# 2017 Annual Report
# HyMARC (Core)

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Project Start Date: September 17th, 2015
Project End Date: September 30th, 2018

## Overall Objectives

- Accelerate discovery of breakthrough storage materials by developing foundational understanding of phenomena governing the thermodynamics and kinetics limiting the development of solid-state hydrogen storage materials.
- Develop community tools and capabilities to enable materials discovery, including computational models and databases, new characterization tools and methods, and tailorable synthetic platforms.
- Provide technical direction 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 ultrahigh 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 SNL multiscale codes to discover new materials and new mechanisms of storing hydrogen, provide input for database development
- Elucidate the role of additives in improving $H_2$ storage adsorption and desorption reactions.

## Fiscal Year (FY) 2017 Objectives

- Demonstrate *in situ* soft X-ray AP-XPS, XAS, XES tools, with sample heating
- Synthesize and characterize library of nanoparticles for one hydride: 1–5 nm, 5–10 nm, >10 nm
- Sensitivity analysis of local binding and second-sphere effets
- Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing $\Delta H°$
- Modify low-energy ion scattering (LEIS) to enable laser-induced thermal desorption.
- Evaluate additive/composite strategies for improving effective $\Delta E$
- Assess bulk additives ($TiF_3$, $TiCl_3$) for their reactivity towards hydrogen.
- Develop prototype hydride surface and interface chemistry kinetic models

## 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:

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(A) System Weight & Volume
(E) Charging/Discharging Rates
(F) Cost, Efficiency, Durability

## 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 2017 Accomplishments

- HyMARC web site brought on line to enhance external communications.
- Extensive suite of modeling capabilities developed, many of which are ready for use through internal and external collaborations.
- Utrahigh-pressure reactor (up to 1000 bar $H_2$ and 400 ºC) is now online and available for use by Seedling projects and other collaborators.
- A series of MOFs was synthesized, characterized at SNL, and sent to HySCORE/NREL for hig.h-accuracy gas sorption measurements to enable model validation and testing of the Chahine rule.
- Extensive high-pressure hydrogen cycling data for several MOFs show that $H_2$ uptake is not always fully reversible.
- Approved Program granted at the Advanced Light Source, providing dedicated access to beam lines for X-ray spectroscopy and Scanning Transmission X-ray Microscopy (STXM) for three years.
- A library of spectroscopic standards was initiated, which contains spectra from NMR, neutron vibrational scattering, and X-ray absorption spectroscopy for hydrides, their decomposition products, and some additives.
- Extensive collaborations among all three laboratories in the HyMARC Core Team occurred, leading to several joint publications.
- Substantial interactions with all five Seedling projects currently in operation, including visits to Sandia by members of Seedling project teams, and exchange of samples for measurements using HyMARC capabilities.
- A Go/No-Go decision point was reached in which improvement strategies for sorbents were ranged according to their potential for increasing the heat of adsorption. Of the six strategies assessed, the two predicted to have the greatest potential are the incorporation of open metal sites into MOFs and related framework materials, and the addition of Lewis-acid sites into porous carbons. A detailed report in the form of a peer-reviewed journal article will be submitted that describes the perspective of the HyMARC team on a wide range of sorbent improvement strategies.
- A model for hydrogen diffusion in Pd was developed, validated by experiment, and extended to the Mg/$MgH_2$ system.
- Several strategies for altering metal hydride uptake and release were evaluated; results indicate that thermodynamics in the Li-M-N-H system can be modified and kinetics of intermediate formation in borohydrides can be altered.
- A method of measuring surface hydrogen diffusion using LEIS was developed.

- An experimental investigation using Sandia and ALS capabilities shows that titanium is not present on the surface during $H_2$ desorption from Ti-doped $NaAlH_4$, supporting the "zipper" mechanism and invalidating several published mechanisms.
- Improved $H_2$ desorption kinetics and intermediate suppression were demonstrated by nanoconfining $LiNH_2$ using a new synthetic route.

