IV.C.1 HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials

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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.

Fiscal Year (FY) 2016 Technical Milestones

- Prepare a library of bulk-phase model storage systems. (first quarter, FY 2016)
- Demonstrate a size control method for one prototype complex hydride nanostructure. (second quarter, FY 2016)
- Demonstrate in situ soft X-ray ambient pressure X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and X-ray emission spectroscopy tools, with sample heating. (third quarter, FY 2016)
- Identify hydride mobile species and diffusion pathways. (fourth quarter, FY 2016)
- Synthesize a library of nanoparticles (1–5 nm, 5–10 nm, >10 nm) for one prototype metal hydride. (fourth quarter, FY 2016)

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

(E) Charging/Discharging Rates

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project will develop foundational understanding and new capabilities that will enable accelerated discovery of breakthrough materials in all classes of storage materials, in particular metal hydrides and sorbents. Specific targets include: (1) validated models of hydrogen uptake and release by storage materials, accounting for all relevant length scales (atomic/molecular to macroscale morphology); (2) databases of thermodynamic and kinetic properties that can be used in materials discovery; and (3) synthetic routes to nanoscale storage materials and a suite of characterization tools for understanding their behavior. It is anticipated that the insights gained from this research, coupled with new synthetic, characterization, modeling, and database tools that will be made available to the hydrogen storage research community, will lead to materials that meet DOE system targets, such as gravimetric and volumetric capacity, system fill time, delivery temperature, and cost.

FY 2016 Accomplishments

- Project teams were established for each of the five tasks (Thermodynamics, Mass Transport, Surface Chemistry, Internal Interfaces, and Additives).
- Four new postdoctoral appointees were hired since the onset of the project.
- User proposals were submitted and approved that permit access by HyMARC staff to the Molecular Foundry, Advanced Light Source, and Spallation Neutron Source.
- A webinar and several invited presentations by HyMARC leadership informed the hydrogen storage community of the new project and its objectives.
- Collaborations with the Hydrogen Storage Characterization and Optimization Research Effort were initiated in the areas of complex metal hydride kinetics, synthesis at ultrahigh pressures (≥700 bar), and vibrational spectroscopy at elevated hydrogen pressure.

- The first journal articles describing HyMARC research were published.

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INTRODUCTION

Storage of hydrogen onboard 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 use 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 targets and deliver hydrogen at lower pressures and higher onboard densities. A successful solution would significantly reduce costs and ensure the economic viability of a United States hydrogen infrastructure.

DOE-supported individual projects and the Centers of Excellence collectively synthesized and characterized hundreds of candidate materials documented in the DOE Hydrogen Storage Materials Database. Although materials meeting some of the key targets were identified, progress continues to be hindered by a lack of understanding of the kinetics and thermodynamics underlying the physical properties of interest. For sorbents, the biggest limitation is volumetric capacity within the target operating temperatures, whereas hydrides are limited by insufficient gravimetric capacity and/or reaction kinetics to meet the fill time target. At a recent (January 2015) Office of Energy Efficiency and Renewable Energy Material-Based Hydrogen Storage Summit, principal investigators (PIs) identified the following high-priority needs for accelerating development of viable solid-state storage materials:

- Validated multi-scale models for determining metal hydride structure-property correlations.
- Computational tools to guide design of nanoporous sorbent pore size distributions.
- Synthetic strategies to increase the strength of hydrogen interactions with sorbent adsorption sites.
- Rates and mechanisms of kinetic processes that limit metal hydride reversibility.
- Design rules for nanostructuring that improve metal hydride kinetics and thermodynamics.
- Models describing the structure, chemistry, and mass transport on surfaces and at interfaces.

APPROACH

The HyMARC consortium seeks to address these needs by leveraging recent advances in predictive multiscale modeling, high-resolution in situ characterization, and material synthesis that were unavailable to the Centers of Excellence. Combined with materials informatics, this strategy embodies the approach highlighted within the Materials Genome Initiative Strategic Plan for accelerated materials development. By focusing on the underlying thermodynamic and kinetic limitations of storage materials, HyMARC will generate foundational understanding that will accelerate the discovery and development of all types of advanced storage materials, including sorbents, metal hydrides, and liquid carriers. Thus, DOE investments will be fully leveraged for future external materials-focused projects.

RESULTS

<u>Organizational aspects</u>: HyMARC was launched in September 2015, with a kickoff meeting held in October. The full team is comprised of approximately 30 individuals, including research staff and postdoctoral appointees, representing the three consortium national laboratories (SNL in Livermore, CA; Lawrence Livermore National Laboratory [LLNL]; and Lawrence Berkeley National Laboratory [LBL]). The leadership structure (Figure 1) includes the consortium director, lead PIs at all three laboratories, and PIs for each of the consortium tasks. The team also includes points of contact at two DOE–Basic Energy Sciences user facilities: the Molecular Foundry and the Advanced Light Source (ALS). Key activities at the full consortium level this year included assembling the full research teams, hiring several new postdoctoral appointees, familiarizing team members with the full set of capabilities represented by the consortium via on-site meetings and lab tours, and establishing a regular series of task meetings for exchange of information. A web data repository was brought on line for internal use; development of an external web site is underway. Finally, HyMARC leadership provided informational briefings about the formation of HyMARC to the national and international hydrogen storage research communities, via a webinar in January 2016 and several presentations at major international conferences.

