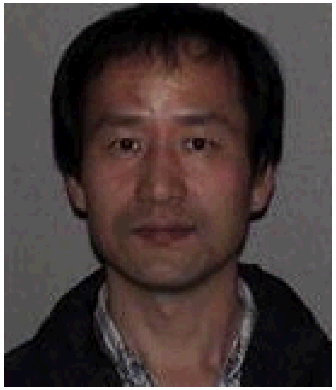
Vitalie Stavila
(Sorbents, hydrides)

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): H_2 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

Sandia National Laboratories

BERKELEY LAB
Lawrence Berkeley National Laboratory

Lawrence Livermore National Laboratory

HyMARC

Thank you for your attention!

We gratefully acknowledge EERE/FCTO for financial support!

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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Technical Back-Up Slides

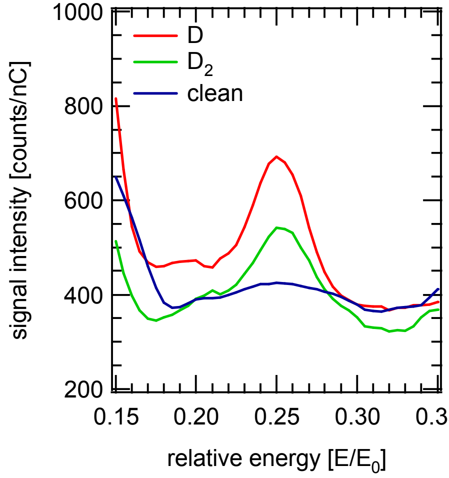
Surface characterization of Ni-doped MgH_2

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.**

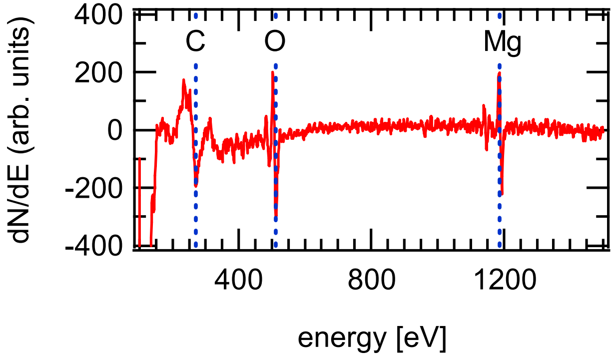
Material: Ni-doped Mg powder (pressed into In foil)



Ion energy spectrum reveals both D2 and D adsorb on the surface. This suggests the Ni dopant promotes D_2 dissociation.

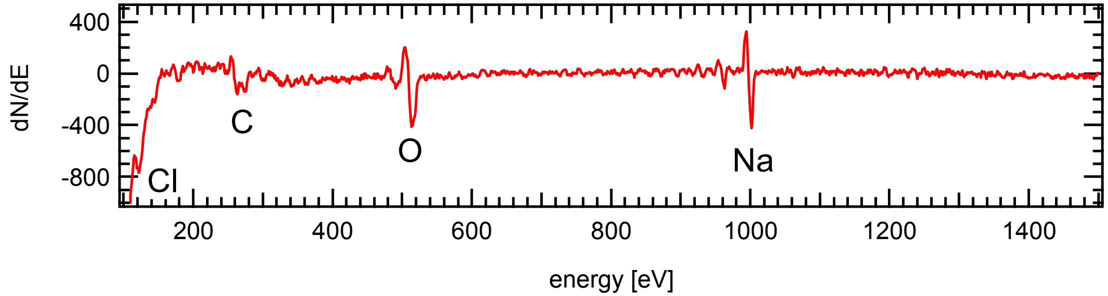
LEIS is the only element-specific way to detect adsorbed hydrogen.

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

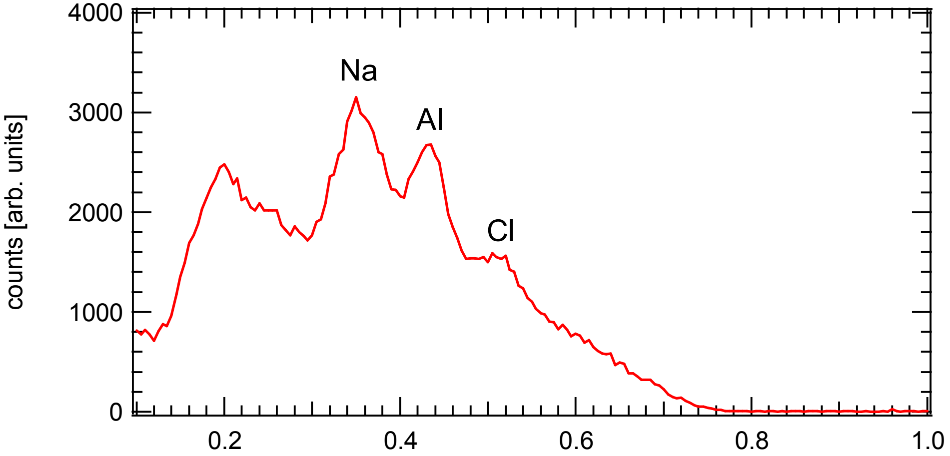


LEIS spectra of $TiCl_3$-doped $NaAlH_4$

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.

