

IV.C.1 HyMARC (Core): SNL Effort

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Project End Date: September 30, 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, and provide input for database development.
- Elucidate the role of additives in improving H₂ storage adsorption and desorption reactions.

Fiscal Year (FY) 2017 Objectives

- Demonstrate in situ soft X-ray ambient pressure X-ray photoelectron spectroscopy (AP-XPS), X-ray absorption spectroscopy (XAS), and X-ray emission spectroscopy tools, with sample heating.
- Synthesize and characterize library of nanoparticles for one hydride with diameters in the ranges of 1–5 nm, 5–10 nm, >10 nm.
- Sensitivity analysis of local binding and second-sphere effects.
- Rank improvement strategies for sorbents per decision criterion: select the two with the greatest potential for increasing ΔH° .
- Modify low-energy ion scattering (LEIS) to enable laser-induced thermal desorption.
- Evaluate additive/composite strategies for improving effective ΔE .
- Assess bulk additives (TiF₃, TiCl₃) 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

- The HyMARC website was brought online to enhance external communications.
- An extensive suite of modeling capabilities was developed, many of which are ready for use through internal and external collaborations.
- The ultrahigh-pressure reactor (up to 1,000 bar H₂ and 400°C) is now online and available for use by Seedling projects and other collaborators.
- An approved program was granted at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, providing dedicated access to beam lines for X-ray spectroscopy and scanning transmission X-ray microscopy (STXM) for three years.
- 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.
- Extensive collaborations among all three laboratories in the HyMARC Core Team occurred, leading to several joint publications.
- 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 metal-organic frameworks (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.
- An experimental investigation using Sandia and ALS capabilities shows that titanium is not present on the surface during H₂ desorption from Ti-doped NaAlH₄, supporting the “zipper” mechanism and invalidating several published mechanisms.
- Extensive high-pressure hydrogen cycling data for several MOFs show that H₂ uptake is not always fully reversible.
- A series of MOFs was synthesized, characterized at SNL, and sent to HySCORE/National Renewable Energy Laboratory for high-accuracy gas sorption measurements to enable model validation and testing of the Chahine rule.
- 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.



INTRODUCTION

Storage of hydrogen on board vehicles is one of the critical technologies needed to create hydrogen-fueled transportation systems that can improve energy efficiency, resiliency, and energy independence and reduce oil dependency. 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. Early-state research to develop a foundational understanding of solid-state storage materials, including novel sorbents and high-density hydrides, is of high importance because of their unique potential to meet all DOE Fuel Cell Technologies Office targets and deliver hydrogen with lower storage pressures and higher onboard densities. However, existing materials suffer from thermodynamic and kinetic limitations that prevent their application as practical H₂ storage media.

Sandia’s objectives and 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 H₂ 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 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.

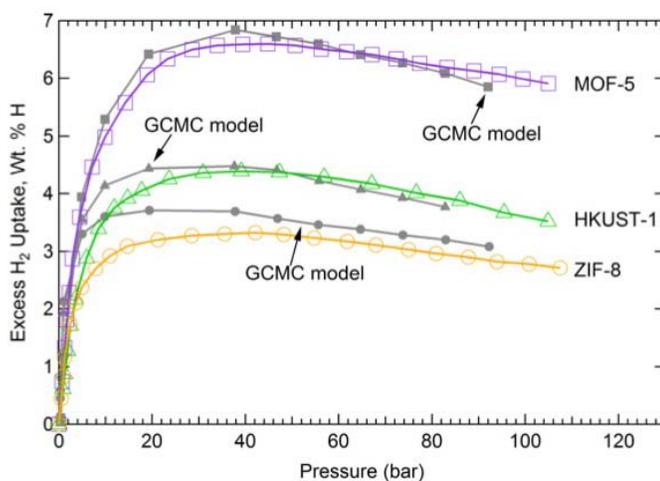
RESULTS

Substantial progress was made on each of the five tasks being performed at SNL, 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

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.

Key results for sorbents: 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 quantum Monte Carlo calculations of the heats of adsorption and grand canonical Monte Carlo (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 1). As part of these experiments extensive high-pressure cycling tests (up to 700 bar) were done for



ZIF – zeolitic imidazolate framework

FIGURE 1. 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.

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.

