

## IV.C.3 HyMARC: Hydrogen Storage Materials Advanced Research Consortium (LLNL Effort)

Brandon Wood (Primary Contact), Tae Wook Heo, Keith Ray, Jonathan Lee, ShinYoung Kang, Stanimir Bonev, Miguel Morales, Roman Nazarov, Patrick Shea, Theodore Baumann, Patrick Campbell

Lawrence Livermore National Laboratory (LLNL)

7000 East Ave., L-413

Livermore, CA 94550

Phone: (925) 422-8391

Email: brandonwood@llnl.gov

DOE Manager: Ned Stetson

Phone: (202) 586-9995

Email: Ned.Stetson@ee.doe.gov

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### Overall Objectives

- Provide community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials.

### Fiscal Year (FY) 2016 Objectives

- Establish protocols for more accurate first-principles computations of hydride and sorbent thermodynamics.
- Adapt methods to account for non-ideal factors (e.g., defects and interfaces) in hydride simulations.
- Devise initial multiscale framework for simulating hydride kinetics, including mass transport and phase evolution, and compare against experiments on a model system.
- Establish protocols for synthesis of tailored carbon sorbents and soft X-ray characterization of hydride materials and catalysts.

### 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 and Volume

(E) Charging/Discharging Rates

### 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. 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

- Demonstrated approaches for computing accurate physisorption energetics of hydrogen on metal organic framework (MOF) metal sites (including hydrogen loadings beyond the dilute limit), and for simulating charge and field effects in carbon sorbents.
- Established protocols for more accurate density functional theory (DFT) computations of hydride thermodynamics accounting for finite temperature contributions, microstructure, and phase morphology.
- Improved thermodynamic phase fraction predictions of Li-N-H system as a function of pressure, temperature, and size within multi-phase framework.
- Developed non-equilibrium statistical approach to quantify effects of non-ideal interfaces and additives on reaction pathways.
- Demonstrated large-scale ab initio molecular dynamics (AIMD) for elucidating possible transport and reaction pathways and enable finite temperature calculations of thermodynamic and spectroscopic quantities.
- Applied coupled atomistic and mesoscale framework combining thermodynamics, mechanical stress, and phase nucleation and growth to model solid phase transition kinetics in an interstitial hydride system (PdH<sub>x</sub>).
- Used X-ray absorption spectroscopy for probing catalyst chemistry and surface versus bulk hydrogenation effects on catalysts within doped hydrides.



## 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 on climate change [1-2]. 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 onboard densities. However, the existing materials suffer from thermodynamic and kinetic limitations that are often poorly understood, which prevent their application as practical hydrogen storage media.

## APPROACH

HyMARC seeks to address these gaps 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. LLNL objectives and responsibilities within HyMARC include (1) providing technical leadership for Tasks 2 (Mass Transport) and Task 6 (Materials Informatics and Databases) and for the theory efforts; (2) providing computational methods for more accurate prediction of sorbent and hydride thermodynamics; (3) developing tools for multiscale modeling of hydride kinetics, including mass transport, chemical kinetics, and phase kinetics; (4) synthesizing carbon frameworks and sorbents with tailored porosity and chemistry; and (5) supporting HyMARC characterization efforts surrounding soft X-ray spectroscopy.

