

IV.C.2 Hydrogen Storage Materials Advanced Research Consortium: Sandia Effort

Mark D. Allendorf (Primary Contact),
Vitalie Stavila, Lennie Klebanoff, Rob Kolasinski,
Farid El Gabaly, Xiaowang Zhao, James White
Sandia National Laboratories
7011 East Avenue
Livermore, CA 94551
Phone: (925) 294-3059
Email: mdallen@sandia.gov

DOE Manager: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

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Overall Objectives

- Provide technical leadership to HyMARC via leadership of Task 1 (Thermodynamics), Task 3 (Gas Surface Interactions) and Task 5 (Additives).
- Provide gas sorption and other property data required to develop and validate thermodynamic models of sorbents and metal hydrides, including the effects of high hydrogen pressure.
- 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 Sandia multiscale codes to discover new materials and new mechanisms of storing hydrogen, provide input for database development.
- Elucidate the role of additives in improving hydrogen storage adsorption and desorption reactions.

Fiscal Year (FY) 2016 Objectives

- Synthesize library of bulk-phase model storage systems.
- Size control method for one prototype complex hydride nanostructure.
- Demonstrate in situ soft X-ray ambient pressure X-ray photoelectron spectroscopy (XPS), X-ray absorption

spectroscopy (XAS), X-ray emission spectroscopy tools, with sample heating.

- Identify hydride mobile species and diffusion pathways.
- Synthesize and characterize library of nanoparticles for one hydride: 1–5 nm, 5–10 nm, >10 nm.
- Assess bulk additives (TiF₃, TiCl₃) for their reactivity towards hydrogen.
- Assess low-energy ion scattering (LEIS) as a tool for measuring H atom surface diffusion on a thermally sensitive surface.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The goal of this project is to develop foundational understanding of phenomena governing thermodynamics and kinetics of hydrogen release and uptake in all classes of hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2020 hydrogen storage targets.

- Cost: \$10/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

FY 2016 Accomplishments

- 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.

- The Sandia high-pressure (up to 1,000 bar) system was upgraded to provide improved temperature control and enable the simultaneous use of multiple reaction cells.
- Synthesized and characterized a suite of metal-organic frameworks (MOFs) to validate quantum Monte Carlo and grand canonical Monte Carlo models of the interaction potentials and predict hydrogen isotherms.
- Established X-ray absorption spectroscopy as a tool for probing metal hydrides, including separate bulk- and surface-sensitive approaches. Used titanium-doped NaAlH_4 as a model system.
- Elucidated the extent to which the bulk additives TiCl_3 and TiF_3 by themselves (no hydride present) are reactive towards hydrogen gas using a combination of X-ray emission spectroscopy, XAS, Fourier transform infrared spectroscopy, and Sieverts hydrogen uptake measurements.
- Developed synthetic protocols for synthesizing ≤ 10 nm particles of $\text{LiNH}_2/2\text{LiH}$ in nanoporous carbons and MOFs.
- Demonstrated that LEIS can be used to measure H atom surface diffusion on the thermally sensitive $\text{Mg}(0001)$ surface.
- Developed clean, air-free techniques for sample transfer for XPS, Auger, XAS, and LEIS in situ studies.



INTRODUCTION

Storage of hydrogen on board vehicles is one of the critical enabling technologies for creating hydrogen-fueled transportation systems that can reduce oil dependency and mitigate the long-term effects of fossil fuels on climate change. Stakeholders in developing hydrogen infrastructure (e.g., state governments, automotive original equipment manufacturers, station providers, and industrial gas suppliers) are currently focused on high-pressure storage at 350 bar and 700 bar, in part because no viable solid-phase storage material has emerged. Nevertheless, solid-state materials, including novel sorbents and high-density hydrides, remain of interest because of their unique potential to meet all DOE Fuel Cell Technologies Office targets and deliver hydrogen with lower storage pressures and higher on-board densities. However, the existing materials suffer from thermodynamic and kinetic limitations, which prevent their application as practical hydrogen storage media.

