HyMARC: LLNL Technical Effort

2017 DOE Hydrogen Annual Merit Review
June 7, 2017
PI: Brandon C. Wood, LLNL


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## Overview

### Timeline

<table>
<thead>
<tr>
<th>Project start date:</th>
<th>9/17/2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase I end date:</td>
<td>9/30/2018</td>
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</tbody>
</table>

### Barriers addressed

- Lack of understanding of hydrogen physisorption and chemisorption (Barrier O)
- System weight and volume (Barrier A)
- Charge/discharge rate (Barrier E)

### Budget

<table>
<thead>
<tr>
<th>FY15 DOE Funding:</th>
<th>$250K</th>
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<tbody>
<tr>
<td>FY16 DOE Funding:</td>
<td>$735K</td>
</tr>
<tr>
<td>FY17 DOE Funding:</td>
<td>$955K</td>
</tr>
<tr>
<td>Total Funds Received:</td>
<td>$1940K</td>
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</tbody>
</table>

### Team -

**Funded Partners:**

- Sandia National Laboratories (lead)
- Lawrence Berkeley National Laboratory
Relevance

**HyMARC provides community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable solid-phase hydrogen storage materials**

### Theory, simulation, data
- High-accuracy physisorption
- *Ab initio* thermodynamics
- *Ab initio* molecular dynamics for bulk/surface/interface chemistry
- Multiscale non-equilibrium mass transport
- Phase-field models for solid-state phase transformation kinetics
- Semiempirical kinetic modeling
- Community software & databases

### Controlled synthesis
- Functionalized carbon and porous nanoconfining media

### In situ characterization
- Soft X-ray absorption and emission spectroscopy
- X-ray spectromicroscopy
Approach: Validated multiscale modeling

Modeling approach prioritizes (1) bridging scales via multiscale integration; (2) improving descriptions of “real” materials; and (3) leveraging experiment-theory feedback.
**Approach:** Using model materials to investigate key phenomena

**We choose model systems that allow us to isolate different physical factors & mechanisms**

**Thermodynamics:**
- Mg-B-H, Li-N-H

**Surface reactions**
- Oxidation (NaAlH₄, Mg(BH₄)₂)
- H₂ dissociation (Mg, MgB₂)

**Sorption**
- MOF-74, CuBTC
- Graphene (doped/functionalized)

**Additives**
- TiF₃/TiCl₃
- Ti in NaAlH₄, MgB₂/Mg(BH₄)₂

**Phase nucleation & evolution**
- Interstitial topotactic interface (Pd/PdHₓ)
- Simple structural transformation (Mg/MgH₂)
- Complex reactive interface (MgBₓHᵧ/MgBₓHₓ)

**Surface/interface diffusion**
- LEIS on model metals (Mg, W)
- Isotropic interstitial diffusion (PdHₓ)
- Anisotropic vacancy diffusion (MgH₂)
- Complex hydride diffusion (Mg(BH₄)₂)

**Bulk diffusion**
- Borohydride decomposition pathways in MgBₓHᵧ

**Chemical bond activation**
# LLNL contributions to HyMARC

## Multiscale modeling

- **Multiscale integration:** Brandon Wood
- **Ab initio molecular dynamics:** Tadashi Ogitsu
- **Mesoscale phase-field kinetic modeling:** Tae Wook Heo
- **Ab initio free energy:** Stanimir Bonev
- **Quantum Monte Carlo:** Miguel Morales

**Postdocs:** ShinYoung Kang, Keith Ray, Patrick Shea, Aurora Pribram-Jones

## Porous carbon synthesis

- **Ted Baumann**
- **Pat Campell**
- **Marcus Worsley**

## X-ray absorption/emission

- **Jon Lee**
- **Alex Baker**
Progress towards milestones with key LLNL activities

FY16Q3: Demonstrate in-situ soft X-ray XAS/XES with sample heating (100%)

FY16Q4: Identify hydride mobile species and diffusion pathways (100%)
• Dynamics and electronic structure computed for pure and defective hydrides in Mg-B-H system
• Multiscale hydrogen diffusion modeling framework established and tested for Mg-H system

