HyMARC: LLNL Technical Effort

2017 DOE Hydrogen Annual Merit Review

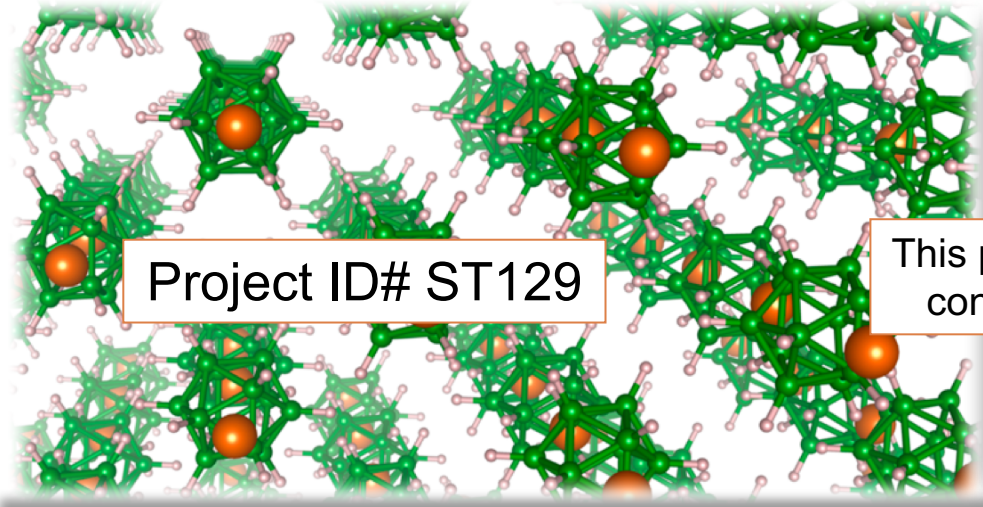
June 7, 2017

PI: Brandon C. Wood, LLNL

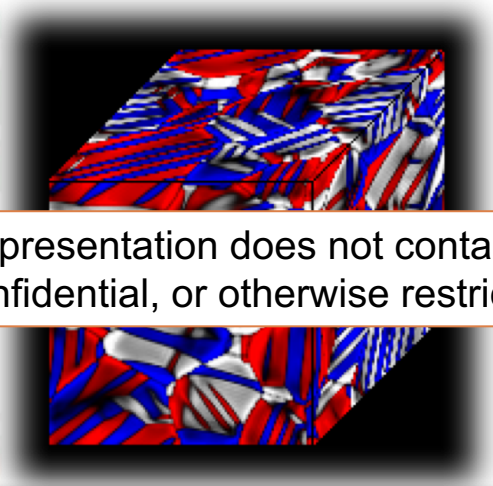
HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling **twice the energy density** for onboard H_2 storage

Team: T.W. Heo, T. Ogitsu, S. Bonev, S. Kang, J.R.I. Lee, A. Baker, P. Shea, K. Ray, A. Pribram-Jones, M. Morales, P. Campbell, T. Baumann



Project ID# ST129



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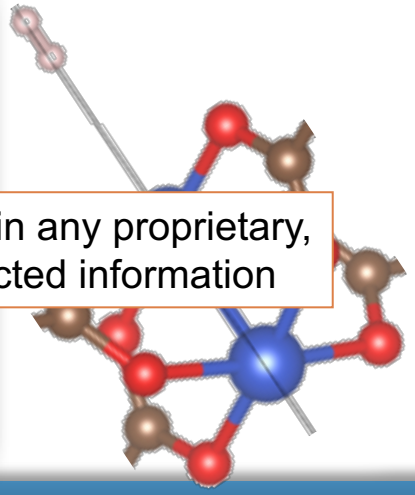

LLNL-PRES-730380

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

Lawrence Livermore National Laboratory

Overview

Timeline

Project start date: 9/17/2015

Phase I end date: 9/30/2018

Barriers addressed

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

Budget

FY15 DOE Funding: $250K

FY16 DOE Funding: $735K

FY17 DOE Funding: $955K

Total Funds Received: $1940K

Team -

Funded Partners:

Sandia National Laboratories (lead)

Lawrence Berkeley National Laboratory

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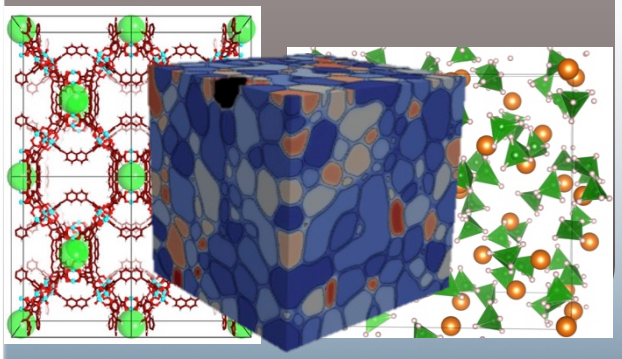
Relevance

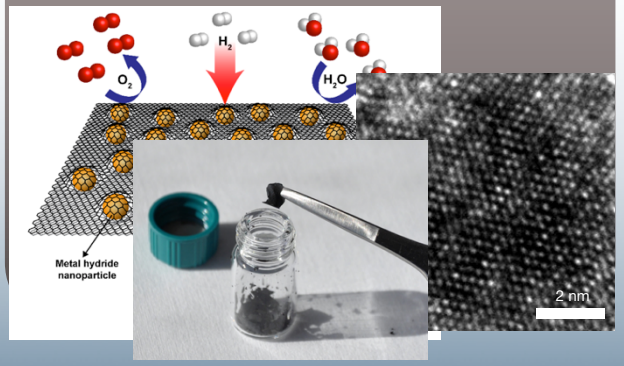
HyMARC provides community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable solid-phase hydrogen storage materials

Theory, simulation, data



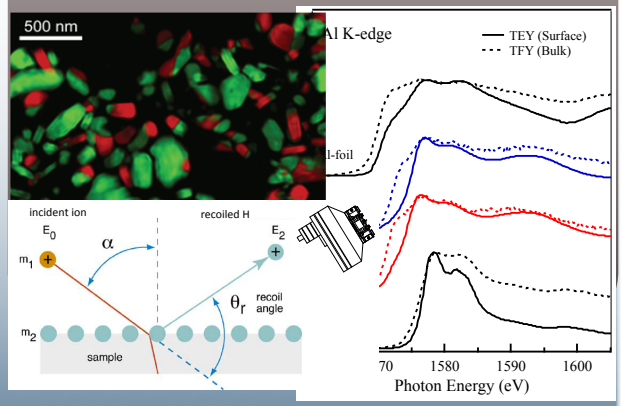
- High-accuracy physisorption
- *Ab initio* thermodynamics
- *Ab initio* molecular dynamics for bulk/surface/interface chemistry
- Multiscale non-equilibrium mass transport
- Phase-field models for solid-state phase transformation kinetics
- Semiempirical kinetic modeling
- Community software & databases