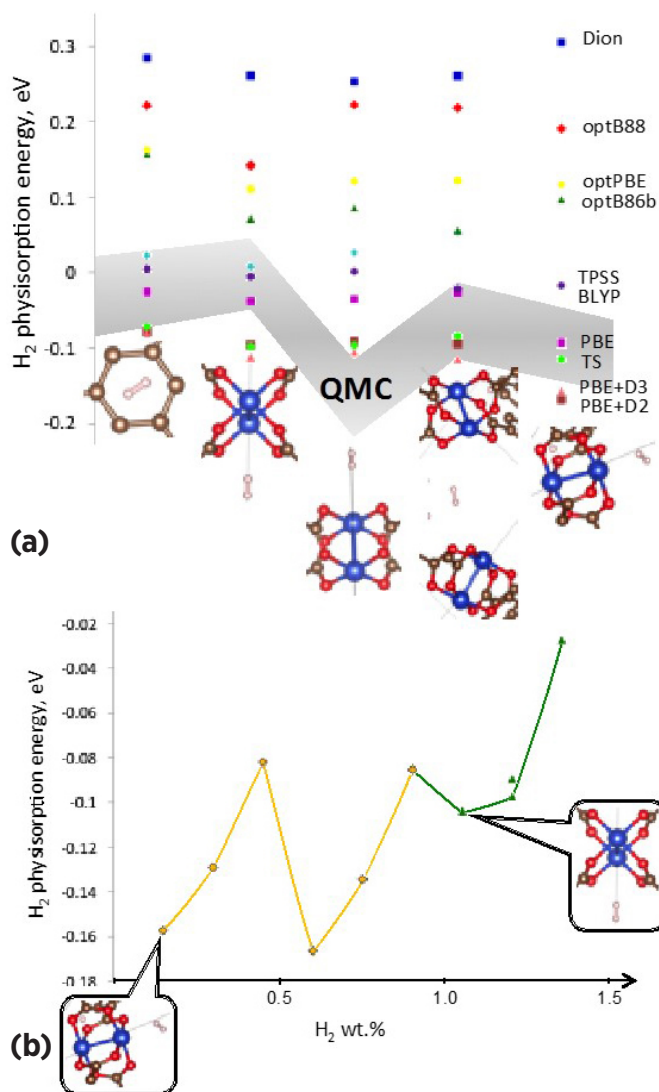
## RESULTS

*Sorbent thermodynamics (Task 1A):* On the sorbent side, our key computational goal is to improve predictions of sorbent-H<sub>2</sub> interaction energetics and provide understanding of beyond-van der Waals (vdW) interactions in sorbents. Three general types of interactions are being considered: metal site coordination (e.g., open metal sites in MOFs), second-neighbor and cooperative interactions (e.g., polarization effects), and charge transfer or electrostatic effects (e.g., Lewis acids, electronic and chemical doping,

and electric field effects). Our strategy relies on more computationally intensive methods that can be used as “gold standards” for energy computations (e.g., quantum Monte Carlo [QMC]), which can benchmark cheaper methods (e.g., vdW-corrected DFT) that can be readily run on many different sorbent systems. Future activities will focus on direct prediction of isotherms (validated against well-characterized MOFs) to provide guidance for MOF design.

MOF-505 was selected as a test sorbent material, with the geometry taken from the CoRE Database [3] and relaxed using DFT. Dilute-limit H<sub>2</sub> physisorption energies were calculated using QMC, which carries significant computational expense but promises chemical accuracy while including the full extended geometry of the substrate [4]. These results were used to evaluate which flavors of vdW-corrected DFT gave reliable binding energies for each possible binding site (Figure 1). Sites were identified by performing AIMD; future efforts will focus on MOFs with sites predetermined via neutron diffraction. Binding geometries amongst different DFT flavors were very consistent, although energies differed by wide margins that were site dependent (up to 500 meV; see Figure 1a). A similar approach will be used to benchmark DFT molecular coordination chemistry calculations and quantify the role of the extended MOF framework in determining binding energetics; indeed, our early calculations suggest extended effects alter bond lengths by as much as 4% with respect to finite clusters. The physisorption energy for higher hydrogen loading on MOF-505 was also computed, taking into account the full interactions between H<sub>2</sub> and the lattice. The results, shown in Figure 1b, demonstrate that the binding energy depends non-trivially on the hydrogen concentration (note that the expected behavior for a weakly interacting system would be flat or monotonic). We conclude that explicit calculations at higher loadings will be necessary for accurate isotherm prediction. The changes in bond lengths with loading should also result in different vibrational modes, which are currently being computed for comparison with infrared spectroscopy performed by partners on the Characterization and Validation team.

Our theoretical investigations on carbon sorbents have centered on the use of electrostatic interactions (charge, field, and polarization effects) to enhance binding of hydrogen, using graphene as a model system to tune the surface charge. These calculations, based on the Effective Screening Medium Method of Otani, et al. [5], show how the application of a strong electric field from positively charged graphene (> +0.025e per carbon atom) is able to introduce enough polarization to bring hydrogen physisorption into the required range. A similarly large change was found in the binding energy and surface diffusion barrier for atomic H, which has possible implications for graphene-induced hydrogen dissociation processes. Efforts towards experimental verification are underway.