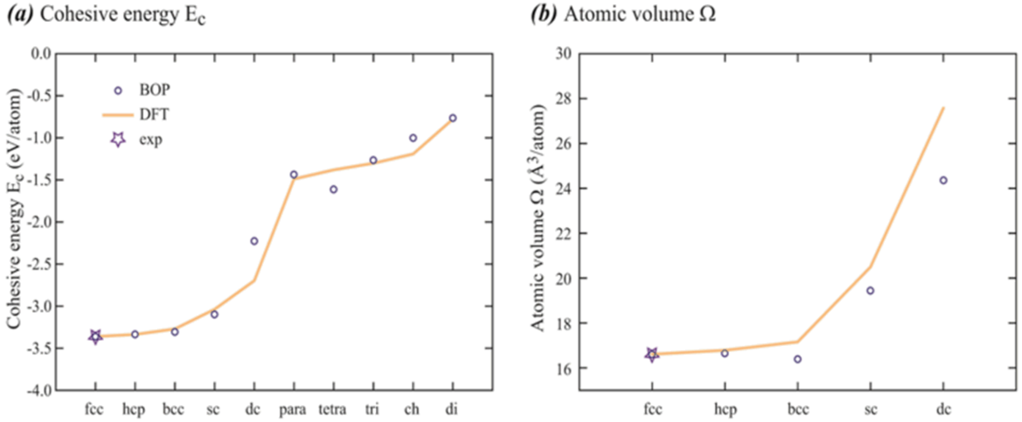
The surface of ball-milled $TiCl_3$-doped sodium alanate (2mol% Ti) is rich in sodium and seems to be oxygen terminated.

High-accuracy Al-H bond order interatomic potentials

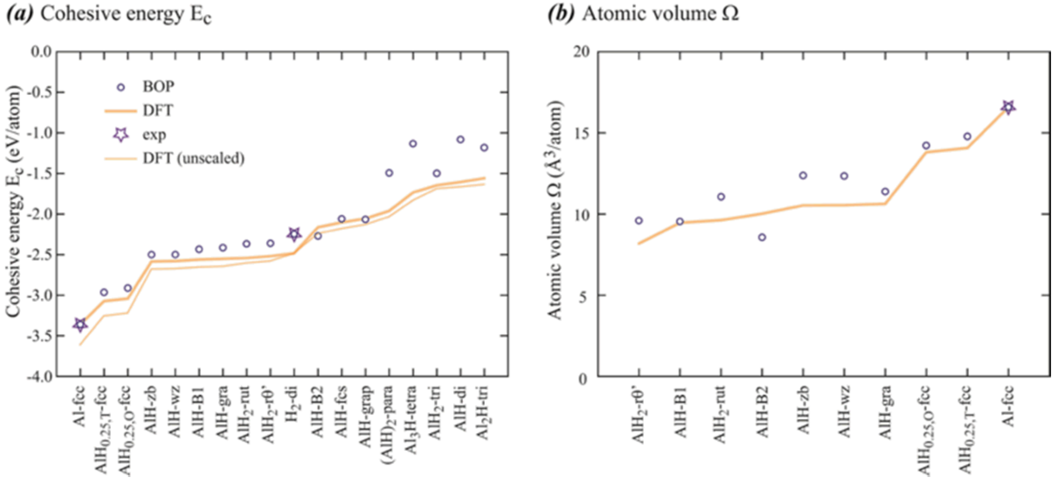
Significant improvement over known potentials:

- 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



Al-H Phases



📖 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)