Controlled synthesis



- Functionalized carbon and porous nanoconfining media

In situ characterization



- Soft X-ray absorption and emission spectroscopy
- X-ray spectromicroscopy

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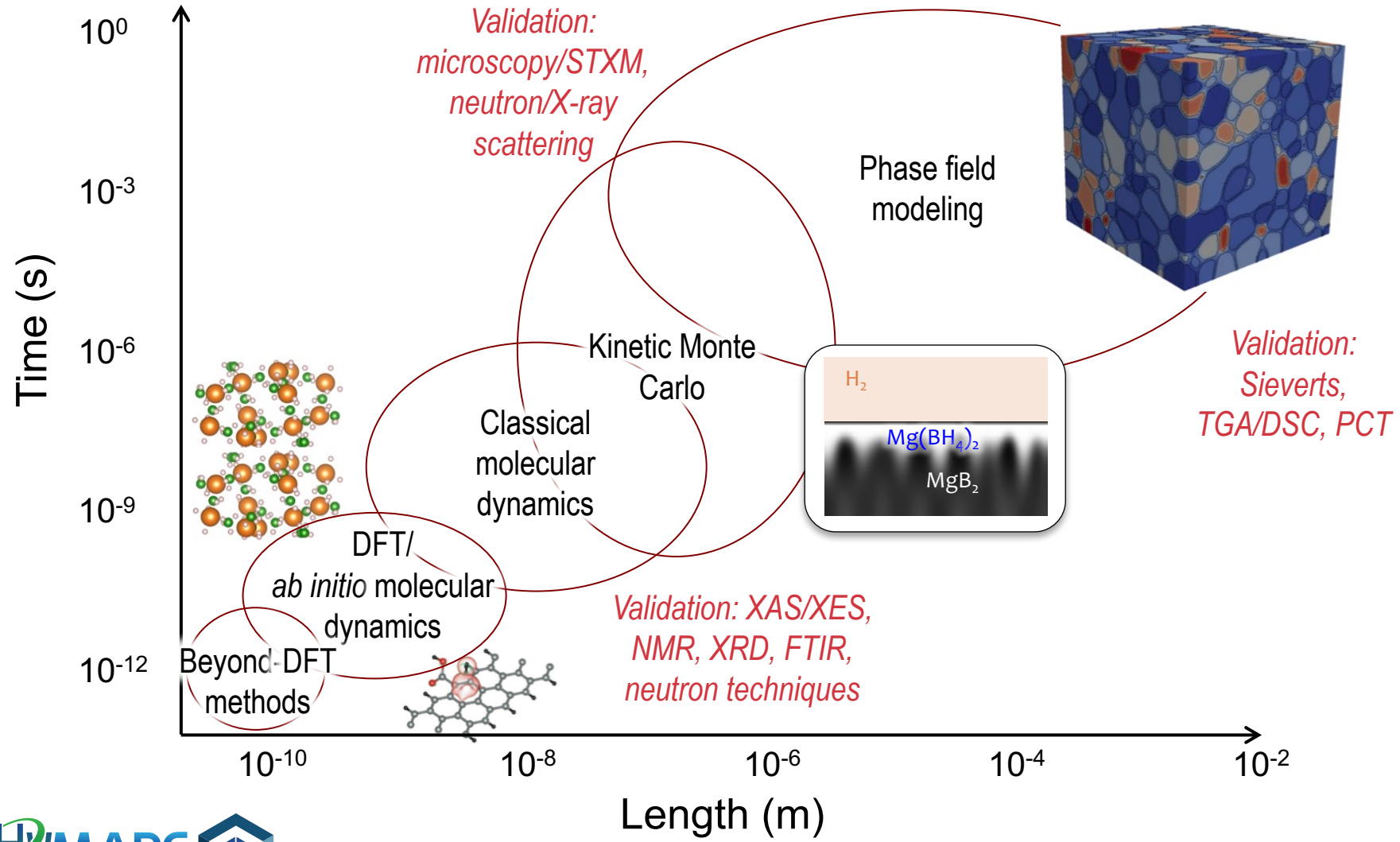
Approach: Validated multiscale modeling

Modeling approach prioritizes (1) bridging scales via multiscale integration; (2) improving descriptions of "real" materials; and (3) leveraging experiment-theory feedback

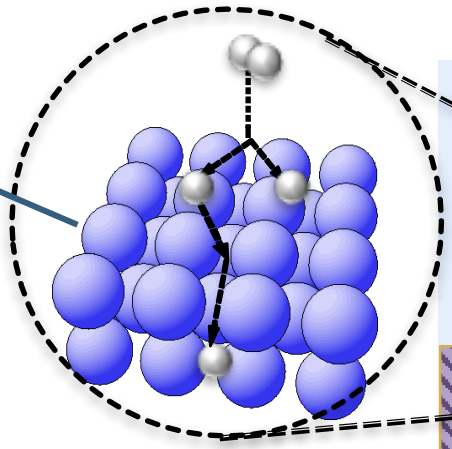


Approach: Using model materials to investigate key phenomena

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

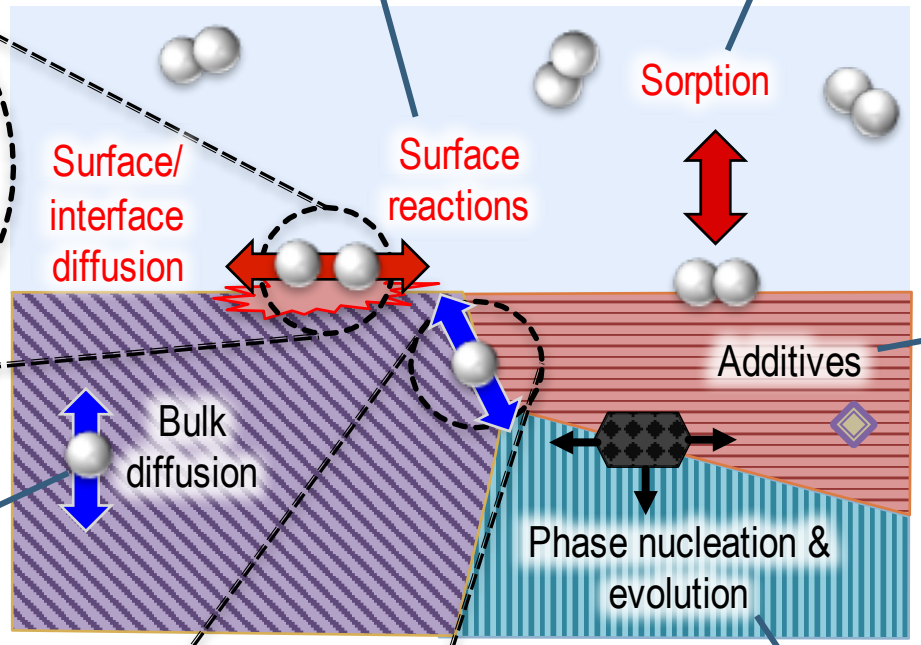
Thermodynamics:
- Mg-B-H, Li-N-H

- LEIS on model metals (Mg, W)



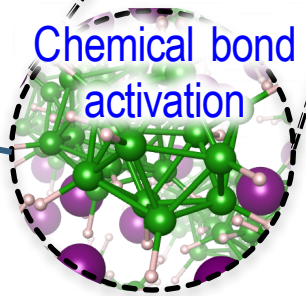
- Oxidation ($NaAlH_4$, $Mg(BH_4)_2$)
- H_2 dissociation (Mg, MgB_2)

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



- $TiF_3/TiCl_3$
- Ti in $NaAlH_4$, $MgB_2/Mg(BH_4)_2$

- Isotropic interstitial diffusion (PdH_x)
- Anisotropic vacancy diffusion (MgH_2)
- Complex hydride diffusion ($Mg(BH_4)_2$)



- Borohydride decomposition pathways in MgB_xH_y

- Interstitial topotactic interface (Pd/PdH_x)
- Simple structural transformation (Mg/MgH_2)
- Complex reactive interface (MgB_xH_y/MgB_nH_m)

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LLNL contributions to HyMARC

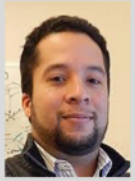
Multiscale modeling

Multiscale integration: Brandon Wood

Ab initio molecular dynamics: Tadashi Ogitsu

Mesoscale phase-field kinetic modeling: Tae Wook Heo

Ab initio free energy: Stanimir Bonev

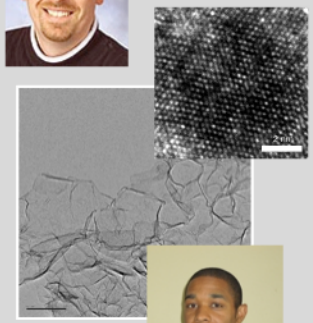


Quantum Monte Carlo: Miguel Morales

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

Porous carbon synthesis

Ted Baumann



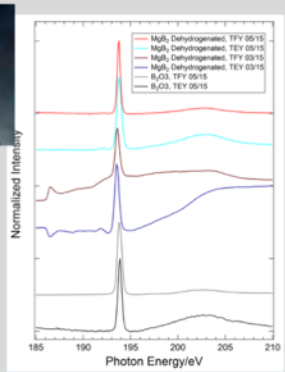
Pat Campell

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 TiF_3 and $TiCl_3$ additives*
- *Completed joint theory-experiment study of confinement stress effects and kinetic enhancements in Ni-doped nanoconfined MgH_2*