**FIGURE 1.** Computed physisorption energies for (a) binding of an H<sub>2</sub> molecule in MOF-505 with geometries shown below each data set (the gray region bounds the high-confidence statistical uncertainty for the QMC results, and the colored symbols are the results for different vdW-corrected DFT functionals); and (b) higher-pressure loading with multiple H<sub>2</sub> adsorption sites (the color change indicates a shift in the preferred site with loading).

On the synthesis end, we have been working to establish reproducible synthesis pathways for three-dimensional graphene macro-assemblies with tailored porosity and chemistry based on previous successes with heat treatment and mechanical compression [6-8]. Graphene oxide-derived aerogels were synthesized with varying crystallinity and pore size, which was achieved by subjecting the aerogels to process temperatures ranging from 1,050°C to 2,500°C. The materials were delivered to HyMARC and Characterization and Validation partners for analysis and use as nano-confinement media.

*Beyond-ideal hydride thermodynamics (Task 1B):* Our computational strategy on the thermodynamics of metal

hydrides have centered on more realistic and accurate assessment of thermodynamics using DFT. Three primary factors are being considered, (1) explicit finite-temperature contributions to the free energy, including anharmonicity and thermal distortions; (2) microstructural effects, including interfaces; and (3) morphological considerations, such as amorphous, defect-rich, or solid solution phases. Alongside experimental validation and characterization partners, HyMARC will quantify these factors to determine which may be relevant for accurate prediction of realistic phase pathways.

One focus area has been the inclusion of anharmonic contributions to the free energy, which are typically associated with molecular modes in complex hydrides. We have devised a model for more accurate computation of these contributions using AIMD, based on separation of diffusive and non-diffusive contributions to the vibrational power spectrum [9]. This formalism has the added advantage of spatially decomposing the entropy density, which can be used to independently assess surface contributions. Successful application to the Mg-B-H system shows that anharmonicity can contribute >12 kJ/mol to stability of certain phases, reflecting the soft anion modes that are connected to the mass transport and phase transformation mechanisms. Significantly greater anharmonic contributions can appear at surfaces due to surface-induced disordering and undercoordination. We conclude that accurate free energy computations of complex hydrides should consider vibrations beyond the ideal harmonic limit.

To study the effects of microstructure, we have used the Li-N-H system as our test case. This system is attractive for isolating phase kinetics and thermodynamics, since Li<sub>3</sub>N and LiNH<sub>2</sub> are known superionic Li conductors and are therefore unlikely to be diffusion limited, and the reaction pathway is well established. Using several model core-shell-derived microstructures based on a careful analysis of previous studies, we computed the predicted thermodynamic phase fractions as a function of pressure, temperature, and particle size (Figure 2). To do so, we developed an extension to the Grand Canonical Linear Programming method [10] by incorporating the effects of interfaces and microstructure in the free energy formulation. Solid interface effects were estimated based on an established semi-empirical procedure for grain boundaries [11], in which the interface energy  $g_{ij}$  is calculated as  $g_{ij} = p_{ij} (s_i + s_j)$ . Here  $s_i$  is the surface energy, which we computed within DFT and averaged over possible exposed facets within the Wulff construction to represent a randomly oriented phase boundary (Figure 2a). Furthermore, to explore the effects of the varying interfacial energies due to the heterogeneity of structural characteristics present in real interphase boundaries (e.g., interfacial coherency, chemical bonding characteristics, contents of additives), we devised a novel approach for analyzing the phase fractions statistically by independently varying the prefactor  $p_{ij}$  and gathering statistics for all sampled configurations of  $p_{ij}$  at