Key results for metal hydrides: 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 equilibrium H_2 pressure increases when small amounts (0.14–10 mol%) of KH were added (Figure 2). We also showed the reactivity of alkali metal $B_{12}H_{12}$ intermediates, which form during decomposition of borohydrides, can be increased, either by applying ultrahigh-pressure hydrogen (700 bar) to shift the equilibrium toward reformation of the parent borohydride, or by heating the $B_{12}H_{12}$ samples in the presence of binary metal hydrides, such as MgH_2 , to further dehydrogenate the intermediates to yield the corresponding 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 H_2 uptake by Li_3N 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. Five weight percent 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 3). Second, we performed in-pore synthesis of nanoscale $Mg(BH_4)_2$ inside MOFs and graphene aerogels. Scanning electron microscopy and energy dispersive X-ray spectroscopy 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 (UHPH) is now fully operational (Figure 4), creating an additional unique HyMARC capability. The reactor achieves H_2 pressures up to 1,000 bar at temperatures up to 400°C, allowing HyMARC to access the highest pressures currently used by new hydrogen fueling stations that are coming online. From a research perspective, the UHPH enables, for example, synthesis of metal hydrides that are unattainable by conventional routes and the probing of 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.

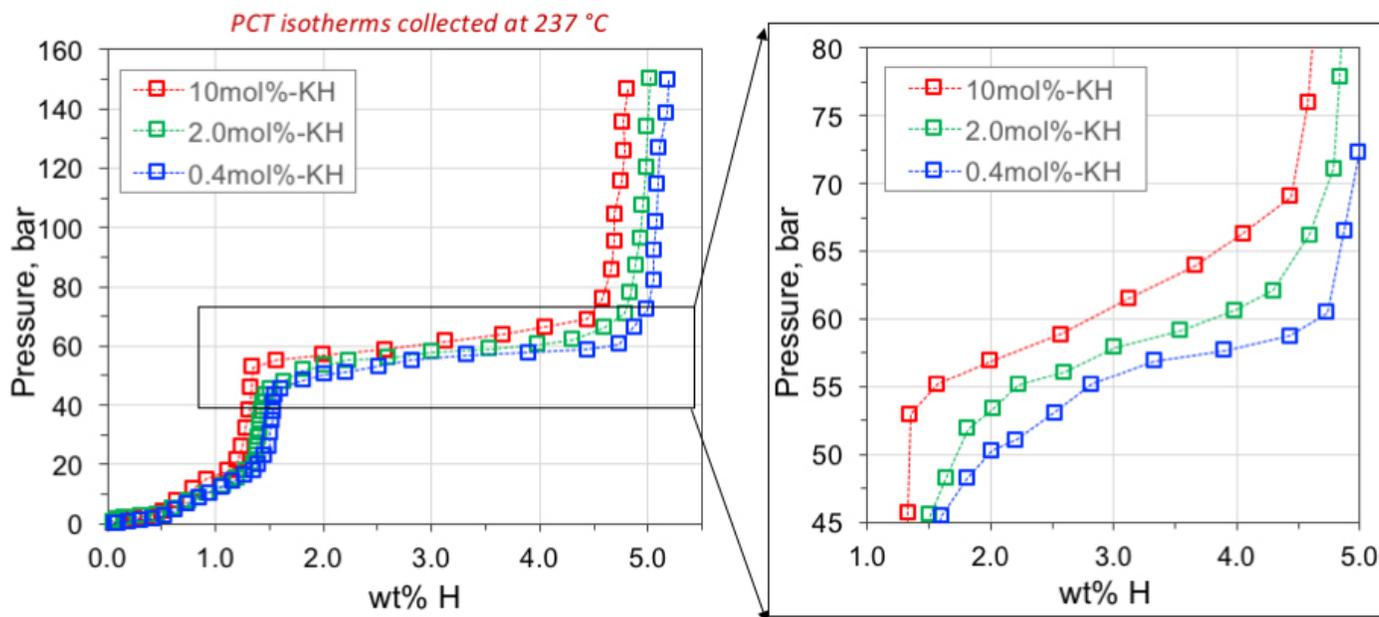


FIGURE 2. Pressure-composition-temperature curves showing that KH doping increases the equilibrium H₂ pressure of the Li-Mg-N-H metal hydride system.