FY17Q2: Go/No-Go: Rank improvement strategies for enthalpy increases in sorbents (100%)
• Provided theory data for aid in ranking strategies

FY17Q4: Prototype hydride surface/interface chemistry kinetic models (100%)
• Models completed and tested for Mg-B-H (diffuse reactive interface), Mg-H (interface with structural transformation), and Pd-H (interface without structural transformation)

FY17Q4: Sensitivity analysis of local binding and second-sphere effects (20%)
• Delays due to postdoc restaffing need (in progress)

FY17Q4: Evaluate additive/composite strategies for improving effective ΔE (20%)
• Completed joint theory-experiment study on hydrogen interaction with TiF₃ and TiCl₃ additives
• Completed joint theory-experiment study of confinement stress effects and kinetic enhancements in Ni-doped nanoconfined MgH₂

FY18Q1: Compute H₂ binding on model MOFs and select appropriate levels of theory (50%)
• Performed comparison between QMC and various flavors of van der Waals DFT on NOTT-100
• Delays due to postdoc restaffing need (in progress)
Accomplishment: B/N-doped graphene aerogels for sorption/encapsulation

Established synthetic protocols for B/N doping of graphene aerogels for hydride infusion (SNL) and direct sorption testing (NREL/HySCORE)

**Boron doping** ($\text{B}_2\text{O}_3$ + annealing)

**Nitrogen doping** (Melamine + annealing)

<table>
<thead>
<tr>
<th>Sample</th>
<th>B (at.%)</th>
<th>N (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-GA 1600C</td>
<td>2.68</td>
<td>1.81</td>
</tr>
<tr>
<td>B-GA 1700C</td>
<td>1.28</td>
<td>1.05</td>
</tr>
<tr>
<td>B-GA 1800C</td>
<td>0.61</td>
<td>0.57</td>
</tr>
<tr>
<td>B-GA 1900C</td>
<td>0.06</td>
<td>0.22</td>
</tr>
<tr>
<td>N-GA 1100C</td>
<td>--</td>
<td>1.96</td>
</tr>
<tr>
<td>N-GA 1300C</td>
<td>--</td>
<td>0.99</td>
</tr>
<tr>
<td>N-GA 1500C</td>
<td>--</td>
<td>0.09</td>
</tr>
<tr>
<td>N-GA 1600C</td>
<td>--</td>
<td>0.92</td>
</tr>
</tbody>
</table>

- Further characterization of local bonding underway with help from theory
- Exploring other schemes (different gel formation precursors for B doping; carbonization in Ar to remove N; $\text{C}_3\text{N}_4$ for N doping) to increase doping and purity

**XPS compositional analysis**

**DOS consistent w/ substitutional doping**

- $sp^2$-boron oxide

**SXE/XAS Intensity (a. u.)**

- Photon Energy/eV

**Normalized XAS Intensity (a. u.)**

- 1000 °C
- 1500 °C
- 2000 °C

**As-prepared B-GA**

M. Worsley, T. Baumann, P. Campbell, A. Baker, J.R.I. Lee
Accomplishment: New theory capabilities introduced in FY17

Seedling needs prioritized development of new theory methods

Improved sorbent isotherms

Recipes for integrating different levels of theory in sorbent isotherm models

Seedling: Chung/PSU

Accurate hydride thermodynamics

Finite-\(T\) free energy, environment- and morphology-dependent thermodynamics

Seedlings: Liu/ANL, Severa/U. Hawaii

Solid mechanics & interfaces in hydrides

Internal and confinement stress effects; reactive diffuse interfaces

Seedlings: Liu/ANL, Severa/U. Hawaii

Kinetic modeling

Semiempirical kinetic modeling and rate analysis; phase evolution kinetics

Seedlings: Liu/ANL, Severa/U. Hawaii

Additional accomplishments in compiling databases and reference libraries (“Task 6”):