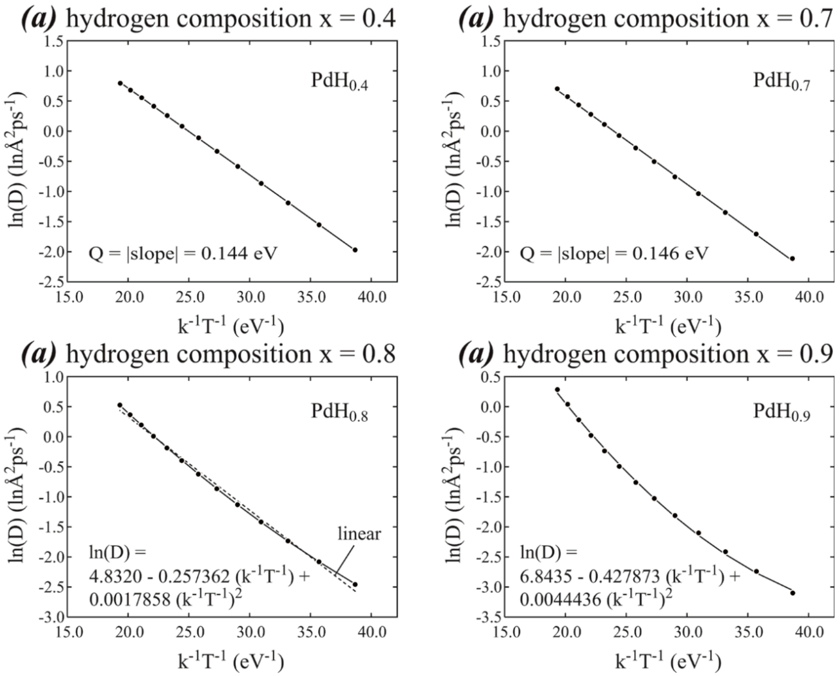
Arrhenius vs. non-Arrhenius type behavior

- 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):

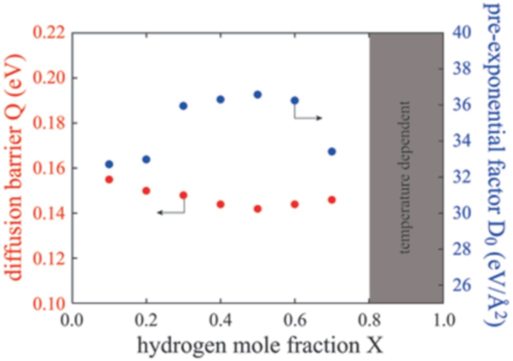
$$D = D_{0,1} \cdot \exp\left(-\frac{Q_{0,1}}{kT}\right) + D_{0,2} \cdot \exp\left(-\frac{Q_{0,2}}{kT}\right)$$