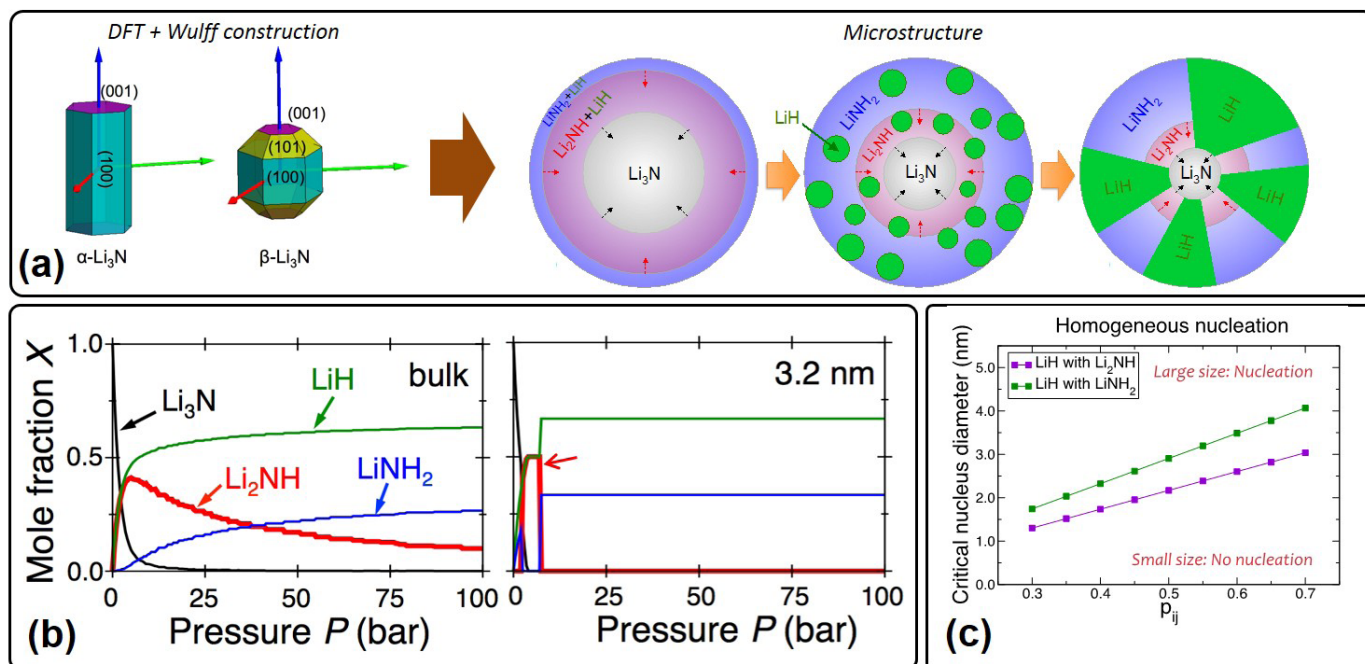


the given hydrogen pressures. For small particles (<20 nm), the interface penalties become sufficiently severe that the ordinarily stable  $\text{Li}_2\text{NH}$  intermediate is suppressed in favor a single-stage reaction pathway between  $\text{Li}_3\text{N}$  and  $\text{LiNH}_2+2\text{LiH}$  for both hydrogenation (at  $P = 100$  bar) and dehydrogenation (at  $P = 1$  bar) processes (Figure 2b shows one case for  $p_{ij} = 0.5$ ). This prediction agrees with measurements performed by HyMARC partners at Sandia, establishing the importance of microstructure and internal interfaces within the particle. Notably, this introduces a new paradigm for progressing towards ultimate hydrogen storage targets by engineering internal microstructure [12]. We are currently working to generalize our phase-fraction prediction code to consider multiple model microstructures.