FY18Q1: Compute H_2 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)*

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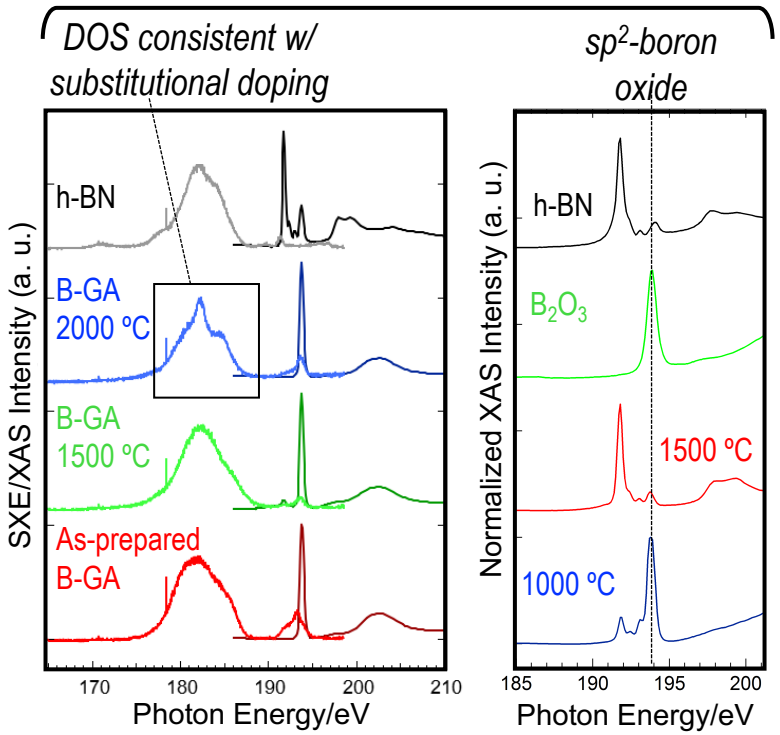
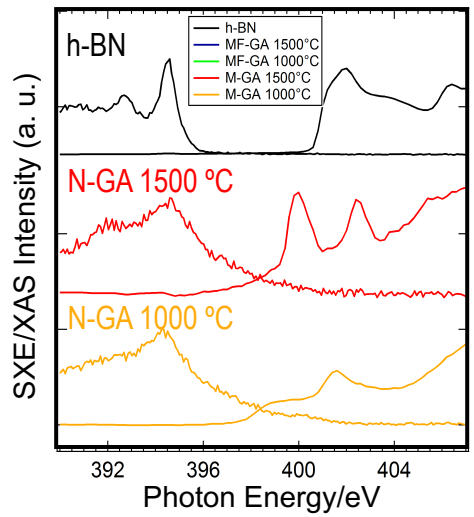
Accomplishment: B/N-doped graphene aerogels for sorption/encapsulation

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

Boron doping (B_2O_3 + annealing)



Nitrogen doping (Melamine + annealing)



XPS compositional analysis

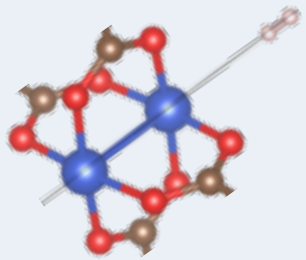
Sample	B (at.%)	N (at.%)
B-GA 1600C	***2.68***	***1.81***
B-GA 1700C	1.28	1.05
B-GA 1800C	0.61	0.57
B-GA 1900C	0.06	0.22
N-GA 1100C	--	1.96
N-GA 1300C	--	***0.99***
N-GA 1500C	--	0.09
N-GA 1600C	--	0.92

- **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; C_3N_4 for N doping) to increase doping and purity**

Accomplishment: New theory capabilities introduced in FY17

Seedling needs prioritized development of new theory methods

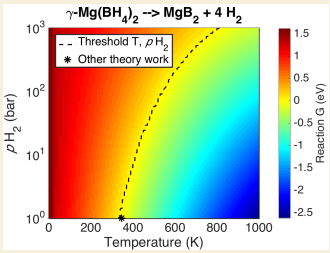
Improved sorbent isotherms



Recipes for integrating different levels of theory in sorbent isotherm models

Seedling: Chung/PSU

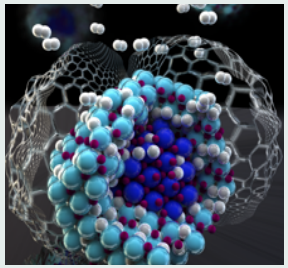
Accurate hydride thermodynamics



Finite-*T* free energy, environment- and morphology-dependent thermodynamics

Seedlings: Liu/ANL, Severa/U. Hawaii

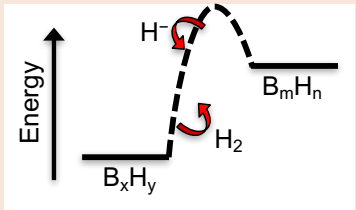
Solid mechanics & interfaces in hydrides



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_xH_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)***

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Accomplishment: Efficient, accurate low-pressure MOF sorption enthalpies

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

Classify motifs via materials informatics *(Haranczyk/LBNL)*

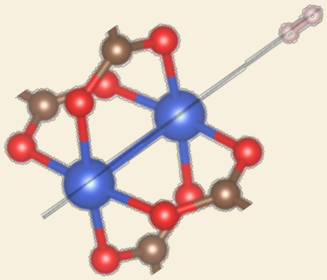
↓

Compute binding energy using suitable theory level *(Pribram-Jones/LLNL & Head-Gordon/HySCORE)*

↓

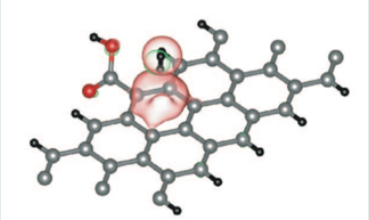
Predict & validate isotherms *(Camp & Haranczyk/LBNL, Stavila/SNL & NREL/HySCORE)*

Open metal sites (OMS)



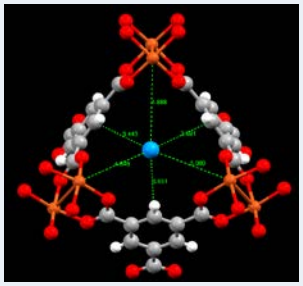
ΔH on OMS varies across DFT flavors from 0 to 15 kJ/mol to in NOTT-100

Linkers/organics



ΔH on linker sites is more consisent across van der Waals DFT flavors in NOTT-100

Extended structure vs. local chemistry



ΔH 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**

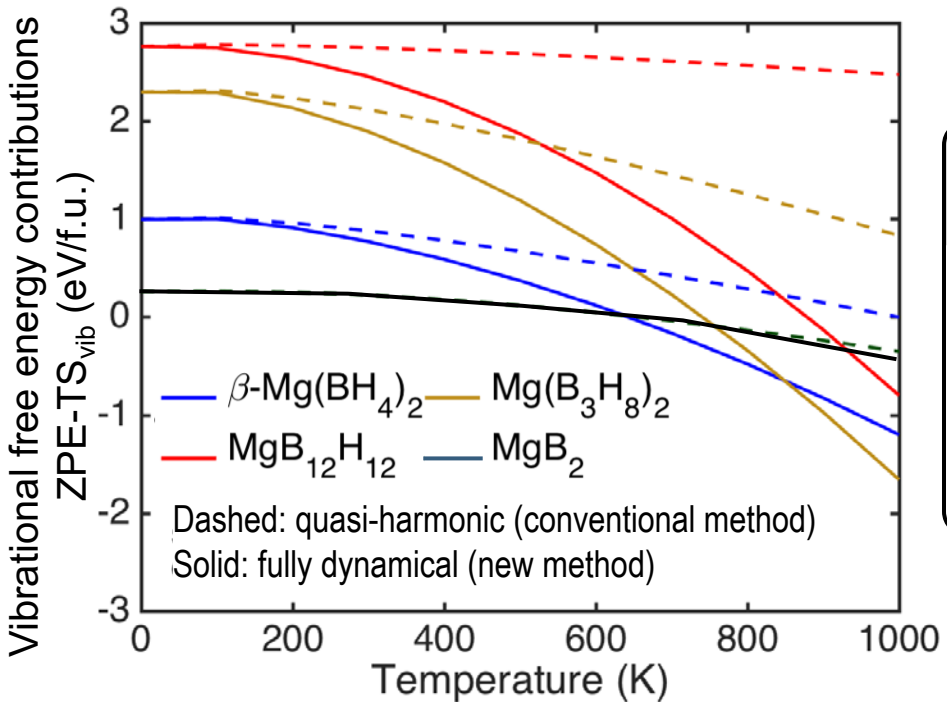
- **Interactions extend through MOF cells, so low-*P* ΔH is mispredicted by local cluster models**
- **Working with HySCORE to benchmark DFT functionals for OMS with accurate Quantum Monte Carlo (downselected three variants for NOTT-100; planning tests on MOF-74)**
- **Working with LBNL to benchmark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

*Lin et al., *JACS* **131**, 2159 (2009)

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*):

