

HyMARC Core Activity: Computational Modeling



Enabling twice the energy density for onboard H₂ storage

Brandon Wood
Lawrence Livermore National Laboratory



This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

Phase II start date: 10/1/2018

Phase II end date: 9/30/2022*

Barriers addressed

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

Budget

Total FY19 funds: \$4.3M

Total FY20 (planned): \$6.25M

Partners

Sandia (lead)

NIST

NREL (lead)

SLAC

PNNL

ORNL

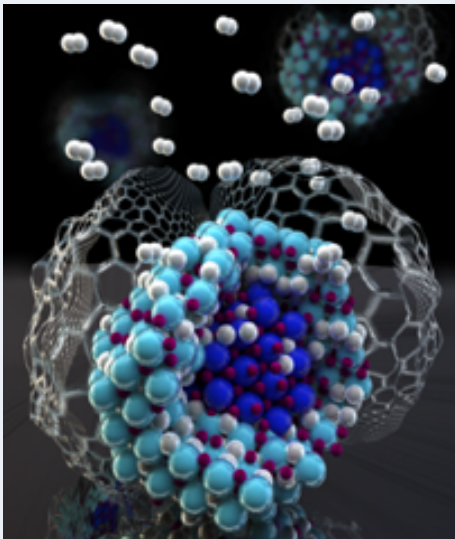
LBNL

LLNL

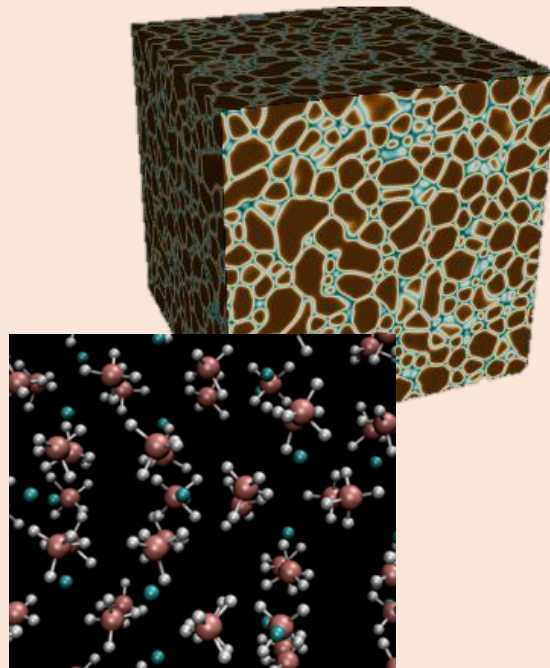
**Project continuation determined annually by DOE*

Relevance: Comprehensive modeling & simulation strategy enables close integration with HyMARC activities

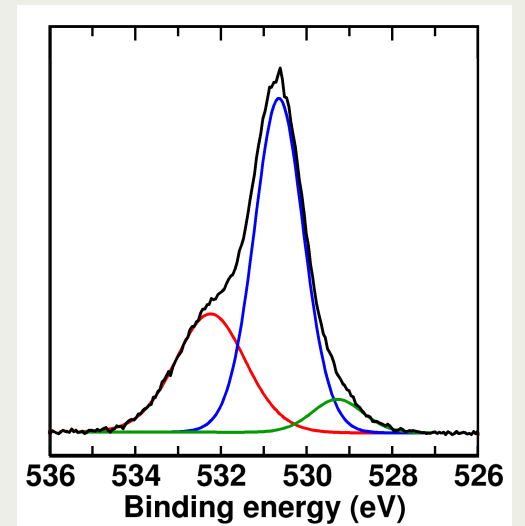
Real materials under real conditions



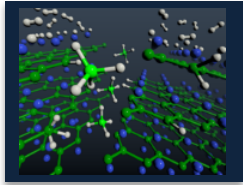
Multiscale modeling



Experiment-theory integration

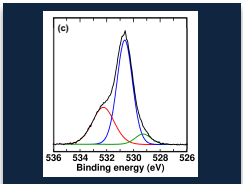


Relevance: How is theory helping with progress towards targets?



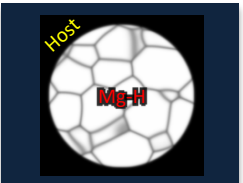
Assess

- Understand physical interaction of hydrogen with existing materials to focus improvement strategies on highest-sensitivity factors



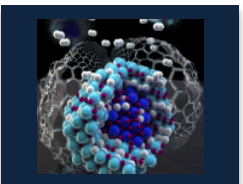
Interpret

- Interpret characterization and testing data in terms of materials chemistry & microstructure to connect composition, processing, and performance



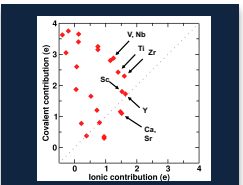
Model

- Create new models and tools to explore the limits of the most promising improvement strategies (e.g., nanoconfinement)