- Simulated & measured spectroscopy database (NMR, FTIR, XAS/XES) for identifying MgB\(_x\)H\(_y\) (preparing manuscript w/LBNL/SNL/HySCORE)
- Library of analytical free energies for Li-N-H (published) and Mg-B-H (preparing manuscript), with validation at a range of pressures via NMR (w/SNL/HySCORE)
- Database of classical potentials for simulating borohydride mixtures and interfaces (w/SNL)
Accomplishment: Efficient, accurate low-pressure MOF sorption enthalpies

**LLNL is benchmarking MOF sorption enthalpies in low-P regime using high-level theory**
*(LLNL is computing higher-P regime using force fields)*

- **Classify motifs via materials informatics**
  (Haranczyk/LBNL)
- **Compute binding energy using suitable theory level**
  (Pribram-Jones/LLNL & Head-Gordon/HySCORE)
- **Predict & validate isotherms**
  (Camp & Haranczyk/LBNL, Stavila/SNL & NREL/HySCORE)

**Open metal sites (OMS)**

\[ \Delta H \text{ on OMS varies across DFT flavors from 0 to 15 kJ/mol to in NOTT-100} \]

**Linkers/organics**

\[ \Delta H \text{ on linker sites is more consistent across van der Waals DFT flavors in NOTT-100} \]

**Extended structure vs. local chemistry**

\[ \Delta H \text{ on OMS changes by 20-50% with loading of other nearby OMS in NOTT-100} \]

Measured \( Q_{st} \) for NOTT-100: 6.3 to 5.4 kJ/mol @ 0 to 1 wt.%H loading*

- Interactions extend through MOF cells, so low-P \( \Delta H \) is mispredicted by local cluster models
- Working with HySCORE to benchmark DFT functionals for OMS with accurate Quantum Monte Carlo (downselected three variants for NOTT-100; planning tests on MOF-74)
- Working with LBNL to benchmark force fields for linkers/organics with vdW DFT


**Progress towards FY17Q2 and FY17Q3 milestones**

A. Pribram-Jones & M. Morales
Accomplishment: New validated finite-T hydride thermodynamics method

**Improved free energy predictions of hydrides by considering explicit thermal effects, with results tested and successfully validated on Mg-B-H system**

- **Run ab initio molecular dynamics** at different $T$
- **Isolate harmonic, anharmonic, and diffusive contributions**
- **Fit to physical equations to obtain analytical $\Delta G(T)$**

Use recipe for high-$T$ equation of state to determine phase fractions at any $(T,P)$:

- Thermal properties from *ab initio* MD
- Zero-K reference energies from DFT and/or Quantum Monte Carlo
- Temperature calibration (e.g., from PCT)

- Anharmonic effects from molecular rotations are critical for predicting free energies
- Predicted phase diagrams and phase fractions of $\text{MgB}_x\text{H}_y$ at several $(T,P)$ (Stavila/SNL) successfully validated via NMR (PNNL/HySCORE) for Wood/LLNL project

S. Kang, S. Bonev, T.W. Heo, T. Ogitsu, B. Wood
**Accomplishment: Morphology/environment-dependent thermodynamics**

Examed stability trends of $B_xH_y$ intermediates beyond the bulk crystalline limit to understand reaction pathways under non-equilibrium reaction conditions.

<table>
<thead>
<tr>
<th>Bulk</th>
<th>Surface/interface</th>
<th>Isolated molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-D</td>
<td>-2.38</td>
<td>-1.28</td>
</tr>
<tr>
<td>2-D</td>
<td>-1.21</td>
<td>-1.15</td>
</tr>
<tr>
<td>1-D</td>
<td>-1.21</td>
<td>-1.14</td>
</tr>
<tr>
<td>0-D</td>
<td>-1.17</td>
<td>-1.14</td>
</tr>
</tbody>
</table>

- Relative stability depends strongly on environment and morphology, so reactions at interfaces are influenced by local compositions and may not follow crystalline trends.
- Building $B_xH_y$ classical potentials database for amorphous and interface thermodynamics (w/ Zhou/SNL) to support Severa/U. Hawaii seedling and Wood/LLNL project.

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Progress towards FY18Q1 and FY18Q2 milestones

S. Kang, T. Ogitsu, B. Wood
Accomplishment: Solid mechanics/strain effect on hydride enthalpy

New capability quantifies the destabilizing effect of internal and external stress on reaction enthalpy due to volume expansion upon hydrogenation.