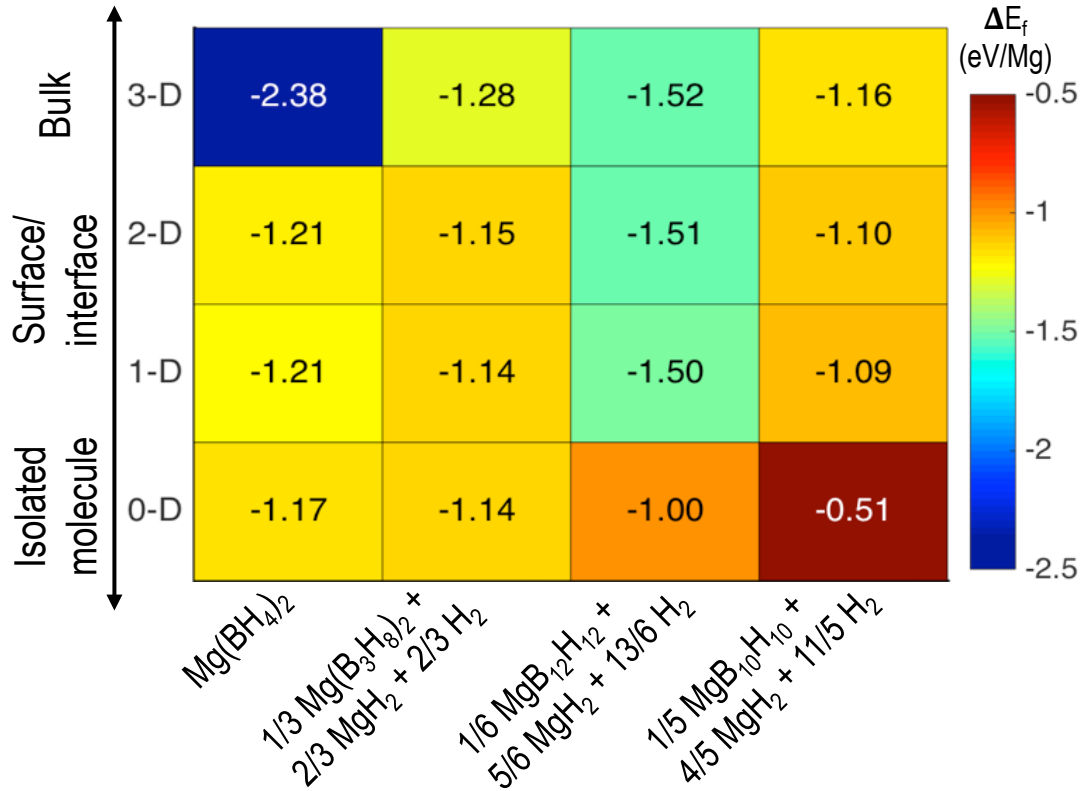
- *Thermal properties from ab initio MD*
- *Zero-K reference energies from DFT and/or Quantum Monte Carlo*
- *Temperature calibration (e.g., from PCT)*

- **Anharmonic effects from molecular rotations are critical for predicting free energies**
- **Predicted phase diagrams and phase fractions of MgB_xH_y at several (*T*,*P*) (Stavila/SNL) successfully validated via NMR (PNNL/HySCORE) for Wood/LLNL project**

Accomplishment: Morphology/environment-dependent thermodynamics

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

Morphology-dependent stability of MgB_xH_y



- **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**

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

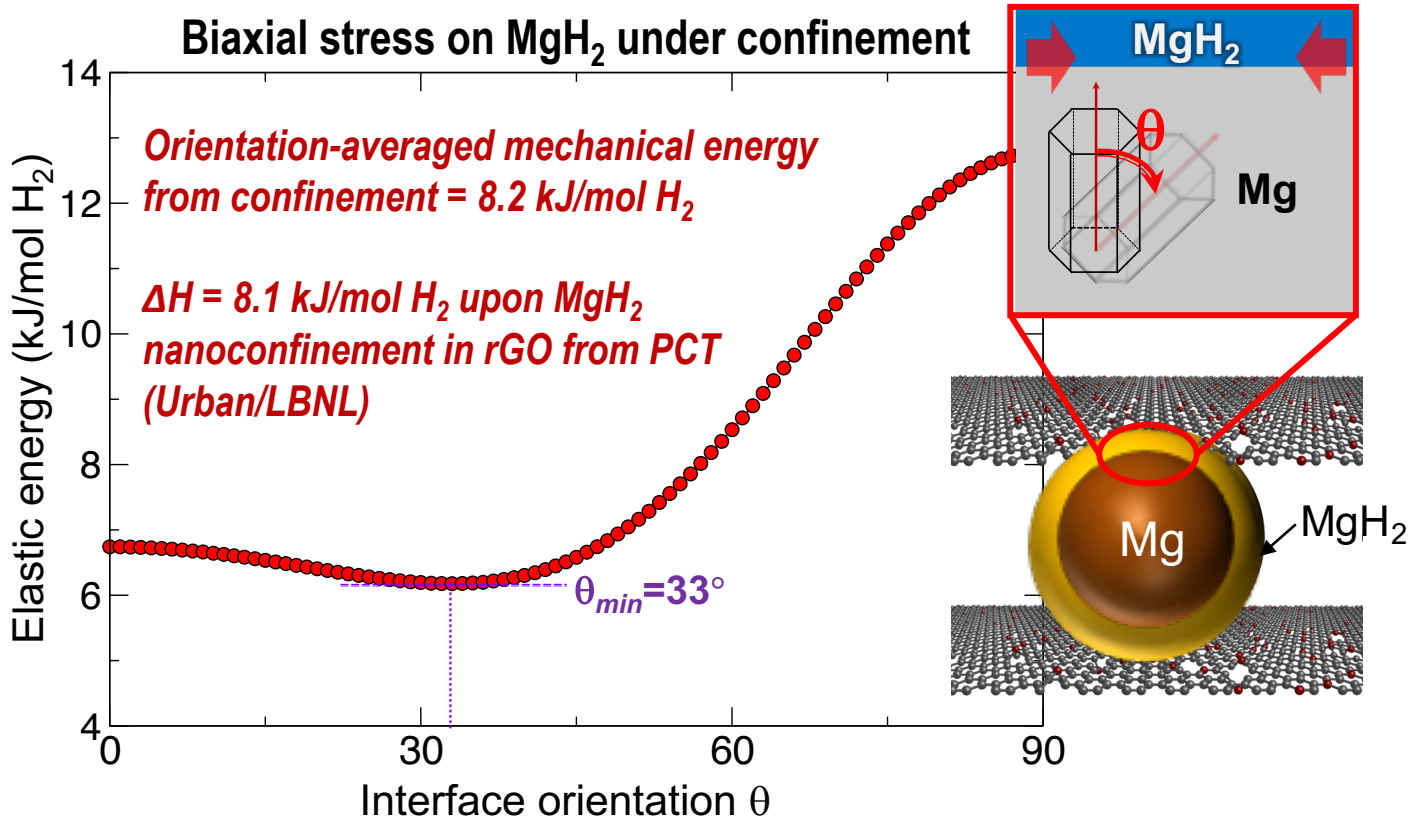
Compute **elastic & lattice constants** from DFT

↓

Compute **mechanical energy** due to internal interface or confinement from elasticity theory