Sandia's objectives/responsibilities within HyMARC are to: (1) provide technical leadership to the consortium at the director level, as well as through leadership of Task 1 (Thermodynamics), Task 3 (Gas-Surface Interactions),

and Task 5 (Additives); (2) provide gas sorption and other property data required to develop and validate thermodynamic models of sorbents and metal hydride storage materials, including the effects of 350 bar and 700 bar hydrogen delivery pressures, serving as a resource for the consortium; (3) identify the structure, composition, and reactivity of gas–surface and solid–solid hydride surfaces contributing to rate-limiting desorption and uptake; (4) provide metal hydrides and MOFs in a variety of formats tailored for specific consortium tasks; (5) develop sample preparation methods and experimental protocols to enable facile use of the new characterization probes employed by the consortium; (6) apply Sandia multiscale codes to discover diffusion pathways and mechanisms of storage materials; (7) elucidate the role of additives in promoting hydrogen storage reactions; and (8) determine if LEIS can be used as a unique tool to measure H atom diffusion on thermally sensitive materials.

APPROACH

HyMARC seeks to address critical gaps in the science of hydrogen storage by leveraging recent advances in predictive multiscale modeling, high-resolution in situ characterization, and novel material synthesis techniques. By focusing on the underlying thermodynamic and kinetic limitations of storage materials, we will generate foundational understanding that will accelerate the development of all types of advanced storage materials, including sorbents, metal hydrides, and liquid carriers.

RESULTS

Substantial progress was made on each of the five tasks being performed at Sandia, with all of the quarterly goals met on time. Sandia principal investigators led the organization of task groups, helping to guide the science in collaboration with our partners, and scheduling and coordinating task team meetings involving all three HyMARC laboratory partners. Technical results include the following:

Task 1: Thermodynamics. A suite of porous carbons, including B- and N-doped materials, were prepared or obtained from other institutions and were characterized to determine pore size distributions and surface areas; these will be used to validate new modeling capabilities. Several MOFs are also included in this test set and were synthesized and characterized by X-ray diffraction (Figure 1) and porosimetry. In collaboration with Task 5 (Additives), pressure–composition–temperature studies on titanium-doped NaAlH_4 show that the adsorption-desorption thermodynamics change as the TiCl_3 dopant concentration increases, indicating that its effect is not purely catalytic (Figure 2), but also thermodynamic. X-ray diffraction shows that a crystalline intermetallic, TiAl , forms when TiCl_3 -doped NaAlH_4 is dehydrogenated.

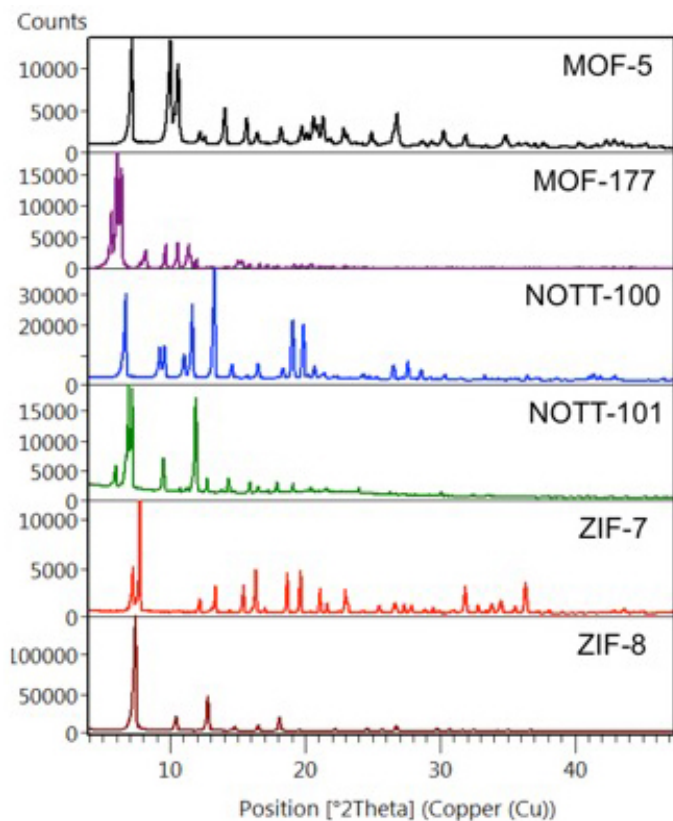


FIGURE 1. X-ray diffraction patterns confirming phase-purity of MOF-5, MOF-177, NOTT-100(101), ZIF-7(8)