- Elastic strain energy can explain confinement effect on $\Delta H$ for MgH$_2$/Mg (Urban/LBNL)
- Stiffness and pore geometry of confining medium can tune thermodynamics
- Adapting formalism to complex borohydrides to support Liu/ANL seedling
Accomplishment: Multiscale method for mass transport

Demonstrated new methods for non-equilibrium mass transport in complex microstructures

- Degree of crystallinity obtained during cycling conditions can impact mass transport
- H depletion geometry influences H surface diffusion kinetics in LEIS (Kolasinski/SNL)
- Extending models to chemically reactive “structural diffusion” in complex hydrides
Accomplishment: Chemical mechanisms at interfaces

Reactive ab initio molecular dynamics simulations of MgB$_2$/H$_2$ and MgB$_2$/etherate interfaces help to elucidate local reaction mechanisms and coordination complexes.

- High-pressure H$_2$ at MgB$_2$ edges prompts initial stages of closoborane and B-H bond formation
  
  ![Diagram](image1.png)

- Al-H bond cleavage and O-H bond formation on oxidized NaAlH$_4$(001)
  
  ![Diagram](image2.png)

- Oxygen coordination complexes formed by THF at the interface with MgB$_2$ edges
  
  ![Diagram](image3.png)

- Boron chemistry activated by charge imbalance (e.g., upon Mg extraction from MgB$_2$)
- Observed MgB$_{x}$H$_y$ chemical intermediates validated via NMR, XAS/XES, FTIR
- O-H bond formation and hydrogen diffusion on oxidized NaAlH$_4$ is consistent with AP-XPS and suggests oxide may play an active role
Accomplishment: New reactive interface phase-field method

- Developed **Diffuse Reactive Interface Nonlinear Kinetics** model for first-ever phase-field simulation of (de)hydrogenation fronts controlled by diffusion and chemical kinetics.

**Chemical kinetics:** Gas-phase energies of MB_xH_y molecules (PNNL/HySCORE)

**Thermodynamics:** Liquid mixtures from new QM/MM approach (LLNL/HyMARC)

- Collaboration with PNNL/HySCORE
- Basis of FY18 interface modeling strategy for complex hydrides
  
  *(FY16 focus: interstitial hydrides using PdH_x
  FY17 focus: simple hydrides using MgH_2)*

**Compute composition-dependent interfacial chemical kinetics**

**Update chemical potentials via nonlinear rate model**

**Recompute free energy & propagate interface**

**New reactive model**

\[ \Delta G_{\beta \rightarrow \alpha} < 0 \]

**Progress towards FY17Q3 milestone**

T.W. Heo, S. Kang, B. Wood
Accomplishment: Foundational understanding of H-catalyst interactions

Examined thermodynamic, kinetic, and electronic effects of TiF₃ catalysts and Ti in borohydrides via DFT and ab initio molecular dynamics

- Isolated TiF₃ is unreactive to H₂ due to high dissociation barrier and low density of H binding sites, so activity is linked to Ti incorporation or solid interface properties
- Ti in Mg(BH₄)₂ creates new gap levels and acts as charge sink to facilitate changes in oxidation state during BₓHᵧ chemistry (comparing w/spectroscopy)

Progress towards FY17Q4 milestone

T. Ogitsu, S. Kang, B. Wood, J.R.I. Lee, A. Baker
Accomplishment: Understanding mechanisms through kinetic rate analysis

*Kinetic analysis elucidated hydrogenation mechanisms in MgB₂ and catalyzed+confined MgH₂*

- Rate analysis suggests that dissociation and diffusion enhancements in Ni-doped, nanoconfined Mg likely from disordered near-surface alloying
- Kinetic models show that dissociation + H binding happen at separate sites in MgB₂

Extracted barriers for H₂ uptake in nanoconfined Mg (in rGO) w/ Urban/LBNL

Extracted barriers and energy landscape for H₂ uptake in MgB₂ w/ Stavila & Klebanoff/SNL and Wood/LLNL project