↓

Determine **relative destabilization** of solid reaction phases

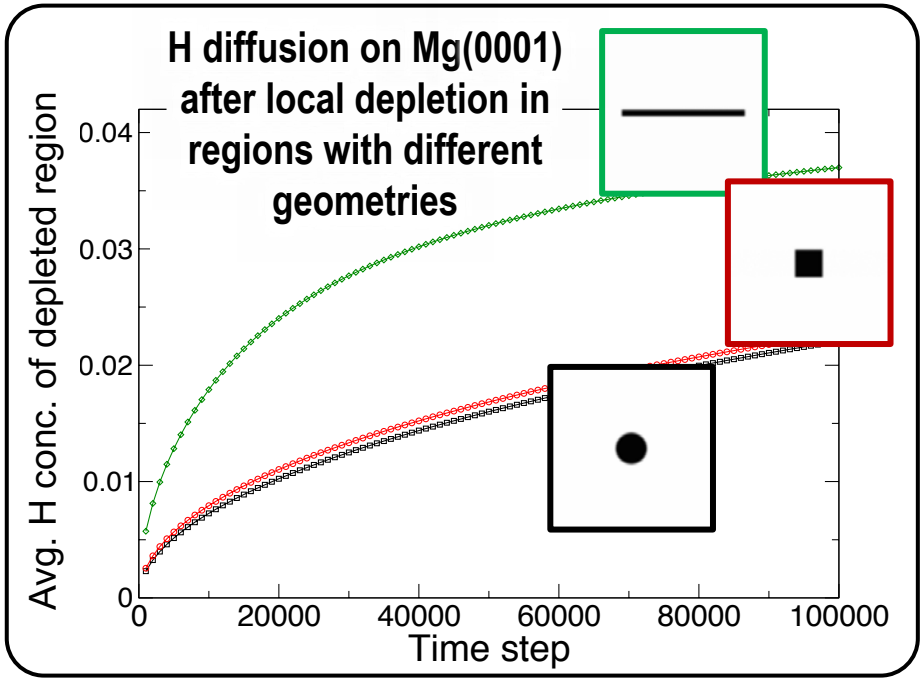


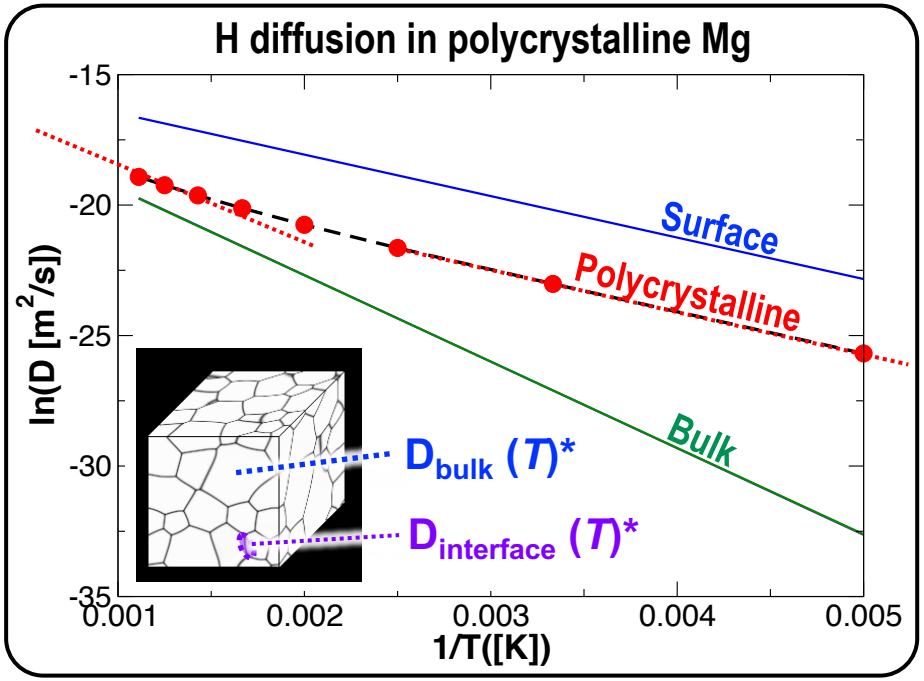
- **Elastic strain energy can explain confinement effect on ΔH for MgH_2/Mg (Urban/LBNL)**
- **Stiffness and pore geometry of confining medium can tune thermodynamics**
- **Adapting formalism to complex borohydrides to support Liu/ANL seedling**

Accomplishment: Multiscale method for mass transport

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

Compute bulk & interface diffusion **pathways & barriers** from DFT/MD → Extract **diffusivity tensors** from kinetic Monte Carlo; Generate **microstructure** from phase-field → Solve continuum equation for **non-equilibrium diffusion kinetics** → Extract **effective diffusivity** tensor





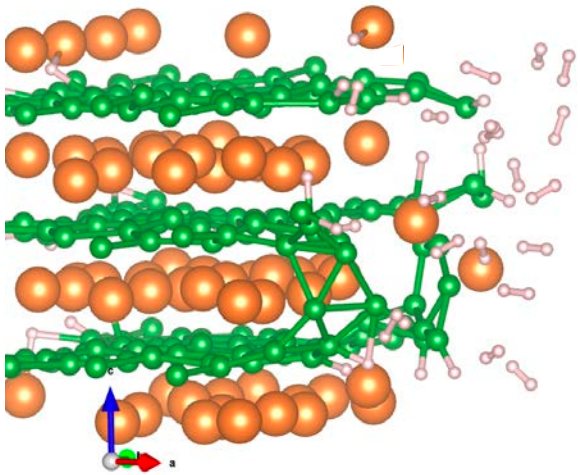
- **Degree of crystallinity obtained during cycling conditions can impact mass transport**
- **H depletion geometry influences H surface diffusion kinetics in LEIS (Kolasinski/SNL)**
- **Extending models to chemically reactive "structural diffusion" in complex hydrides**

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

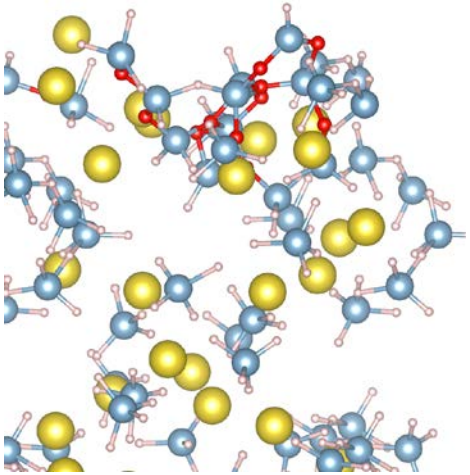
w/Wood/LLNL individual project



Al-H bond cleavage and O-H bond formation on oxidized $NaAlH_4$(001)

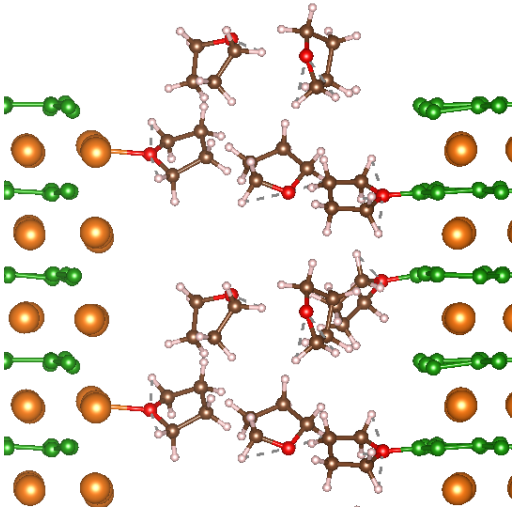
w/AP-XPS

(El Gabaly, White/SNL)