Task 2: Kinetics of Mass Transport. A new molecular dynamics-based modeling capability was developed to simulate hydrogen diffusion through solids. Hydrogen diffusion through aluminum and hydrogenated palladium (PdH_x) were modeled as test systems (Figure 3), employing thousands of simulations to determine appropriate values of the numerous independent parameters in such calculations. The calculated energy barrier for H transport in Al, determined from the Arrhenius plot of diffusion constants obtained at several temperatures, was found to be ~ 0.4 eV, matching experimental results. Hydrogen diffusion in PdH_x is found to be independent of composition below $x = 0.7$, with an activation energy of 0.15 eV. However, above that threshold, at least two diffusion pathways are active. This new tool allows hydrogen transport in an evolving material to be modeled, such as a metal hydride undergoing dehydrogenation.

Task 3: Surface Science. Several new surface analytical techniques were deployed, both at Sandia and at the Advanced Light Source. New “clean transfer” sample holders that prevent exposure to air and moisture were designed and fabricated for both the Auger electron spectroscopy/LEIS and XPS systems at Sandia, and for ambient-pressure XPS at the Advanced Light Source. Data from a model system, TiCl_3 -doped NaAlH_4 , provide new insight into the chemistry

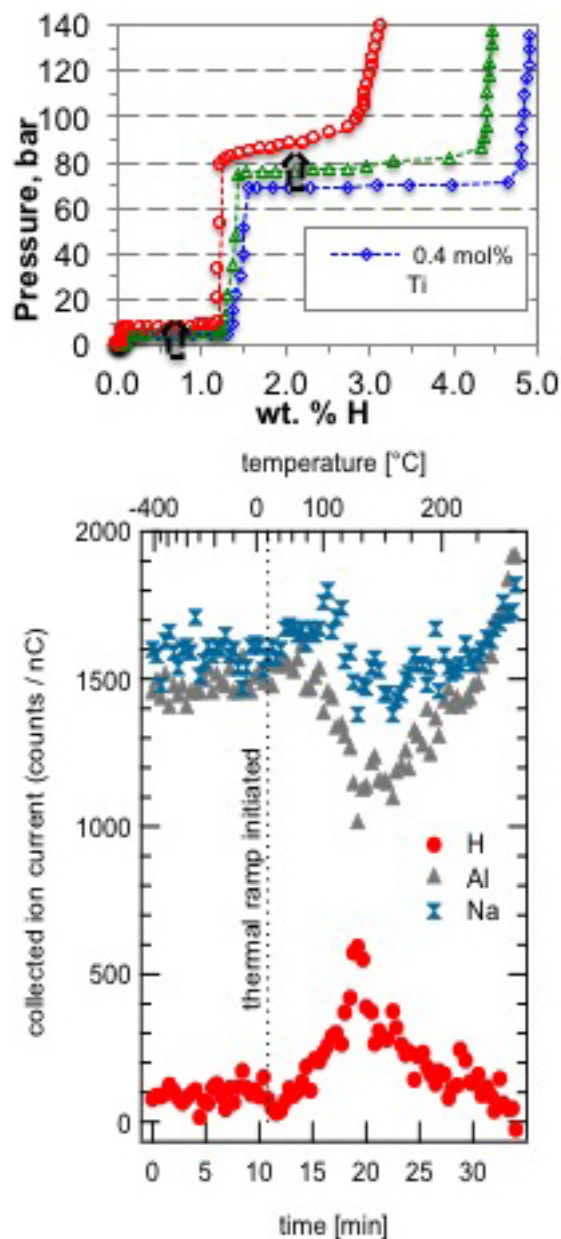


FIGURE 2. Top: Pressure–composition–temperature isotherms of NaAlH_4 doped with differing amounts of TiCl_3 , showing increases in plateau pressures with higher loadings. Bottom: LEIS measurements of 2 mol% TiCl_3 -doped NaAlH_4 during sample heating.