## 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 OEMs, 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/FCTO 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 $H_2$ 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 Tasks 1 (Thermodynamics), 3 (Gas-Surface Interactions) and 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 and 700 bar $H_2$ 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 SNL multiscale codes 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 PIs 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.* Sandia's effort to elucidate the factors contributing to the thermodynamics of hydrogen uptake and release by sorbents and metal hydrides provided new data and contributed to the foundational understanding of these materials.

<u>Key results for sorbents</u>: protocols for the reproducible synthesis of MOFs were developed. The $H_2$ isotherms at 77 K for a library of these materials were measured to provide data for comparison with QMC calculations of the heats of adsorption and GCMC predictions of gas sorption isotherms.

Simulations and experiment are in agreement within a 10-20% band of uncertainty; this uncertainty is primarily the result of different equations of state and variations in the $H_2$ potential used in the force field. A detailed analysis of these effects is underway. (Figure A) As part of these experiments extensive high-pressure cycling tests (up to 700 bar) were done for several MOFs; these showed, surprisingly, that in some cases the surface area and capacity degraded after as few as 100 cycles. The reasons for this are unclear but X-ray diffraction suggests that it is not due to structural degradation.

<u>Key results for metal hydrides</u>: The effect for potassium hydride doping on the thermodynamics of $H_2$ release from hydrides in the Li-Mg-N-H system were conducted. The results show that the equlibrum $H_2$ pressure increases when small amounts (0.l4-10 mol%) of KH were added (Figure B). We also showed that the reactivity of alkali metal $B_{12}H_{12}$ intermediates, which form during decomposition of borohydrides, can be increased by either applying high-pressure $H_2$ to shift the equilibrium to form borohydrides or by dehydrogenation to form metal borides. This is significant because it suggests strategies for avoiding kinetic dead ends that prevent materials with attractive thermodynamics, such as $Mg(BH_4)_2$, from being practical storage materials.

In a second major effort, we advanced our understanding of nanoscale effects on the thermodynamics and kinetics of metal hydrides. First, we demonstrated that the kinetics of H2 uptake by Li3N can be dramatically improved by confining the material within porous carbons. A new one-step synthetic route involving liquid $NH_3$ infiltration achieves high $Li_3N$ loadings (>50 wt%) into pores < 12 nm. 5 wt% reversible $H_2$ cycling and suppression of the detrimental $Li_2NH$ species were shown to occur using $Li_3N$ within 6-nm porous carbon (Figure D). Second, we performed in-pore synthesis of nanoscale $Mg(BH_4)_2$ inside MOFs and graphene aerogels. 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 enables efficient infiltration of high-capacity metal borohydrides, which is critical to minimize the weight penalty associated with the dead volume associated with a host material.

Finally, the Sandia ultra-high-pressure hydrogen reaction station is now fully operational (Figure E), creating an additional unique HyMARC capability. The reactor achieves $H_2$ pressures up to 1000 bar at temperatures up to 400 ºC, allowing HyMARC to access the highest pressures currently used by new hydrogen fueling stations that are coming on line. From a research perspective, the UHPR enables, for example, synthesis of metal hydrides that are unattainable by conventional routes and probe the destabilization of *closo*-borane intermediates.

*Task 2: Kinetics of Mass Transport.* This year we continued our development of validated models of hydrogen diffusion, which are used in models to determine whether mass transport is a rate-limiting factor in the desorption or release of $H_2$ from metal hydrides. Our approach begins with model systems of progressively higher complexity so that we can validate individual aspects of model performance. Initially, we considered $PdH_x$, an interstitial hydride with well-understood properties that undergoes no phase transition upon hydrogen uptake. We validated the diffusion rate of H in bulk Pd by comparison with experimental data in the literature; in particular, our model is consistent with experiments showing that H segregates on Pd(111) surfaces. Next, which applied our modeling approach to diffusion of hydrogen in $MgH_2$, at material with covalent Mg-H bonds that undergoes a phase transition and large change in unit cell volume upon uptake of hydrogen.