Oxygen coordination complexes formed by THF at the interface with MgB_2 edges

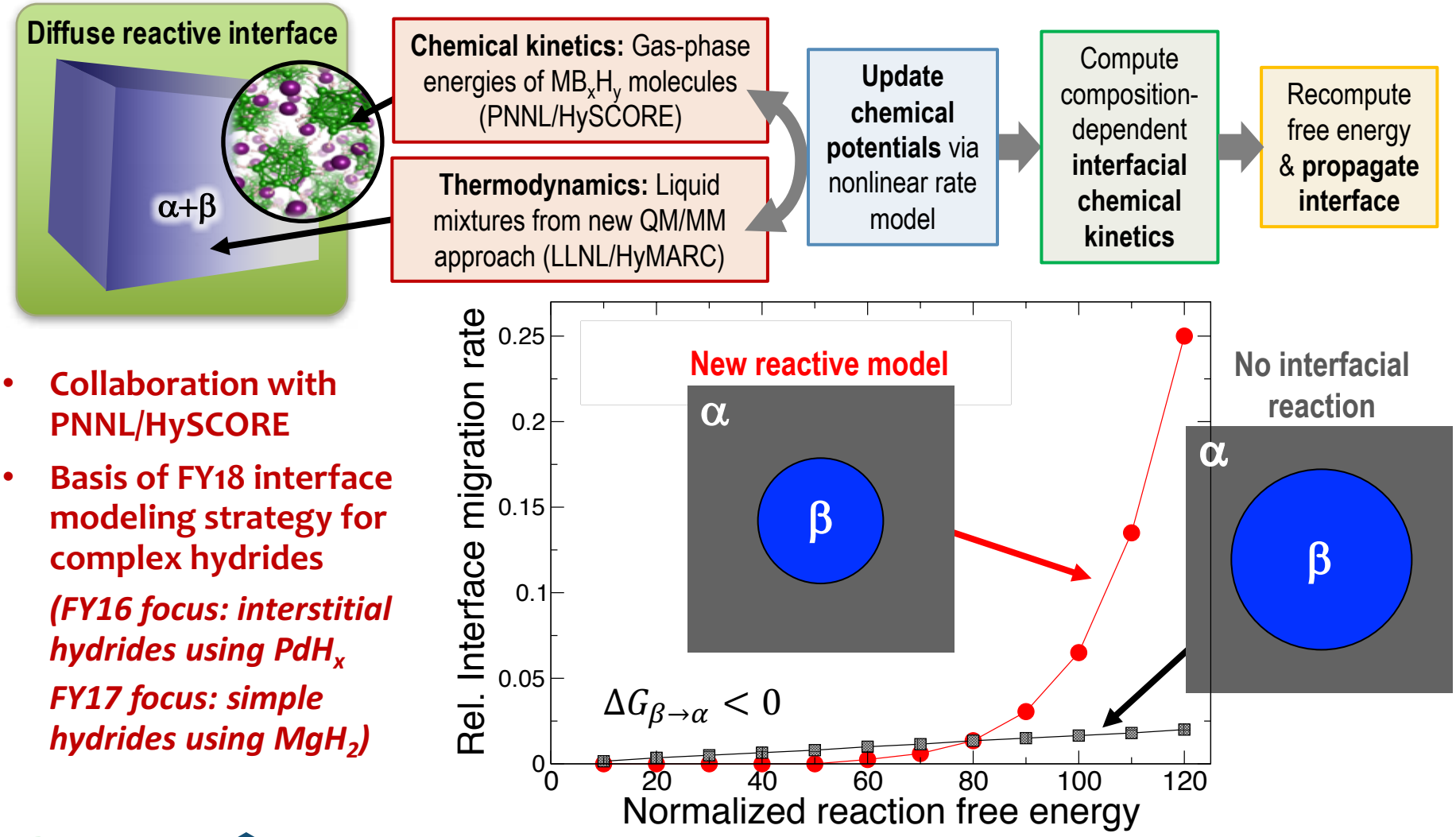
w/Severa/U. Hawaii seedling



- **Boron chemistry activated by charge imbalance (e.g., upon Mg extraction from MgB_2)**
- **Observed MgB_xH_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



- **Collaboration with PNNL/HySCORE**
- **Basis of FY18 interface modeling strategy for complex hydrides**

  (FY16 focus: interstitial hydrides using PdH_x

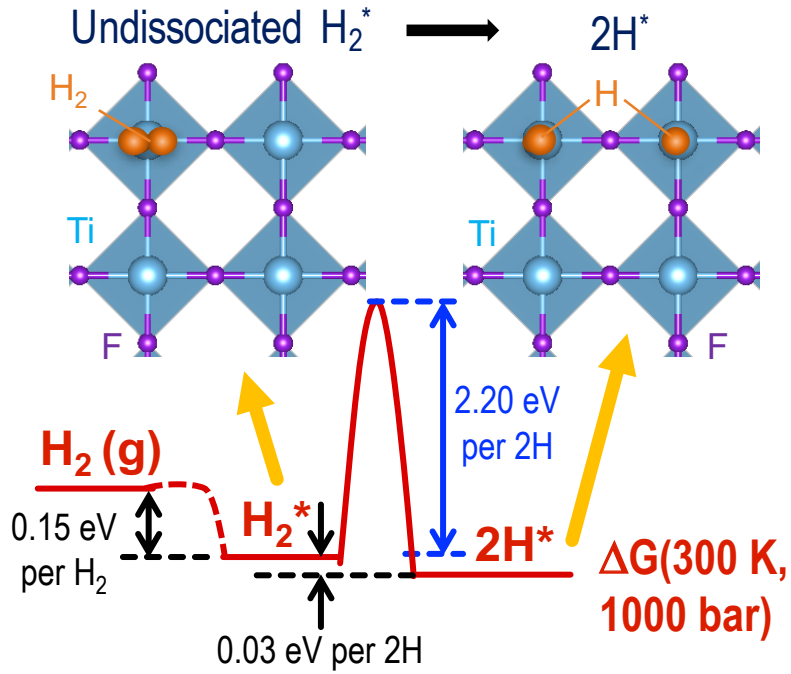
  FY17 focus: simple hydrides using MgH_2)

Accomplishment: Foundational understanding of H-catalyst interactions

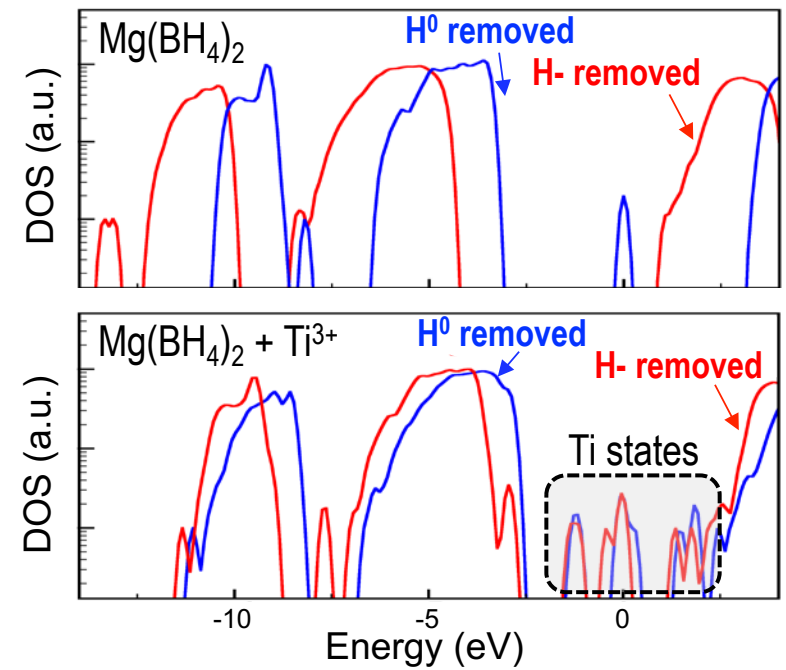
Examined thermodynamic, kinetic, and electronic effects of TiF_3 catalysts and Ti in borohydrides via DFT and ab initio molecular dynamics

Energy landscape for H_2 interaction w/TiF_3

w/ Klebanoff/SNL



Electronic effects of Ti in $Mg(BH_4)_2$



- **Isolated TiF_3 is unreactive to H_2 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 $Mg(BH_4)_2$ creates new gap levels and acts as charge sink to facilitate changes in oxidation state during B_xH_y chemistry (comparing w/spectroscopy)**

Accomplishment: Understanding mechanisms through kinetic rate analysis

Kinetic analysis elucidated hydrogenation mechanisms in MgB_2 and catalyzed+confined MgH_2

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

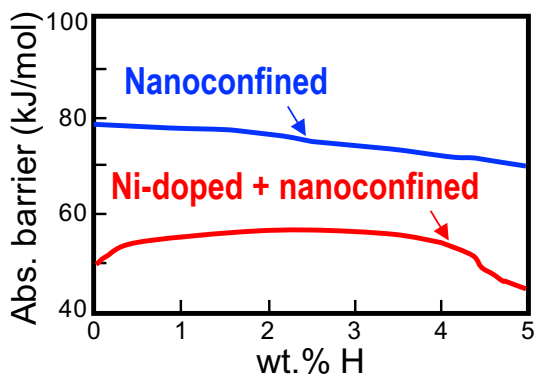
Create kinetic model based on proposed mechanisms

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

Downselect or **validate** possible mechanisms

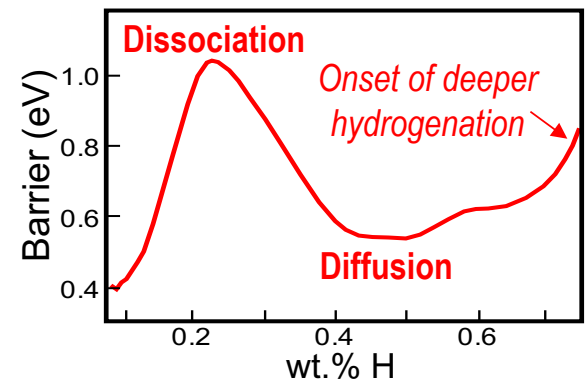
Extracted barriers for H_2 uptake in nanoconfined Mg (in rGO)

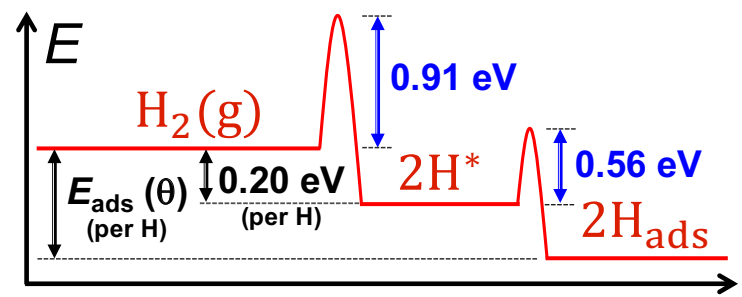
w/ Urban/LBNL



Extracted barriers and energy landscape for H_2 uptake in MgB_2

w/ Stavila & Klebanoff/SNL and Wood/LLNL project





- **Rate analysis suggests that dissocation 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 MgB_2**