of hydrogen desorption. After ball-milling, Ti is undetectable by XPS or Auger electron spectroscopy, indicating that it is present only in the bulk. Both in situ and ex situ studies show that surface Al-H decreases upon heating to 150°C and metallic Al increases as dehydrogenation proceeds. LEIS, which can detect hydrogen at the gas-surface interface, indicates that surface H increases during hydrogen release from the decomposing sample (Figure 2). The surface also becomes sodium-rich and surface Al (in all forms) is

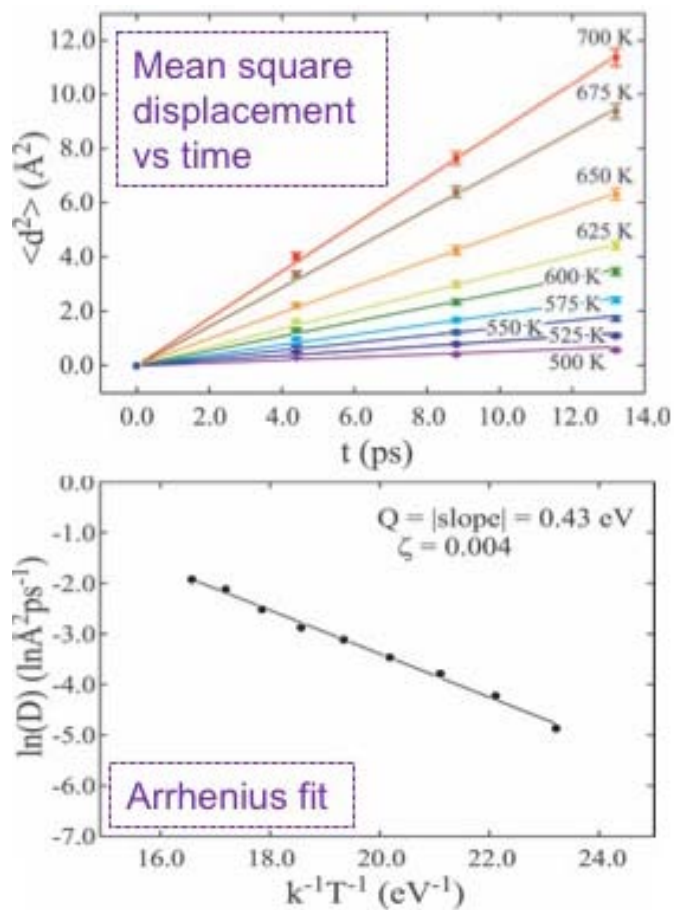


FIGURE 3. Molecular dynamics calculations of mean-square displacements and the corresponding Arrhenius plots of hydrogen diffusion in aluminum at various temperatures

depleted. LEIS was also employed to probe the diffusion of hydrogen on surfaces, using the Mg(0001) surface for demonstration purposes. This newly developed capability involves dosing the surface with hydrogen, followed by creating a well-defined H-free surface region using the low-energy ion beam. Hydrogen is then detected by LEIS as the cleared region is repopulated. LEIS can now be applied to other materials and will be used in conjunction with theory being developed to determine rates of two-dimensional hydrogen transport.