<table>
<thead>
<tr>
<th>wt.% H</th>
<th>Eads (θ)</th>
<th>E_ads (per H)</th>
<th>E₂H_ads</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20 eV</td>
<td>0.20 eV</td>
<td>0.56 eV</td>
<td>0.91 eV</td>
</tr>
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</table>

Dissociation

Onset of deeper hydrogenation

Diffusion

Create kinetic model based on proposed mechanisms

Inform model from extracted barriers + DFT energies and compare simulated behavior to measurements

Downselect or validate possible mechanisms

Extract composition-dependent barriers from rates and compare to barriers for known processes

Collaborations

Engagement with HyMARC seedlings

• Predicting thermodynamics and kinetics of graphene-wrapped hydrides (Liu/ANL ST136)
• Modeling interfaces and complexation of ethers around MgB₂ (Severa/U. Hawaii ST138)
• Methods for describing physisorption interactions in polymers (Chung/PSU ST140)
• Monthly webinars with ANL and U. Hawaii

External collaborations

• Kinetic Monte-Carlo for solid-state diffusion: H. Kreuzer (Dalhousie U.)
• Phase-field model development: H.-C. Yu (U. Michigan)
• Hybrid quantum-classical simulations of borohydride interfaces: M. Otani (AIST, Japan)

HySCORE collaborations

• Mg-B-H chemistry, NMR, borohydride reaction modeling (T. Autrey et al., PNNL)
  • Biweekly webinars discussing modeling and weekly webinars discussing experiments, plus bilateral visits
  • HyMARC focus on solid-state aspects and MgB₂ rehydrogenation; HySCORE focus on borohydride chemistry during Mg(BH₄)₂ dehydrogenation
• DFT computations of H₂ physisorption on MOFs (M. Head-Gordon, LBNL)
  • HyMARC focus on extended systems & high-level theory; HySCORE focus on cluster chemistry
• Neutron diffraction/spectroscopy of borohydrides (T. Udovic, NIST)
• Sorption tests of doped graphene aerogels (T. Gennett et al., NREL)

LLNL theory team @PNNL (Feb. 2017)

Also extensive collaborations within HyMARC
Remaining challenges/barriers & mitigation strategies

• **Computational expense complicates highly accurate sorbent predictions**
  • *Our sorbent strategy uses high-level methods to benchmark more affordable approaches that can be directly integrated within classical uptake models*

• **Difficult to paramaterize free energy landscape for amorphous materials**
  • *Working with SNL to synthesize amorphous materials for testing. Also pursuing novel techniques for estimating properties of amorphous materials from melts and mixed quantum-classical dynamics through new collaboration with AIST, Japan.*

• **Microstructural information is needed for model validation**
  • *We will soon be initiating STXM measurements as part of our ALS Approved Program, which will directly provide microstructural information with minimal beam damage. Also investigating the possibility of performing TEM.*

• **Difficult to validate chemical kinetics predictions in diffuse reactive interfaces**
  • *HyMARC will pursue in situ spectroscopic methods for understanding interfacial chemistry, focusing on kinetic trends with polycrystallinity and other variables. We are also collaborating with PNNL/HySCORE to perform ex situ NMR analysis of molecular species as a function of exposure time, which will be used to validate LLNL kinetic models.*

*Note: Departure of postdoc working on sorbent modeling has led to a staffing issue that we are currently working to fill within budgetary constraints*
Proposed future work

Task 1A (Sorbents):
• Complete B/N doping studies & send samples for sorption (HySCORE) and hydride infiltration (SNL)
• Apply physisorption framework to understand & validate effects of geometry and levels of theory on open metal sites for MOF-74 (w/LBNL & SNL)

Task 1B (Hydride thermodynamics):
• Refine thermodynamics of amorphous materials and interfaces in Mg-B-H (w/SNL & HySCORE)
• Extend solid mechanics formalism to borohydrides (Mg(BH₄)₂ & NaBH₄) (w/LBNL & ANL seedling)

Task 2/Task 3 (Transport and surface phenomena):
• DFT study of hydrogen-oxide interactions and surface diffusion on oxidized NaAlH₄ (w/SNL & LBNL)