With LLNL, LBNL and ALS

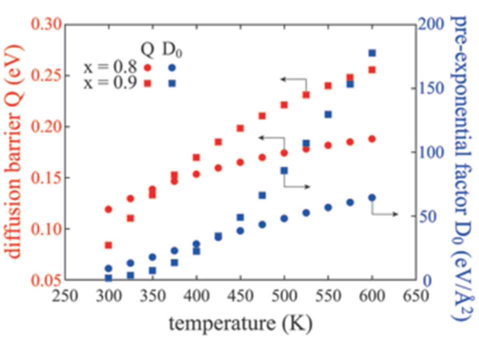
Arrhenius Plots



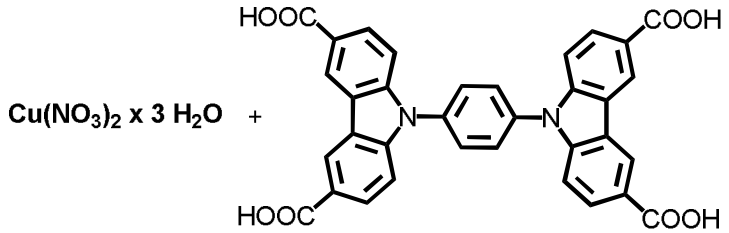
Barrier vs. Composition



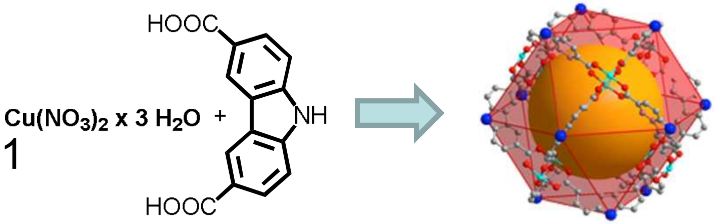
Barrier vs. Temperature

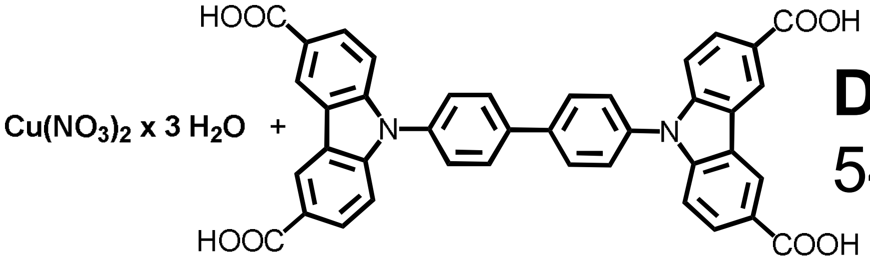


High-surface area MOFs

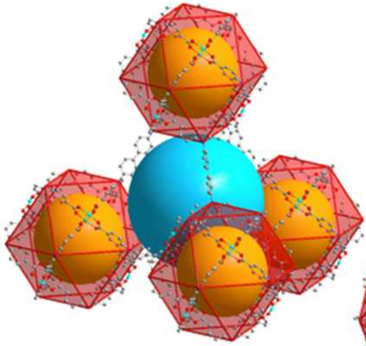


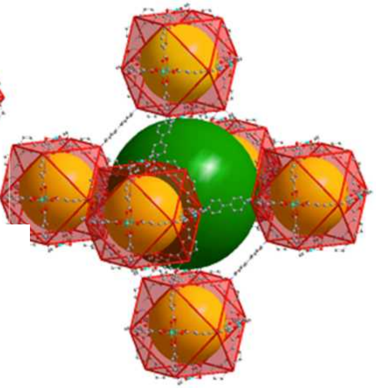
DUT-48
4898 $m^2\ g^{-1}$

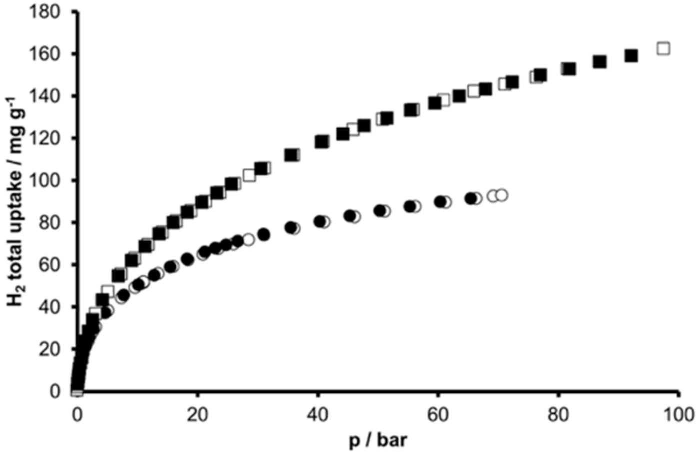


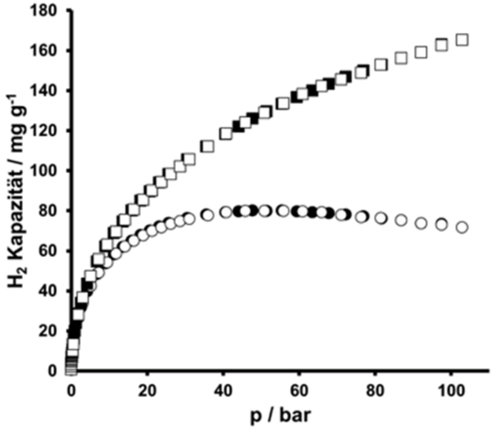


DUT-49
5476 m^2g^{-1}









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

Reviewer-Only Slides

Critical assumptions and issues

- **Assume that synthetic methods being developed for nanoscale binary metal hydrides will apply to complex hydrides**
    - *Will explore several strategies to achieve nanosizing, including wet-chemistry and solid-state approaches to nanostructured complex metal hydrides*
- **Assume that potentials developed for model metal hydrides and sorbents will be transferable to other classes of storage materials**
    - *Will perform QMC and DFT computations on sorbents to correlate the results*
    - *Will perform experiments to validate multiscale theory models*
- **Capability of monitoring the surfaces and interfaces *in situ* during hydrogen release and absorption**
    - *Multiple characterization techniques (spectroscopy, soft X-ray techniques, electron microscopy) will be used to correlate the results and determine mechanisms and hydrogen diffusion pathways*

Publications and presentations

Presentations:

- V. Stavila, B. Wood, L. Klebanoff, T.W. Heo, et al. “Nanoscale effects in complex metal hydrides”, Pacifichem-2015, Honolulu, HI, December **2015**.
- V. Stavila, L. Klebanoff, E. Majzoub, J. Vajo. “Phase minimization as a promising strategy to improve hydrogen storage properties of complex metal hydrides” MRS Spring Meeting, Phoenix, AZ, April **2016**.

Publications:

- X. W. Zhou, F. El Gabaly, V. Stavila, M. D. Allendorf, “Molecular Dynamics Simulations of Hydrogen Diffusion in Aluminum”, *J. Phys. Chem. C*, **2016**, *v. 120*, p. 7500.
- B.C. Wood, V. Stavila, et al., “Nanointerface-driven reversible hydrogen storage in the nanoconfined Li-N-H system,” *submitted for review*.

Patents:

- V. Stavila, L. Klebanoff. “Nanostructured metal amides and nitrides for hydrogen storage”, US Patent Application 62/235,930, **2015**.