Task 4: Solid-Solid Interfaces. A novel ammonia solution-based method was developed that allows LiNH_2 and Li_3N to be incorporated into porous carbons with average pore sizes from 3–12 nm. The presence of Li-containing species confined within the pores was confirmed by EELS mapping (Figure 4). The hydrogenation and dehydrogenation of this nano-confined Li_3N is found to be a single-step process, unlike the two-step mechanism in bulk Li_3N . Moreover, complete cycling occurs 180°C lower than the bulk, allowing up to 4 wt% H incorporation (Figure 4). Theoretical predictions in collaboration with LLNL

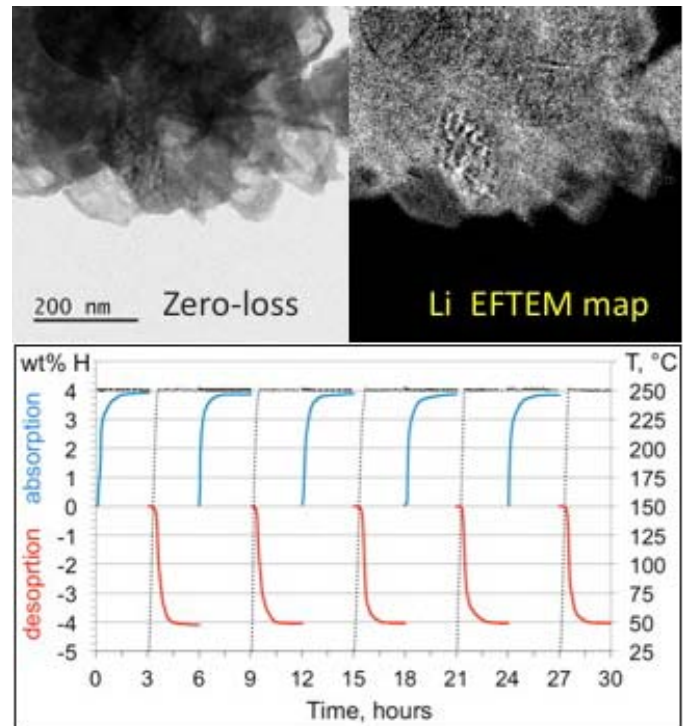


FIGURE 4. Top: Zero-loss transmission electron microscopy and energy filtered transmission electron microscopy (EFTEM) Li elemental maps in nano-confined $\text{Li}_3\text{N}@3.2\text{nm}$ -carbon. Bottom: Sieverts data showing 4 wt% reversible hydrogen uptake and release in $\text{Li}_3\text{N}@3.2\text{nm}$ -carbon.

indicate nanoscaling Li_3N particles effectively eliminates the metastable Li_2NH intermediate due to its high interfacial energy.

Task 5: Additives. The additives TiF_3 and TiCl_3 , which are known to be catalytic for the cycling of NaAlH_4 , were studied in pure form to determine their hydrogenation reactivity. XAS, which can detect TiCl_3 in concentrations at least as low as 0.4 mol%, was employed to monitor the Ti chemistry. TiCl_3 and TiF_3 exposed to 120 bar hydrogen at both room temperature and 200°C for 17 h exhibit negligible hydrogen uptake. The XAS spectra show no changes in the local electronic structure at Ti or F for TiF_3 upon H_2 exposure, and the Ti local electronic structure remained unmodified. Vibrational spectroscopy indicates no change in the chemical properties of the bulk additives upon exposure to H_2 under the same conditions.

CONCLUSIONS AND FUTURE DIRECTIONS

In the first year of HyMARC the SNL team developed new synthetic, modeling, and diagnostic tools that provide new insights into seemingly well-understood storage materials such as Ti-doped NaAlH_4 , magnesium, and titanium hydrides. These tools are now available, through

collaborations with the HyMARC team, to accelerate development of new storage materials. Future work will extend these to more complex, less understood, storage materials that can meet DOE targets, such as $\text{Mg}(\text{BH}_4)_2$. Highly accurate quantum Monte Carlo calculations are expected to provide new understanding of H_2 binding to open metal sites in MOFs and other sorbents. In addition, a database development task will commence, with the objective of creating web-based tools to allow the hydrogen storage community to access HyMARC results.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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

FY 2016 PUBLICATIONS/PRESENTATIONS

Publication

1. 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.

Presentations

1. V. Stavila, B. Wood, L. Klebanoff, T.W. Heo, et al. “Nanoscale effects in complex metal hydrides,” Pacificchem-2015, Honolulu, HI, December 2015.

2. 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.