As part of this effort, we developed new methods to accelerate force field optimization, which is typically a very time-consuming process. A new capability to fit forces for any atom in any specified phase was added to our existing force field parameterization tools, which can fit energy, lattice constant, and elastic constants of a variety of phases. This new capability was used to apply further constraints to the Mg-H bond order potential parameterization, resulting in much more robust parameterization. We also developed new analysis tools that require only a few seconds of labor to launch a job to analyze molecular dynamics data and 30 minutes of computing time to obtain the final results. Our previous automated tools could submit hundreds of MD jobs. However, analysis of the results became a labor-limiting factor. For example, our bulk diffusion analysis alone is done at 10 compositions and 13 temperatures for any hydride. Data reduction for these 130 simulations could easily take several days of labor time. These new analytical tools are a unique HyMARC capability that will be extended to more complex hydrides in the coming year.

*Task 3: Surface Science.* Development of HyMARC's comprehensive suite of diagnostics to probe chemical phenomena at all relevant length-scales continued this year, with the development of a method to measure surface diffusion using LEIS. The new LEIS diffusion capability uses the ion beam to clear the surface area of H, then uses ion scattering to monitor diffusion from the periphery (Figure C). The approach can detect surface H and ~ 0.1 monolayer levels, avoids thermal damage to sensitive samples, and can detect the refilling of the clear space by H within seconds. With this new method we can now probe chemical composition at the first monolayer (< 1nm) using LEIS, near-surface region (< 10 nm) using XPS or AP-XPS, and the bulk using STXM or XAS. We applied all of these tools to understand the desorption of hydrogen from Ti-doped $NaAlH_4$ (see additional details under Task 5) and are now applying them to complex hydrides that are much more poorly understood, such as $Mg(BH_4)_2$.

*Task 4: Solid-Solid Interfaces.* The primary contribution of the Sandia team to this task was the development of sample preparation techniques for STXM measurements at the ALS. As part of the HyMARC ALS AP, which provides dedicated beam time for three years, we conducted STXM measurements during fifteen eight-hour shifts using Ti-doped $NaAlH_4$, $Li_3N$, and Mg nanoparticles as test cases for method development. Sandia also contributed XAS data to a collaborative effort involving HyMARC investigators at PNNL, NIST, and LBNL to generate a library of spectroscopic standards to facilitate understanding of novel storage materials.

*Task 5: Additives.* New understanding concerning the role of titanium in accelerating the desorption of $H_2$ from complex metal hydrides was obtained using HyMARC's suite of surface diagnostics and soft X-ray spectroscopies. Among the most heavily studied systems and yet least understood is titanium-doped $NaAlH_4$ ($Ti@NaAlH_4$), for which there exist more than 2000 papers in the literature. Many of the proposed mechanisms involve surface titanium in some form. Using samples ball-milled for long times and cycled to simulate a material used in a fuel tank, LEIS, AP-XPS, STXM, and FTIR data together indicate that no Ti-containing species exist during $H_2$ desorption from $Ti@NaAlH_4$. The Ti is located in the bulk and reemerges upon exposure to $H_2$ during the regeneration phase. These results contradict several proposed mechanisms and support the so-called "zipper model," in which Ti-containing surface species are destabilized when sodium diffuses to the surface during desorption. Moreover, it is clear from these investigations that bulk titanium halides themselves do not promote $H_2$ dissociation, showing that Ti-containing additives must be chemically altered to have a catalytic effect. A final important conclusion of this investigation is the critical need for reliable assignments of XAS and XPS spectroscopic features, for which there is disagreement in the hydrogen storage literature. The spectroscopic standards effort under Task 4 coupled with computational spectroscopy performed by HyMARC investigators at the Molecular Foundry, are addressing this issue.

*Interactions with Seedling projects and collaborations.* HyMARC expertise and capabilities have been accessed extensively by several of the current Seedling projects. Researchers from three of the projects were hosted for periods of up to a month. Capabilities used include the UHPR, XPS, LEIS, XRD, FTIR, and high- and low-pressure porosimetry. Due to the exceptional complexity of metal borohydride hydrogen chemistry, HyMARC investigators are collaborating with NIST and PNNL to perform a detailed mechanistic investigation of hydrogen release and uptake by $Mg(BH_4)_2$.