<u>HyMARC capabilities</u>: Achieving the HyMARC goal of developing a suite of modeling tools that span all length and time scales relevant to hydrogen storage requires a combination of facile, controllable synthetic approaches, high-performance computing hardware, and state-of-the-art characterization tools that can be used to test and validate these models. The scope of the HyMARC modeling initiative is illustrated in Figure 2, which indicates that phenomena from the atomic to the macroscale must be addressed. Access to high-performance computing capabilities at the three consortium laboratories was in

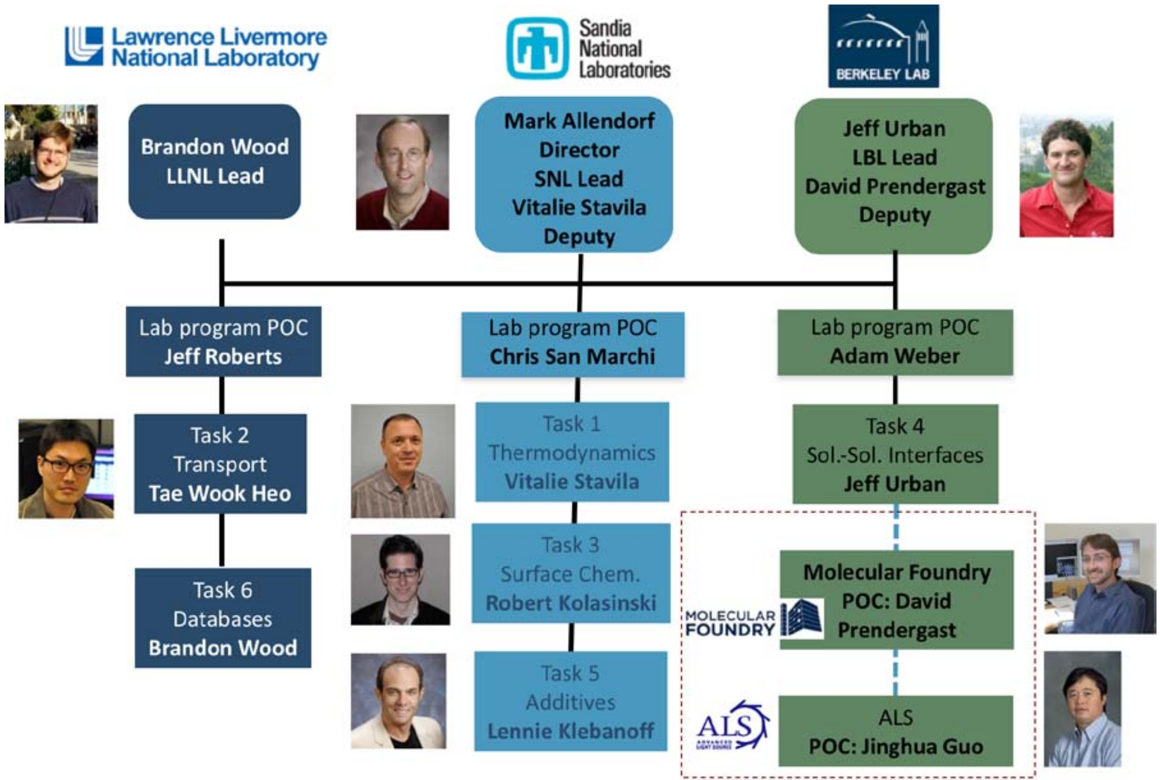

FIGURE 1. HyMARC organizational structure and key points of contact

place at from the outset of HyMARC, as were a number of unique diagnostic and synthetic capabilities. However, some of the most powerful characterization tools available today are located at DOE–Basic Energy Sciences user facilities, which require approval of submitted research proposals to obtain time on the instrument. To this end, the HyMARC team submitted user proposals to the Molecular Foundry, ALS, and Spallation Neutron Source, all of which were approved. At the Molecular Foundry, access was approved to use the first-principles computational spectroscopy models for interpreting data obtained at the ALS, and to the electron microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy available in the Imaging and Manipulation of Nanostructures Facility. At the ALS, an "Approved Program" proposal was granted that allocates a block of dedicated time for three years on two beam lines. The first of these provides access to soft X-ray spectroscopies (e.g. X-ray absorption and emission), which will be used to probe composition and coordination environment. This tool can also distinguish the bulk chemical environment from that of the near-surface region. The second beam line will be used for scanning transmission X-ray microscopy measurements, which enable composition, phase, and microstructure to be probed with 30-nm resolution. At the Spallation Neutron Source, a user proposal was approved that provides access to the VISION vibrational spectrometer, which provides information about molecular structure, chemical bonding, and intermolecular interactions. Experiments at all three user facilities have already been conducted or are scheduled as of the writing of this report.