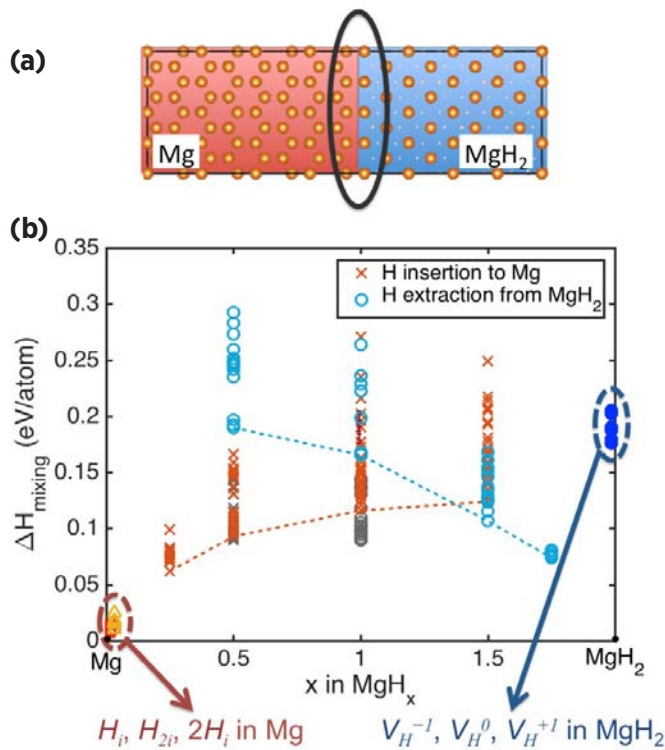
*Modeling interfaces and defects (Tasks 1 & 4):* Within our kinetic phase transformation modeling framework (see sections below), one of the most important yet challenging ingredients for predicting accurate kinetics is the computation of reliable solid interface energies and compositions. Semi-empirical approaches based on surface energy calculations benefit from simplicity but lack much of the physics of the complex models and may therefore be limited in their predictive capability. Within HyMARC, we are pursuing several additional strategies for computing interfacial energies and benchmarking against kinetics experiments using model materials. In this way, we hope to select a practical solution that balances accuracy with

reasonable computational cost and can be applied to a wide variety of materials.

For interstitial hydrides, free energies of interfaces can be computed explicitly with full finite-temperature effects using large-scale molecular dynamics, which captures the full interface complexity (an example based on Pd-H is discussed in further detail below [13]). For somewhat more complicated hydrides where charge transfer is relevant and large-scale molecular dynamics may be impractical, we are exploring methods based on zero-temperature DFT. Here, our model system is the Mg-H system, with interface kinetics characterization supplied from HyMARC partners at Lawrence Berkeley National Laboratory. For simple hydrides (e.g., Mg-H), the interface enthalpy can in principle be calculated within DFT using large supercells; however, accurately accounting for the possibility space of interface orientations, thicknesses, and structural defects is extremely costly, motivating development of an improved heuristic model. Mechanical strain contributions ( $E_{\text{mech}}$ ) are relatively straightforward to include by computing the elastic strain energy from the strain tensor and the elastic stiffness tensors. For the remaining chemical contributions ( $E_{\text{chem}}$ ) associated with bond breaking and atomic rearrangement, we treat the immediate interface region as a mixed phase and investigate the mixing enthalpy (Figure 3). Considering the distinct atomic arrangements of host Mg ions in *hcp* Mg and  $\text{MgH}_2$ , H insertion and extraction were considered in both lattice frameworks. This approach is currently being evaluated



**FIGURE 2.** (a) Illustration of the phase fraction calculation procedure that combines DFT-derived interfacial energies with model microstructures for the Li-N-H system; (b) computed mole fractions of relevant phases as a function of  $\text{H}_2$  upon isothermal hydrogenation of the bulk material (left) and  $d = 3.2$  nm (right), showing size-induced suppression of  $\text{Li}_2\text{NH}$ ; and (c) estimated critical nucleus diameter of a LiH crystallite within  $\text{LiNH}_2$  or  $\text{Li}_2\text{NH}$  for different values of  $p_{ij}$  representing different interface energy approximations.



**FIGURE 3.** (a) Schematic of the atomistic Mg/MgH<sub>2</sub> interface; and (b) calculated composition-dependent mixing enthalpy of Mg-H in the *hcp* Mg lattice framework (orange cross: lattice parameter fixed to pristine Mg) and in the pyrite MgH<sub>2</sub> lattice framework (blue circle: lattice parameter fixed to pristine MgH<sub>2</sub>), based on testing multiple atomic configurations. The dotted lines connect the lowest-energy configurations, and the grey circles show values with a fully relaxed lattice parameter. The defect formation energies of hydrogen interstitials ( $H_i$ ) and vacancies ( $V_H$ ) in Mg and MgH<sub>2</sub>, respectively, are also shown.

against full interface energy computations for Mg/MgH<sub>2</sub> for select interface orientations.