## Conclusions and Future Directions

The Sandia HyMARC team continued its development of new synthetic, modeling, and diagnostic tools that are providing new insights into all major classes of storage materials, ranging from relatively simple systems such as $PdH_x$ and $MgH_2$, to exceptionally complex ones, such as the metal borohydrides, as well as materials thought to be very well-understood, such as Ti-doped $NaAlH_4$. This unprecedented suite of capabilities, capable of probing all relevant length scales within storage materials, is already having a significant impact, as they are now being used by both Seedling projects and collaborators at other laboratories within HyMARC. We expect this impact to grow as new Seedling projects begin and through collaborations with other scientists outside HyMARC. In the coming year, Sandia efforts will focus on the highest impact problems, in coordination with the other HyMARC National Laboratory partners, to provide the foundational science necessary to accelerate the discovery of new hydrogen storage materials.

## Special Recognitions & Awards/Patents Issued

1. V. Stavila, L. Klebanoff. "Nanostructured metal amides and nitrides for hydrogen storage", US Patent Application 62/235,930, November, 2016.
2. V. Stavila. "Solid state synthesis of alkali metal borohydrides", US Patent Application 63/237,752, March, 2017.

## FY 2016 Publications/Presentations

### Publications:

1. B. C. Wood, V. Stavila, N. Poonyayant, T.-W. Heo, K. Ray, L.E. Klebanoff, T.J. Udovic, J.R.I. Lee, N. Angboonpong, J.D. Sugar, P. Pakawatpanurut "Nanointerface-Driven Reversible Hydrogen Storage in the Nanoconfined Li–N–H System", cover feature *Adv. Mater. Interfaces*, **2017***, 4,* 1600803.
2. M. Dimitrievska, J.L. White, W. Zhou, V. Stavila, L.E. Klebanoff T.J. Udovic, "Structure-dependent vibrational dynamics of $Mg(BH_4)_2$ polymorphs probed with neutron vibrational spectroscopy and first-principles calculations," *Phys. Chem. Chem. Phys.*, **2016**, *18*, 25546.
3. X. W. Zhou, et al. "Molecular Dynamics Simulations of Hydrogen Diffusion in Aluminum", *J. Phys. Chem. C*, 120, 7500 (2016).
4. E. S. Cho, et al. "Graphene Oxide/Metal Nanocrystal Multilaminates as the Atomic Limit for Safe and Selective Hydrogen Storage" *Nature Commun.*, 2016, 7, 10804.

### Presentations:

9 presentations (1 keynote and 4 invited) were delivered at National and International conferences and symposia over the past 12 months.

## Acronyms

ALS: Advanced Light Source. AP: Approved Program. GCMC: Grand Canonical Monte Carlo. HyMARC: Hydrogen Storage Materials Advanced Research Consortium. FTIR: Fourier Transform Infrared spectroscopy. LEIS: Low Energy Ion Scattering. MD: molecular dynamics. MOF: Metal-Organic Framework. QMC: Quantum Monte-Carlo. XAS: X-ray Absorption Spectroscopy. STXM: Scanning Transmission X-ray Microscopy. UHPR: Ultra-High-Pressure Reactor. (AP)-XPS: (Ambient-Pressure)X-ray Photoelectron Spectroscopy.

# Figures

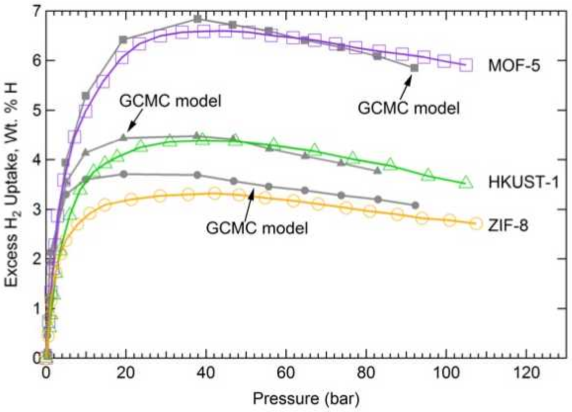

**Figure A.** Comparison of measured $H_2$ uptake with GCMC predictions. The best combination of $H_2$ potential and equation of state identified from an evaluation of several common ones in the literature were used for the GCMC calculations.

