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# Hydrogen Materials-Advanced Research Consortium: Sandia Efforts for Understanding Hydrogen Storage Systems

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## Aims of HyMARC and Sandia's Objectives

*Provide foundational understanding of phenomena governing thermodynamics and kinetics and develop a knowledge base to accelerate the development of on-board $H_2$ storage materials.*

-Develop and validate thermodynamic models of hydrogen adsorption and metal hydride reactivity, including effects of $H_2$ pressures of up to 700 bar.

-Identify structures, compositions, and diffusion processes for gas-surface and solid-solid interfaces and their role in the kinetic processes. .

-Determine mechanisms by which additives can promote improved hydrogen storage performance.

-Apply multiscale codes to gain clarity on the physical mechanisms of hydrogen storage materials that may impact behavior and the ability of any material to achieve or surpass DOE performance targets.

-Leverage specialized and *in-situ* capabilities and expertise: a high-pressure (up to 1000 bar) $H_2$ system, low-energy ion scattering spectroscopy, air-free transfer systems compatible with ALS, and high-throughput molecular dynamics calculations.

| Theory/modeling | Synthesis | Characterization |
|---|---|---|
| DFT, Classical MD, database development | Bulk and nanoscale synthesis of MOFs, metal hydrides, high-pressure $H_2$ synthesis, controlled additives studies | LEIS, porosimetry/gas sorption, *in situ* XRD, FTIR, soft X-ray synchrotron techniques (XAS, XES, AP-XPS) |

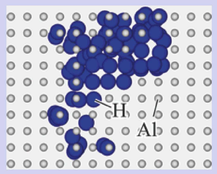
## Diffusion of Hydrogen

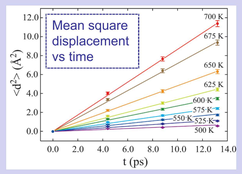
**Objective:** Calculate and measure bulk and surface *transport rates* of hydrogen to understand **kinetics** of hydrogenation and dehydrogenation.

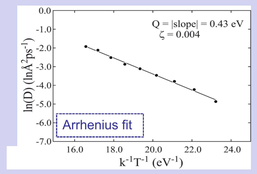
### Molecular Dynamics Simulations of H in Aluminum

- Relate myriad diffusion jump pathways to overall diffusion behavior
- Generate dynamic evolution of structures and positions of H atoms

LAMMPS

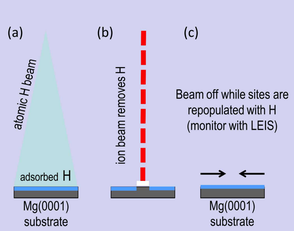


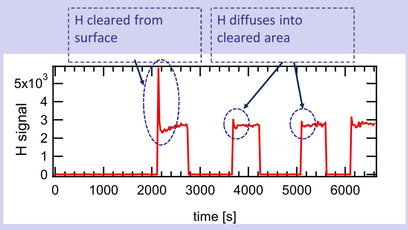




### Low-Energy Ion Scattering (LEIS) Measurements on Magnesium

- Proven LEIS can be used to monitor hydrogen surface diffusion
- The LEIS approach allows surface diffusion studies on thermally sensitive samples.



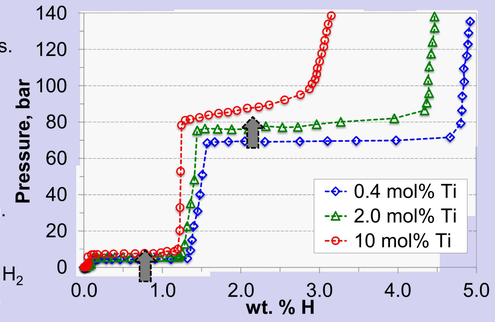




## Model Bulk Metal Hydride: Ti-doped $NaAlH_4$

**Objective:** *Understand factors controlling enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) of $H_2$ adsorption and desorption, including the role of titanium dopants in the **thermodynamics** of $NaAlH_4$, to develop validated multi-scale models for computational materials design.*

### Pressure-Composition-Temperature Studies

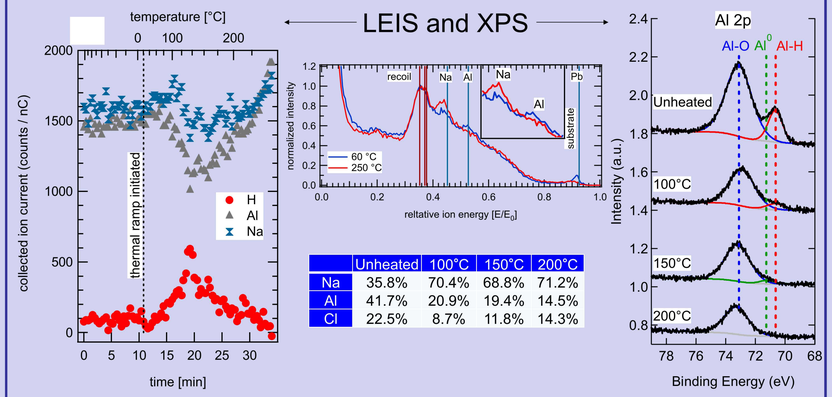
- $TiCl_3$ is known to enable reversibility and improve kinetics.
- Increasing the concentration of $TiCl_3$ increases the plateau (equilibrium) $H_2$ pressures, indicating a shift in the thermodynamics.
- Need to study interactions between Al and Ti in the system.