T. W. Heo, P. Shea, S. Kang, K. Ray, A. Baker, J.R.I. Lee, B. Wood

Collaborations

Engagement with HyMARC seedlings

- Predicting thermodynamics and kinetics of graphene-wrapped hydrides (Liu/ANL ST136)
- Modeling interfaces and complexation of ethers around MgB_2 (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 MgB_2 rehydrogenation; HySCORE focus on borohydride chemistry during $Mg(BH_4)_2$ dehydrogenation*
- DFT computations of H_2 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

HyMARC Hydrogen Materials Advanced Research Consortium

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 ($Mg(BH_4)_2$ & $NaBH_4$) (w/LBNL & ANL seedling)*

Task 2/Task 3 (Transport and surface phenomena):

- *DFT study of hydrogen-oxide interactions and surface diffusion on oxidized $NaAlH_4$ (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/MgH_2 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 $TiF_3/TiCl_3$ on MgB_2 using DFT (w/SNL)*

Task 6 (Databases):

- *Publish MgB_xH_y spectroscopy standards study (w/HySCORE, SNL, and LBNL)*
- *Complete library of pairwise intermolecular potentials for B_xH_y (w/SNL)*

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

HyMARC Hydrogen Materials Advanced Research Consortium

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

HyMARC
Hydrogen Materials Advanced Research Consortium

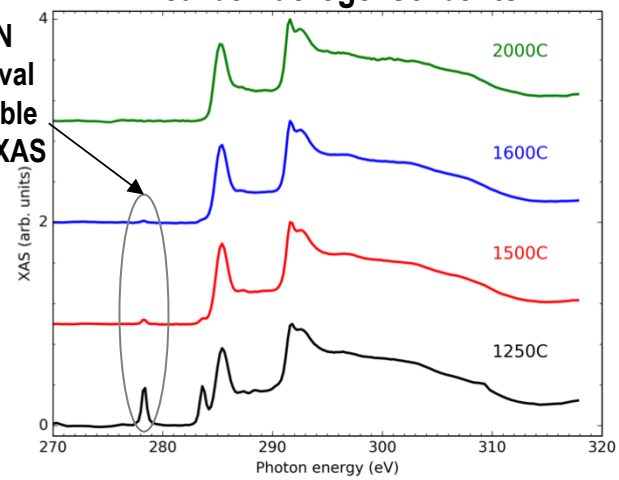
Technical backup slides

Backup: Crosscutting collaborative LLNL synchrotron efforts

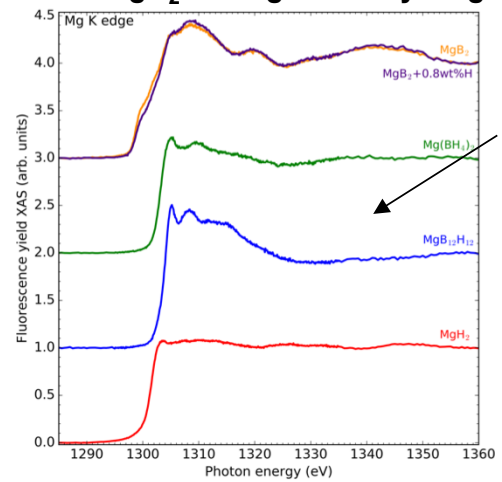
ALS Approved Program involves collaboration between all three core labs on synchtron soft X-ray spectroscopy (LLNL: A. Baker, J. Lee; SNL: L. Klebanoff, V. Stavila; LBNL: Y.-S. Liu)

Local bonding character of dopants in carbon aerogel sorbents

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



Evolution of MgB_2 during initial hydrogenation

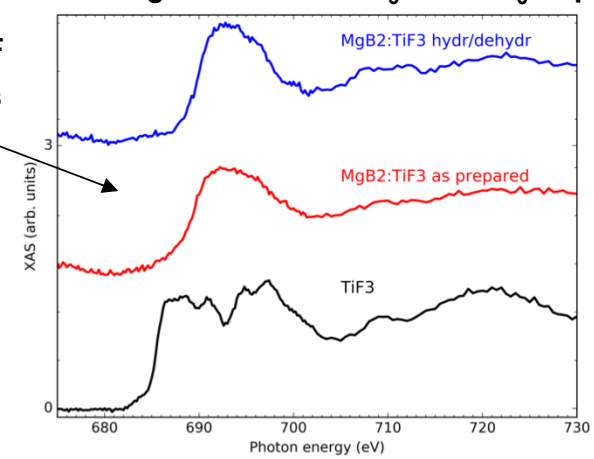


Mg K-edge XAS elucidate mechanisms: no evidence for MgH_2 formation during initial hydrogenation

- **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**

Understanding the role of $TiCl_3$ and TiF_3 dopants

Dramatic changes in F K-edge XAS upon TiF_3 doping of MgB_2



A. Baker, J.R.I. Lee

Backup: Multiscale solid interfaces in simple hydrides

Predicted the preferred orientation and strain energy for solid interfaces in Mg/MgH_2, which affects the structure and reactivity of the parent phases

Predicted Mg/MgH_2 phase boundary orientation and energy

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

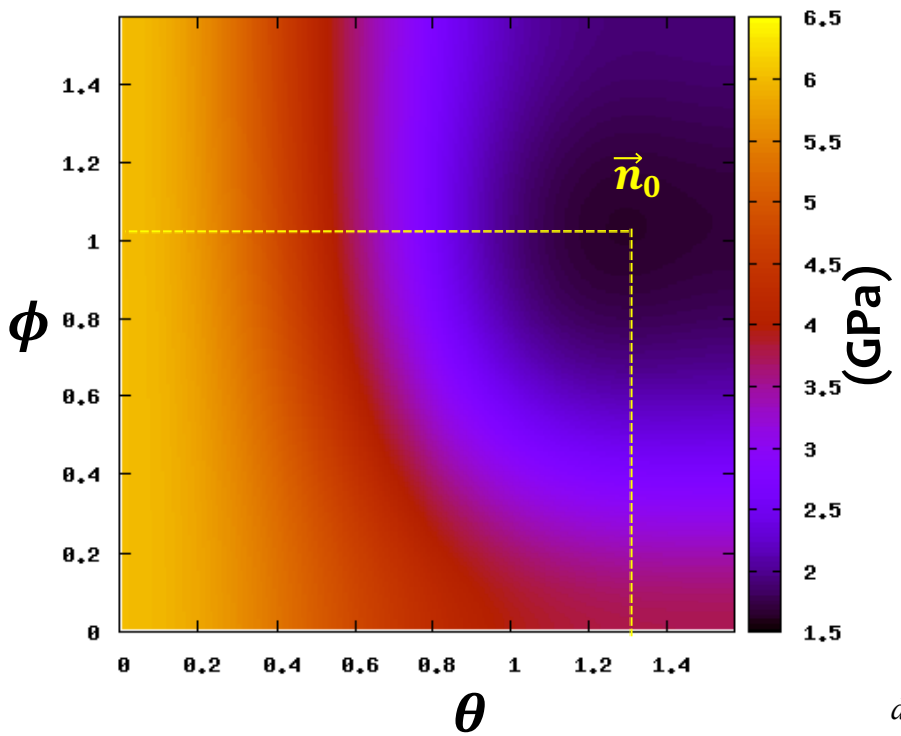
Elastic constants & lattice constants (DFT)

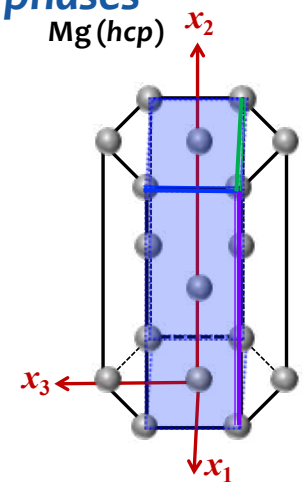
↓

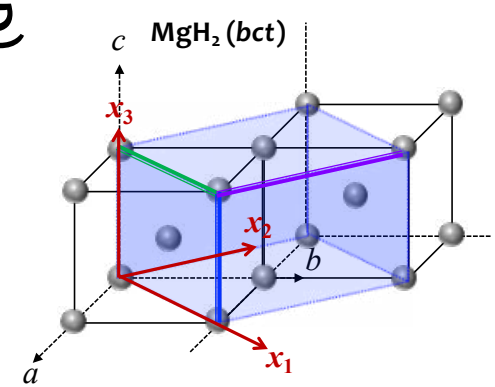
Interface orientation (Microelasticity theory)

↓

Explicit interface model (DFT and/or MD)