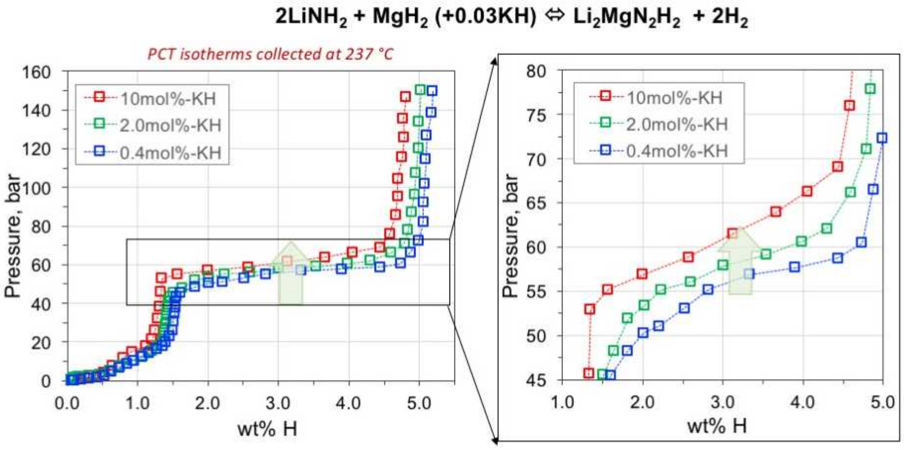

**Figure B.** PCT curves showing that KH doping increases the equilibrium $H_2$ pressure of the Li-Mg-N-H metal hydride system.

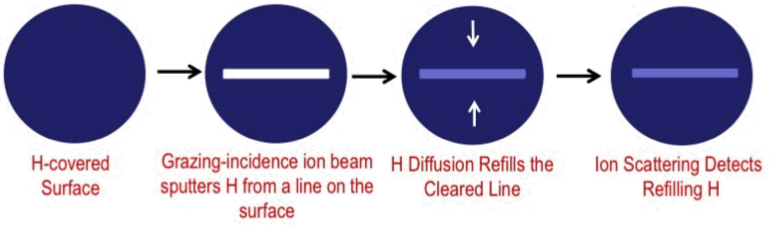

**Figure C.** New methodology for probing surface diffusion using LEIS.

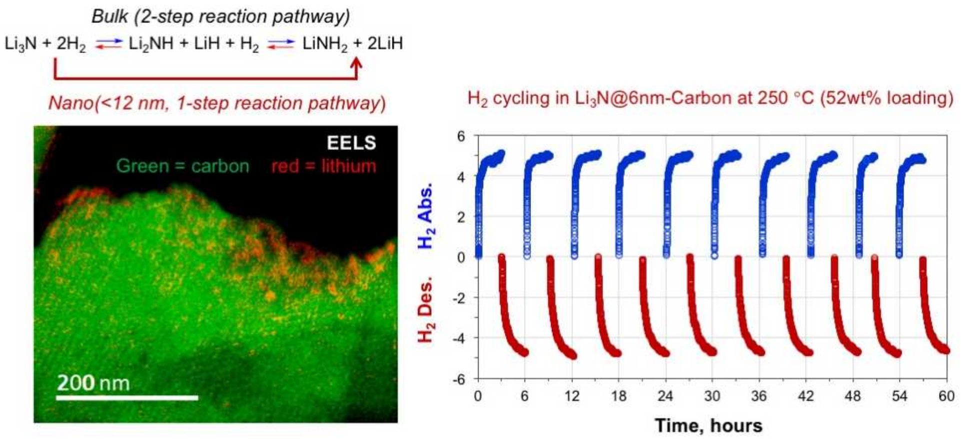

**Figure D.** Nanoscale $Li_3N$ formed within 6-nm porous carbon and the reproducible cycling of $H_2$ release at high gravimetric loading.

**Figure E.** New Ultra-High-Pressure Reactor station now available for use at Sandia.