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

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

### *In situ* Surface Analysis with Heating

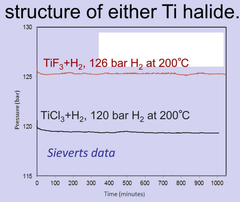


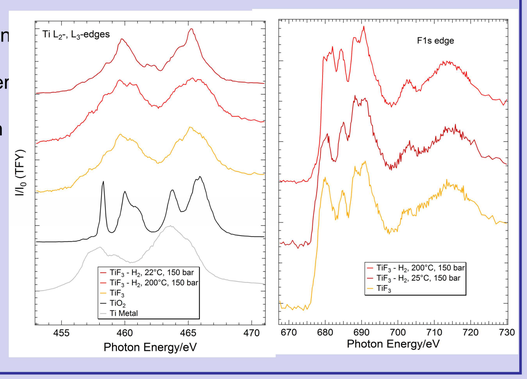

| | Unheated | 100°C | 150°C | 200°C |
|---|---|---|---|---|
| Na | 35.8% | 70.4% | 68.8% | 71.2% |
| Al | 41.7% | 20.9% | 19.4% | 14.5% |
| Cl | 22.5% | 8.7% | 11.8% | 14.3% |

- LEIS indicates segregation of H to the surface as hydride is heated to 150˚C.
- Able to measure hydrogen directly as it thermally desorbs.
- Al 2p XPS spectrum shows conversion of Al-H to $Al^0$ upon heating to 150 ˚C.
- Rehydrogenated material again has peak for Al-H.
- Ti not detected by either method (even at 10 mol%) without sputtering off surface layer.
- Surface becomes enriched with Na during heating, and Al becomes depleted.
- New clean transfer capabilities preserve hydride without additional oxidation.

### Examination of Ti-based Catalytic Additives

- Determine whether Ti halides are active for hydrogenation on their own.
- Heat $TiF_3$, $TiCl_3$ at 200˚C under 120 bar $H_2$ for 17 hours.
- XAS, FTIR show no change in electronic or vibrational structure of either Ti halide.

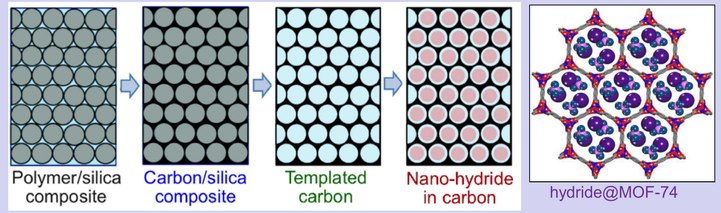



## Nanoscale Effects and Nanointerfaces

**Objective:** *Use nanostructuring to improve **kinetics**, alter **reaction pathways**, and study the effects of particle size, defects, and nanointerfaces on **thermodynamics**.*

### Infiltration of Hydride Nanoparticles into Porous Materials




### Nanoconfined $Li_3N$ Bypasses $Li_2NH$ Intermediate

Bulk (two steps):

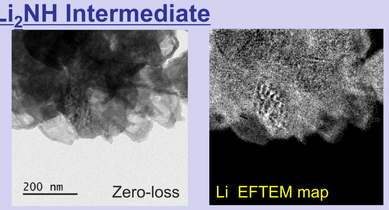
$Li_3N + H_2 \rightleftarrows Li_2NH + LiH$

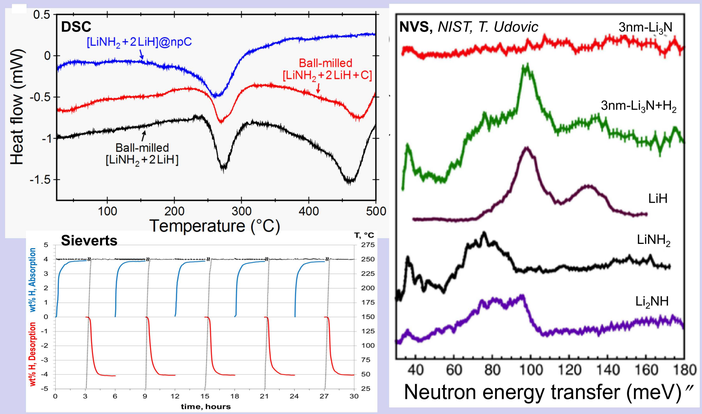
$Li_2NH + LiH + H_2 \rightleftarrows LiNH_2 + 2LiH$

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

Nano (one step, $Li_3N$ in 3-10 nm npC):

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




## Summary and Conclusions

- Hydrogen diffusion rates in metals has been measured experimentally and modeled using molecular dynamics codes developed at Sandia.
- Established Ti-doped $NaAlH_4$ displays concentration effects on the $H_2$ plateau equilibrium.
- Hydrogen surface speciation was detected i*n situ* by LEIS and XPS upon heating of $NaAlH_4$.
- Bulk Ti-based additives $TiCl_3$ and $TiF_3$ alone are unreactive to hydrogenation.
- Methods for infiltrating complex metal hydrides into porous hosts have been developed.
- $Li_3N$ synthesized and confined in nanoporous carbon can be fully hydrogenated in one step.
- LEIS can be used to measure hydrogen surface diffusion on thermally sensitive materials.

## Publications and Patents:


- Zhou, X. W.; El Gabaly, F.; Stavila, V.; Allendorf, M. D. *J. Phys. Chem. C*, **2016**, *120*, 7500-7508
- Wood, B. C.; Stavila, V.; Poonyayant, N.; Heo, T. W.; Ray, K.; Klebanoff, L. E.; Udovic, T. J.; Lee, J. R. I.; Angboonpong, N.; Pakawatpanurut, P. *submitted*
- Stavila, V.; Klebanoff, L.E. U.S. "*Nanostructured metal amides and nitrides for hydrogen storage*" Patent filed, application # *62/235,930*, **2015**.


## Acknowledgments:

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