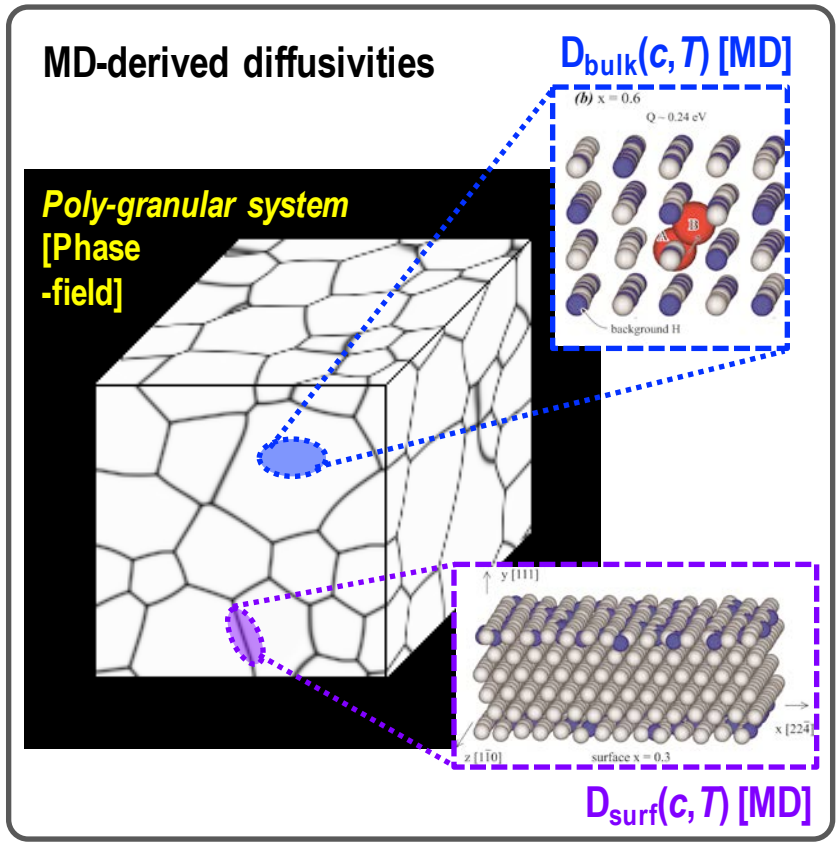


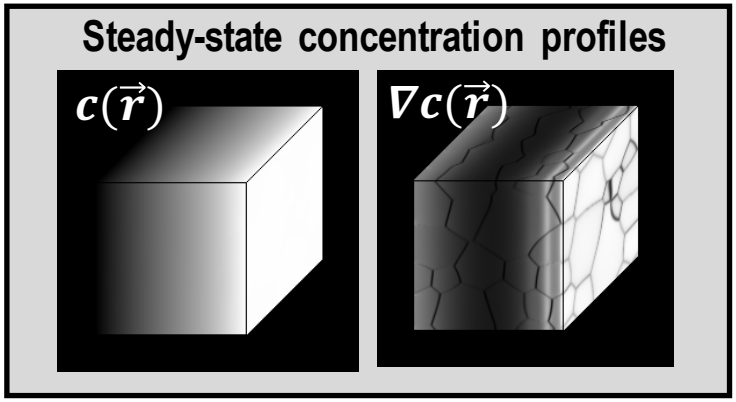


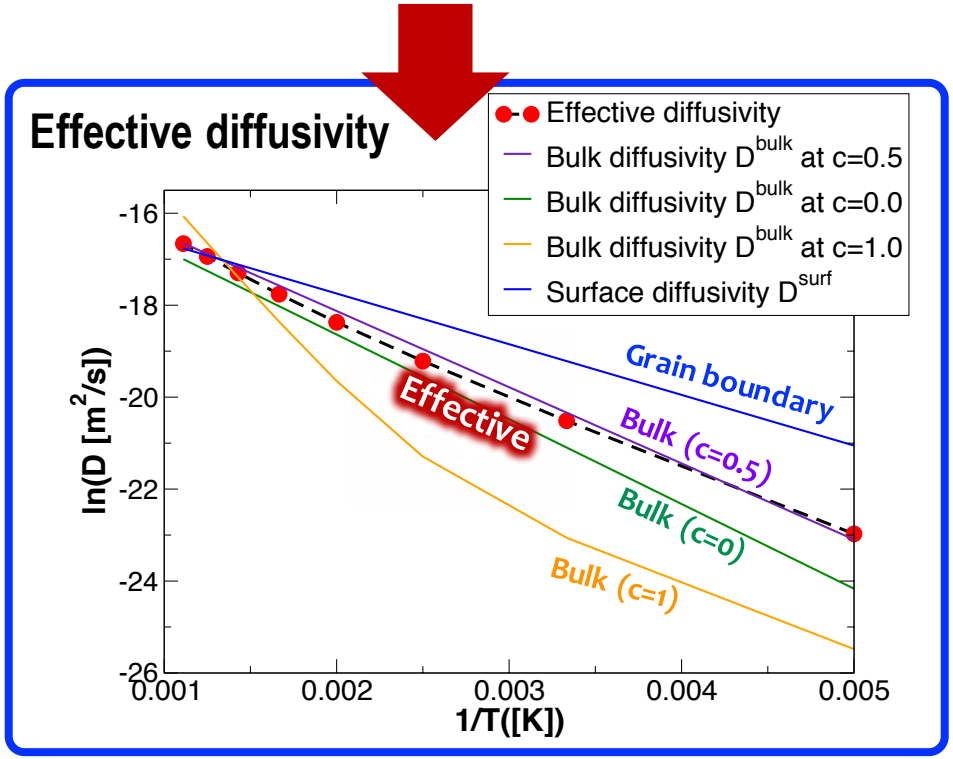
- **High interfacial strain due to volume expansion upon hydrogenation means interface is likely partially disordered (semicoherent)**
- **Currently testing in phase-field model of MgH_2 dehydrogenation with LBNL validation**

Backup: Computed effective diffusivity in polygranular Pd-H

Computed effective diffusivity in Pd-H using full c- and T-dependent diffusivities from classical MD (Zhou/SNL)





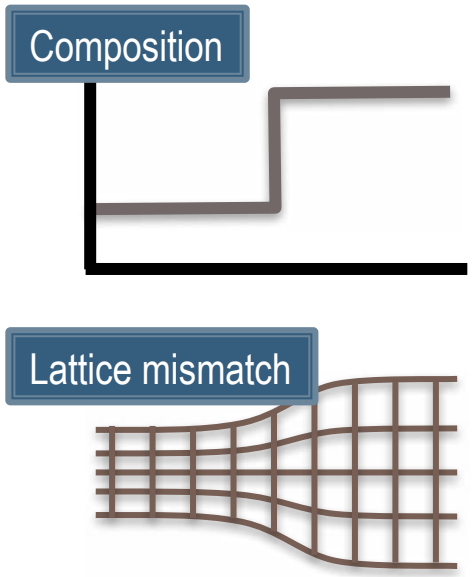


Backup: New approaches for modeling solid interfaces in metal hydrides

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

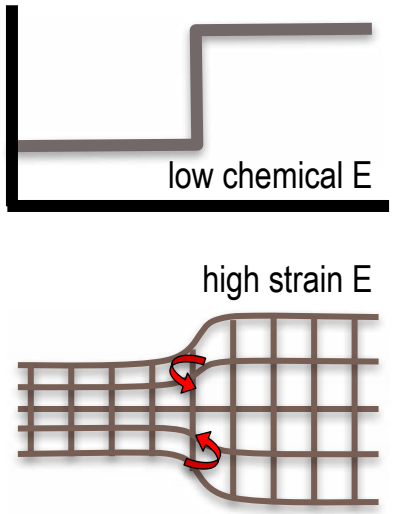
Interstitial
(topotactic coherent)



Model for study:
- Pd-H system

FY17

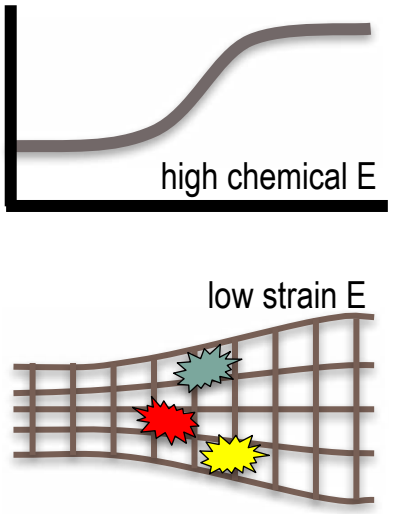
Structure change
(semi-coherent)



Model for study:
- Mg-H system

FY17-FY18

Diffuse interface
(incoherent) +
chemically reactive



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