Complex hydrides, which have more realistic potential to achieve ultimate targets, introduce additional complexities that require an entirely new approach. Here, various reactions between constituents must be considered and interface alignments are generally ill defined due to phase incommensurability. Accordingly, we are developing a new model based on a diffuse interface that combines mass transport near the interface boundaries with chemical reactivity and solution thermodynamics in the interface interior. This formalism, being developed in collaboration with the Characterization and Validation team and tested on the Mg-B-H system, is currently based on chemical kinetics computed with DFT, although high-temperature AIMD simulations are also being pursued as an avenue to extract possible chemical pathways. Further development and validation of this complex hydride interface model will be a key future direction for HyMARC.

#### *Chemical pathways and diffusion (Tasks 2 & 3):*

Understanding the kinetics of mass transport is a critical ingredient for developing a more comprehensive mechanistic model of hydrogen storage in metal hydrides. Our theory efforts in this regard have centered on two activities. The first is the computation of defect formation energies and mobilities using zero-temperature approximations to identify which hydrogen-bearing species can diffuse effectively in the bulk materials. The defect formation energies are computed as function of electronic and atomic chemical potentials, which allow varying defect concentrations to be integrated directly within our mesoscale models that consider changes in chemical potential at interfaces and surfaces. Our second activity involves the use of AIMD to investigate transport pathways at surfaces and interfaces. A Python-based framework has been developed to automate setup and execution of the AIMD simulations, which will facilitate rapid application to other materials.

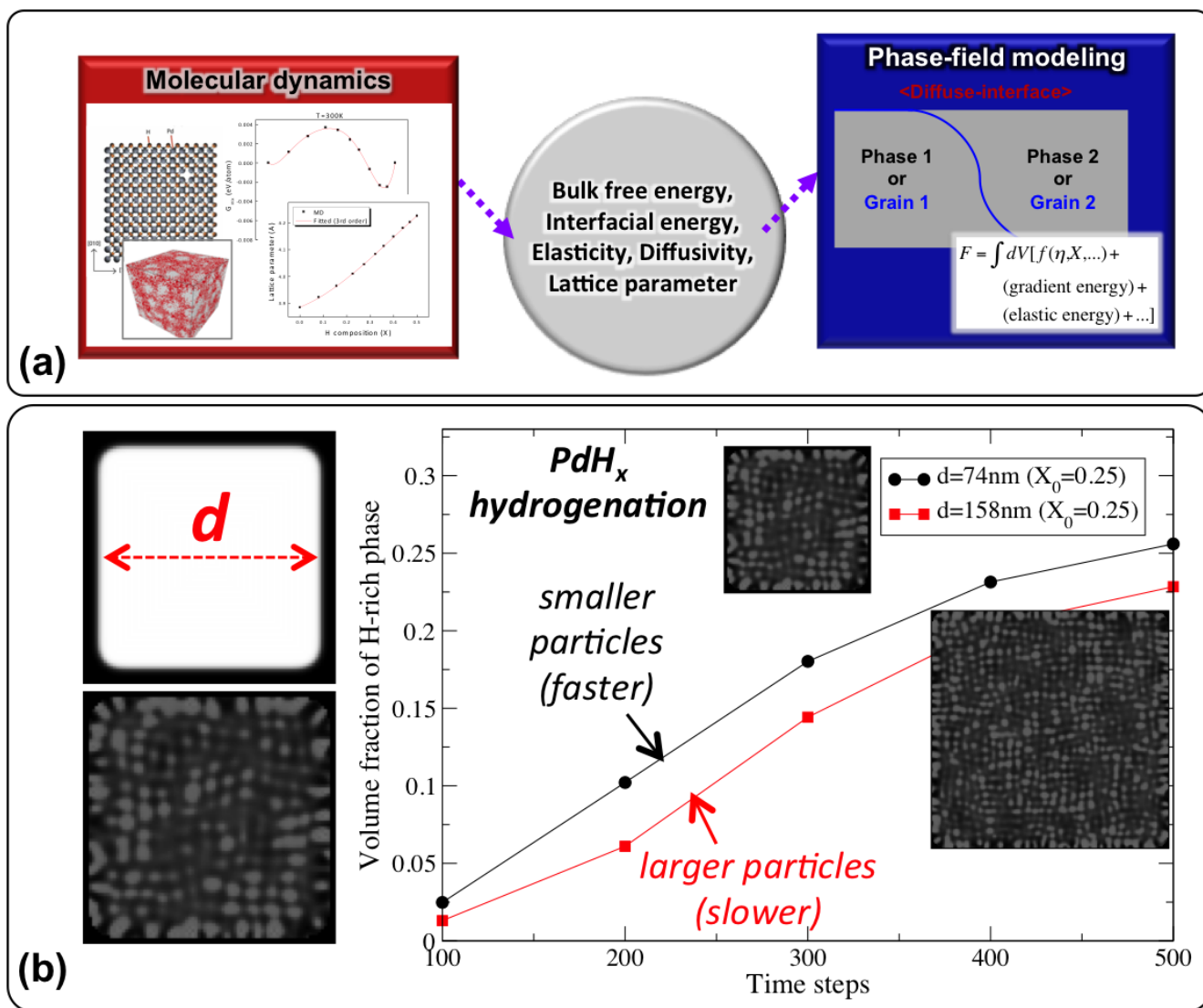
Both the defect-based and AIMD-based approaches have been applied to investigate the Mg-B-H system, focusing on MgH<sub>2</sub>, Mg(BH<sub>4</sub>)<sub>2</sub>, and several potential B<sub>x</sub>H<sub>y</sub>-containing intermediates. The results point to the possibility of low-barrier interfacial and surface hydrogen structural diffusion pathways that are accessible to the picosecond timescales of AIMD. In certain cases, for instance, in  $\beta$ -Mg(BH<sub>4</sub>)<sub>2</sub>, these facile pathways emerge even though bulk diffusion is inhibited [14]. The different bulk, surface, and interface mobilities can be combined into an effective polycrystalline diffusivity, which we will integrate into our mesoscale models. Notably, the diffusion kinetics can also be matched to direct analysis of experimental uptake curves in regimes where diffusion limitations are expected; indeed, more closely connecting the theoretical and experimental kinetics analysis will be a key future focus.