Collaborations: The geographical colocation of the three partner laboratories strongly enhances the ability of the HyMARC team to collaborate in a fluid and responsive way. This was readily apparent this year, as efforts to employ the unique consortium tools at all three laboratories were initiated. Task meetings routinely involved in-person participation by representatives of all three laboratories. A number of joint investigations were initiated, in which staff from one partner laboratory went on site to a partner laboratory to be trained on relevant equipment and conduct experiments. Use of precious beam time at the ALS was also greatly facilitated by the proximity of SNL and LLNL to LBL. The ability to plan experiments by in-person meetings with various beam-line scientists and transport equipment and samples easily from one site to another greatly simplified logistics for staff involved in experiments running around the clock.

In addition, several collaborations with the Hydrogen Storage Characterization and Optimization Research Effort were initiated, with the twin objectives of facilitating information exchange and to assemble powerful interdisciplinary teams combining the unique capabilities of each team to address the most challenging problems. The first

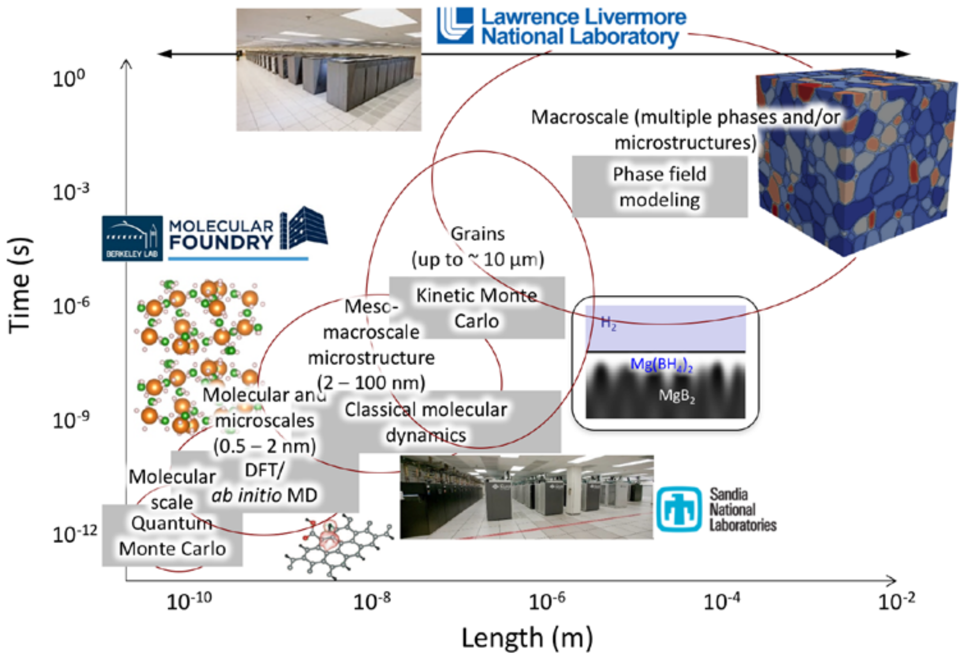

FIGURE 2. Length and time scales relevant to hydrogen storage material properties and corresponding modeling tools employed by HyMARC to address these. Supercomputing facilities at all three consortium laboratories are being employed to develop a suite of modeling tools spanning the atomic/molecular to macroscale/multiphase materials.

of these is a joint effort to understand the complex kinetics of hydrogen desorption and uptake by magnesium borohydride ($Mg(BH_4)_2$). HyMARC investigators are focusing on hydrogen uptake kinetics, while the Hydrogen Storage Characterization and Optimization Research Effort team is developing mechanisms of hydrogen desorption. Sample exchanges and jointly planned experiments are underway.

Technical progress: Details of the progress toward FY 2016 milestones (listed above) are provided in the individual annual reports for the three consortium laboratories. Briefly, however, as of the writing of this report, Milestones 1 and 2 are complete and Milestones 3, 4, and 5 are in progress. Noteworthy, the first two journal publications resulting from HyMARC research appeared in the literature, one describing a new molecular dynamics approach to computing hydrogen diffusion constants through materials, the other an exciting new method for synthesizing metal hydride nanoparticles.

FY 2016 PUBLICATIONS/PRESENTATIONS

Publications

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.

2. E.S. Cho, A.M. Ruminski, S. Aloni, Y.-S. Liu, J. Guo, J.J. Urban "Graphene Oxice/Metal Nanocrystal Multilaminates as the Atomic Limit for Safe and Selective Hydrogen Storage," *Nature Comm.* 2016, *vol. 7*, p. 10804.

Presentations

1. M.D. Allendorf "Hydrogen Materials Advanced Research Consortium," FCTO Overview Webinar, January 7, 2016.

2. M.D. Allendorf, B.C. Wood, j. J. Urban, J. Guo, T. W. Heo, L.E. Klebanoff, R. Kolasinski, V. Stavila "HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials," *Int. Symp. Hydrogen & Energy*, Febuary 22–26, 2016, Sendai, Japan.

3. M.D. Allendorf "HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials," Toyota Central R&D Laboratories, Febuary 26, 2016, Nagoya, Japan.