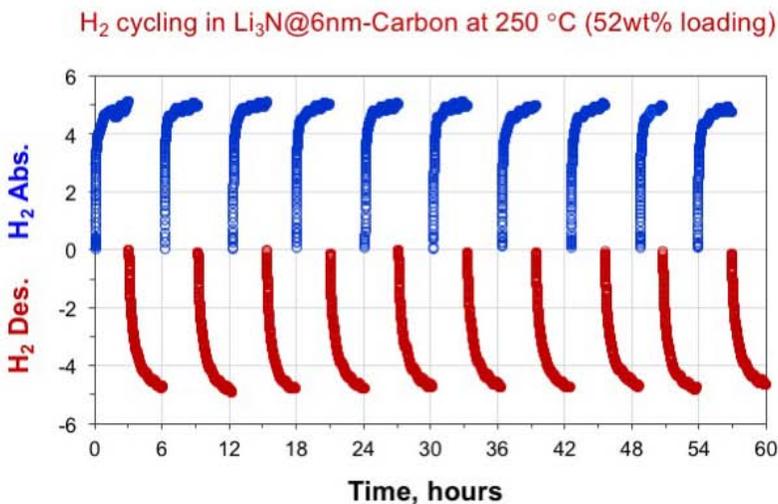
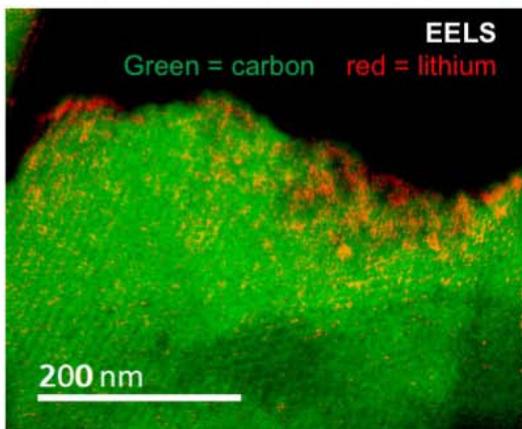
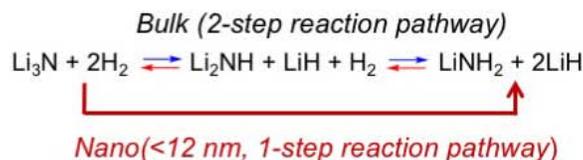


FIGURE 3. Nanoscale Li₃N formed within 6-nm porous carbon and the reproducible cycling of H₂ release at high gravimetric loading.

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 MgH₂, a material with covalent Mg-H bonds that undergoes a phase transition and large change in unit cell volume upon uptake of hydrogen.



FIGURE 4. New UHPR station now available for use at Sandia.

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

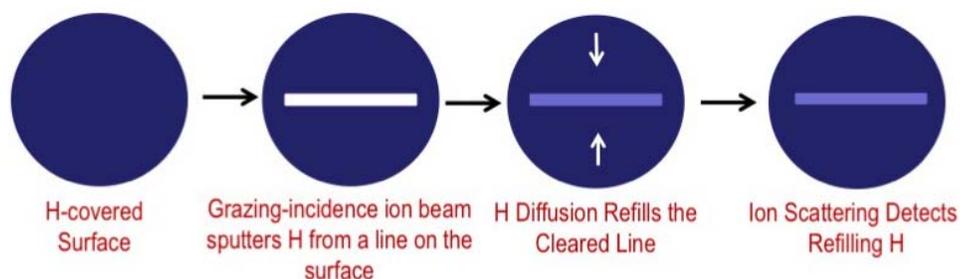


FIGURE 5. New methodology for probing surface diffusion using LEIS.

using standard institutional cluster machines. 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 5). 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 (<1 nm) 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 $\text{Mg}(\text{BH}_4)_2$.

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 approved program, which provides dedicated beam time for three years, we conducted STXM measurements during 15 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 Pacific Northwest National Laboratory, the National Institute of Standards and Technology, and Lawrence Berkeley National Laboratory

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 desorption of H₂ from complex metal hydrides was obtained using HyMARC's suite of surface diagnostics and soft X-ray spectroscopies. Among the most heavily studied and yet least understood systems is titanium-doped NaAlH₄ (Ti@NaAlH₄), for which there exist more than 2,000 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, we employed a suite of diagnostic tools that probe all relevant length scales in the reaction (probe depth given in parentheses): LEIS (1 monolayer), AP-XPS (5 nm; ~15 atomic layers), STXM (bulk), and Fourier transform infrared (bulk). Together, the data obtained from these diagnostics indicate that no Ti-containing surface or near-surface species exist during H₂ desorption from Ti@NaAlH₄. The Ti is located in the bulk and reemerges upon exposure to H₂ 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 H₂ 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, X-ray diffraction, Fourier transform infrared spectroscopy, and high- and low-pressure porosimetry. Due to the exceptional complexity of metal borohydride hydrogen chemistry, HyMARC core lab investigators are collaborating with HySCORE researchers at National Institute of Standards and Technology and Pacific Northwest National Laboratory to perform a detailed mechanistic investigation of hydrogen release and uptake by Mg(BH₄)₂.

CONCLUSIONS AND UPCOMING ACTIVITIES

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 MgH₂, to exceptionally complex ones, such as the metal borohydrides, as well as materials thought to be very well-understood, such as Ti-doped NaAlH₄. 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 2017 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(BH₄)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

1. Nine presentations (one keynote and four invited) were delivered at national and international conferences and symposia over the past 12 months.