Another activity, which is being pursued in close collaboration with HyMARC partners at Sandia performing low-energy ion scattering (LEIS) experiments, involves coupling atomistic surface diffusion models to concentration-driven continuum Fickian diffusion. This multiscale approach carries a twofold purpose. First, it is intended to improve the quantitative interpretation of LEIS data in terms of self-diffusion coefficients. Second, it will improve understanding of mass transport under the non-equilibrium conditions of (de)hydrogenation, in contrast to conventional DFT-based nudged elastic band or AIMD mobility calculations that can only probe diffusion under equilibrium conditions. As an initial test, we are investigating hydrogen migration on Al, Mg, and graphene, since the carefully controlled and well-defined nature of these surfaces allows for better experimental validation of models. However, the framework should be generalizable to any surface. A more complete analysis comparing the theoretical predictions with the experimental results on these materials is forthcoming.

*Hydride phase transformation kinetics (Task 4):*

To understand the phase transformation kinetics and associated microstructural features of metal hydrides, it is important to analyze the relevant phase transition mechanisms for products and intermediates, which often occur through nucleation and growth. Using the DFT-derived thermodynamics and statistically sampled interfacial energies created upon nucleation (see discussion above), we evaluated the critical nuclei sizes and corresponding nucleation barriers employing classical nucleation theory. Applying this framework to predict the critical nuclei size of LiH crystallites showed that crystalline LiH is unlikely to nucleate in small particles until very late in the reaction (see Figure 2c), offering more accurate picture of microstructure evolution in the nanoscale Li-N-H model storage system [12].