Task 4 (Interfaces):
• Perform sensitivity analysis of morphology and microstructure for model hydrides
• Continue AIMD of Mg-B-H in ether and analyze coordination (w/LBNL & U. Hawaii seedling)
• Test fully integrated kinetics framework for Mg/MgH₂ interface propagation (w/LBNL)
• Parameterize diffuse reactive interface phase field model and test on Mg-B-H (w/SNL)

Task 5 (Additives):
• Study chemistry of TiF₃/TiCl₃ on MgB₂ using DFT (w/SNL)

Task 6 (Databases):
• Publish MgBₓHᵧ spectroscopy standards study (w/HySCORE, SNL, and LBNL)
• Complete library of pairwise intermolecular potentials for BₓHᵧ (w/SNL)

Any proposed future work is subject to change based on funding levels
Summary

• Integrated theory/synthesis/characterization framework of HyMARC aims to provide foundational understanding and new tools for solid-state hydrogen storage

• LLNL works closely with the HyMARC core lab team and with HySCORE to investigate key phenomena that govern the performance and viability of hydrogen storage materials

• FY17 LLNL synthesis tasks focused on establishing key strategies for tailored doped carbons

• FY17 LLNL characterization tasks focused on spectroscopic changes upon hydrogenation (part of ALS Approved Program with participation from all three labs)

• FY17 LLNL modeling tasks broadly focused on multiscale integration, experiment-theory feedback, and beyond-ideal materials modeling

• Developed several new modeling techniques for describing kinetics of complex materials, including the first integrated chemical + diffusive phase transformation kinetics model of (de)hydrogenation

• Improved theory-experiment feedback by providing mechanistic understanding and interpretation of observed phenomena, and by validation of phase diagram predictions

• Applying tools for interaction with seedlings to model thermodynamics and kinetics of confined hydrides and MgB$_2$ etherates, as well as H$_2$ physisorption on tailored polymers
Technical backup slides
ALS Approved Program involves collaboration between all three core labs on synchrotron soft X-ray spectroscopy (LLNL: A. Baker, J. Lee; SNL: L. Klebanoff, V. Stavila; LBNL: Y.-S. Liu)

- Synchrotron experiments are tightly coupled with computational spectroscopy efforts (LLNL/LBNL)
- LLNL is leading a manuscript on spectroscopic standards for Mg-B-H intermediates, featuring XAS/XES results from all three core labs plus PNNL/HySCORE

Evidence of N dopant removal at high T visible in C K-edge XAS

Mg K-edge XAS elucidate mechanisms: no evidence for MgH₂ formation during initial hydrogenation

Understanding the role of TiCl₃ and TiF₃ dopants

Dramatic changes in F K-edge XAS upon TiF₃ doping of MgB₂
Predicted the preferred orientation and strain energy for solid interfaces in Mg/MgH₂, which affects the structure and reactivity of the parent phases

Predicted Mg/MgH₂ phase boundary orientation and energy

\[ \vec{n}_0 = [0.4875, 0.8281, 0.2766] \quad (B(\vec{n}_0) = 1.651 \text{ GPa}) \]

- High interfacial strain due to volume expansion upon hydrogenation means interface is likely partially disordered (semicoherent)
- Currently testing in phase-field model of MgH₂ dehydrogenation with LBNL validation

T.W. Heo, S. Kang
Computed effective diffusivity in Pd-H using full c- and T-dependent diffusivities from classical MD (Zhou/SNL)
Backup: New approaches for modeling solid interfaces in metal hydrides

Progress towards integration of diffusion, chemical kinetics, and phase kinetics within our phase-field model requires step-by-step approach to different types of interfaces, with validation on carefully chosen model systems.

FY16
- Interstitial (topotactic coherent)
  - Composition
  - Lattice mismatch

Model for study:
- Pd-H system

FY17
- Structure change (semi-coherent)
  - low chemical E
  - high strain E

Model for study:
- Mg-H system

FY17-FY18
- Diffuse interface (incoherent) + chemically reactive
  - high chemical E
  - low strain E

Model for study:
- Mg-B-H complex hydride

S. Kang, T.W. Heo, B.C. Wood