Furthermore, we established an integrated atomistic and mesoscale framework for modeling interface kinetics and internal phase microstructure evolution within metal hydrides. The approach combines the atomistically derived materials thermodynamic and kinetic parameters with the phase-field modeling approach as illustrated in Figure 4a. We have applied this integrated approach to a Pd-H system as the simplest model interstitial hydride for which the phase transformation is governed exclusively by diffusional processes without any crystallographic structural change. The phase-field model was fully parameterized using temperature- and composition-dependent Gibbs free energies, elastic moduli, lattice parameters, interfacial energies, and diffusion coefficients derived (by HyMARC partners at Sandia) from classical molecular dynamics simulations using an embedded-atom potential [15]. Isothermal phase-



**FIGURE 4.** (a) Illustration of the integrated atomistic and mesoscale modeling framework, and (b) examples of simulated phase transformation kinetics for a Pd-H system.



field simulations for two different particle sizes successfully captured experimentally measured differences in phase evolution kinetics as shown in Figure 4b [13]. Encouraged by this successful demonstration, we are now extending this same formalism to the other systems that involve both diffusional and crystallographic structural transformations.

*Additives (Task 5):* To better understand the role of additives in metal hydrides, LLNL has been working closely with the other HyMARC partners to measure and interpret X-ray absorption and emission spectroscopy of TiCl<sub>3</sub>-doped NaAlH<sub>4</sub>. Because the system has been studied extensively with other techniques, we can leverage the wealth of published information to validate and further inform our interpretations. Synchrotron X-ray absorption spectroscopy experiments performed by the LLNL team at the Advanced Light Source to probe the Ti L<sub>2</sub> and L<sub>3</sub> edges of TiCl<sub>3</sub>-doped NaAlH<sub>4</sub> show that hydrogen-induced chemical changes to the Ti environment are signaled by a change in signal strength that increases dramatically at higher additive concentrations. This indicates a likely change in the surface concentration of Ti upon exposure to hydrogen. Further analysis is underway, including accompanying theoretical modeling and comparison to proposed mechanisms in the literature [16].

## CONCLUSIONS AND FUTURE DIRECTIONS

- Accurate binding energy calculations on MOF-505 suggest H<sub>2</sub> interactions carry a significant dependence on H<sub>2</sub> loading, leading to likely deviations from model isotherms.
- Internal interfaces can modify the reaction pathway for nanoscale Li<sub>3</sub>N, suggesting microstructure and morphology engineering as a new strategy for improving hydrides.
- Multiscale integration of atomistic and continuum approaches can reproduce size-dependent phase kinetics of model interstitial hydride systems.
- *Future direction:* Use benchmark calculations to select a computational strategy for sorbent thermodynamics that balances accuracy and computational efficiency.
- *Future direction:* Apply improved hydride thermodynamic calculation protocols to other model hydride systems for quantitative evaluation.
- *Future direction:* Demonstrate multiscale surface transport simulation for validation and interpretation of LEIS results.
- *Future direction:* Evaluate different approaches for interface modeling and apply phase kinetics framework to a complex metal hydride.

- *Future direction:* Work with HyMARC partners to develop interpretation of soft X-ray spectra on catalyzed hydride materials.

## FY 2016 PUBLICATIONS/PRESENTATIONS

1. Wood, B.C. et al., “Nanointerface-driven reversible hydrogen storage in the nanoconfined Li-N-H system,” *Materials Research Society Spring Meeting*, Phoenix, AZ, April 2016.
2. Wood, B.C., V. Stavila, N. Poonyayant, T.-W. Heo, K. Ray, L.E. Klebanoff, T.J. Udovic, J. Lee, N. Angboonpong, J.D. Sugar, and P. Pakawatpanurut. “Nanointerface-driven reversible hydrogen storage in the nanoconfined Li-N-H system.” *Submitted* (2016).

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and P. Pakawatpanurut, “Nanointerface-driven reversible hydrogen storage in the nanoconfined Li-N-H system.” *Submitted* (2016).

**13.** Zhou, X.W., T.W. Heo, B.C. Wood, V. Stavila, and M.D. Allendorf. “Molecular dynamics analysis of thermodynamic and kinetic parameters controlling hydriding/dehydriding of palladium hydrides.” *Manuscript in preparation* (2016).

**14.** Wolverton, C., et al. *U.S. DOE Hydrogen and Fuel Cells Program Annual Report* (2013).

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