Explain

- Provide foundational insight into origins of experimental successes that are “moving the bar”

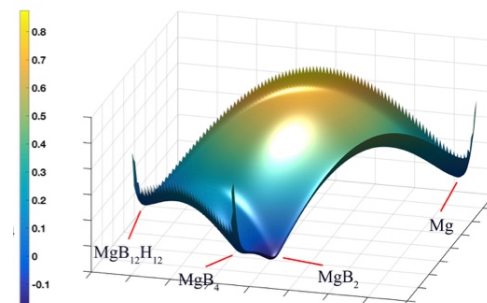


Design

- Guide strategies for new materials design and connect system-level performance models to materials-level parameters

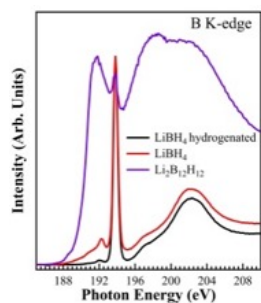
Approach: Capabilities address key HyMARC priorities

- Accurate physisorption energies (vdW DFT)
- Thermodynamic prediction & calibration (DFT & AIMD)
- Chemical mechanisms at interfaces (DFT & AIMD)
- Spectroscopy modeling (DFT)
- Confinement and nanoscale effects (DFT, effective medium)
- Non-equilibrium mass transport (MD, KMC, phase field)
- Solid-state phase transformation kinetics (phase field)
- Semiempirical kinetic analysis (continuum)
- Catalyst pathways, stability, and microkinetic modeling (DFT, hybrid DFT/continuum)



Approach: Simulations span multiple scales

Atomic/molecular
(0 – 1 nm)



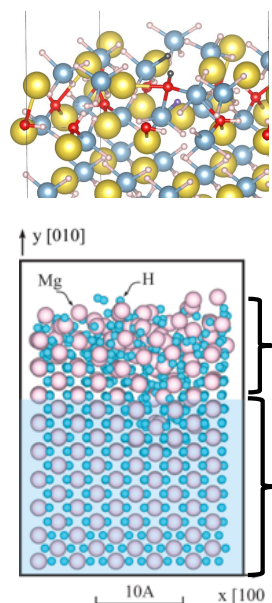
Computational Spectroscopy

Hydrogen chemisorption & physisorption

Density functional theory & ab initio molecular dynamics

10⁻¹⁰

Molecular/micro
(0.5 – 2 nm)

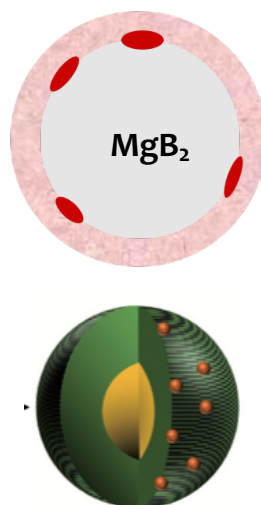


Surface/interface chemistry

Classical molecular dynamics & microkinetic modeling

10⁻⁸

Mesoscale
(2 - 100 nm)

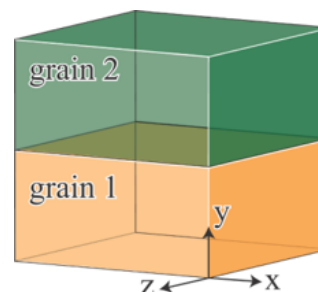


Nucleation kinetics
Phase microstructures

Phase-field modeling & microelasticity

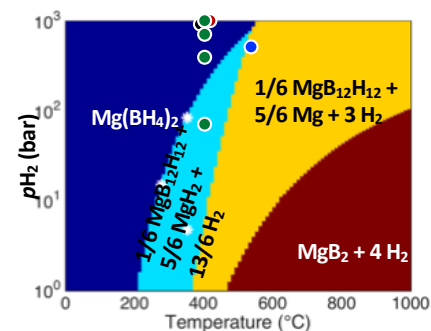
10⁻⁶

Grains
(≤ 10 μm)



Grain boundaries
Particle size effects
Stress/strain

Macroscale/Bulk



Thermodynamics
Mixing

Ab initio thermodynamics

10⁻⁴

10⁻²

Length (m)

Accomplishments and progress towards modeling milestones

FY19Q3: Develop computational approach for screening additives to activate B-B bonds in MgB₂ (100%)

- *Screening approach was finalized and prepared for publication*

FY19Q4: Demonstrate >6% reversible capacity for Li-N-H based on predicted composition (100%)

- *Theory contribution predicted size-dependent thermodynamics including surface entropy*

FY20Q1: Data Hub determination of HyMARC data needs (100%)

- *Coded predicted reaction diagrams for backend implementation*

FY20Q2: Assemble computational database of metal hydride thermodynamic properties (100%)

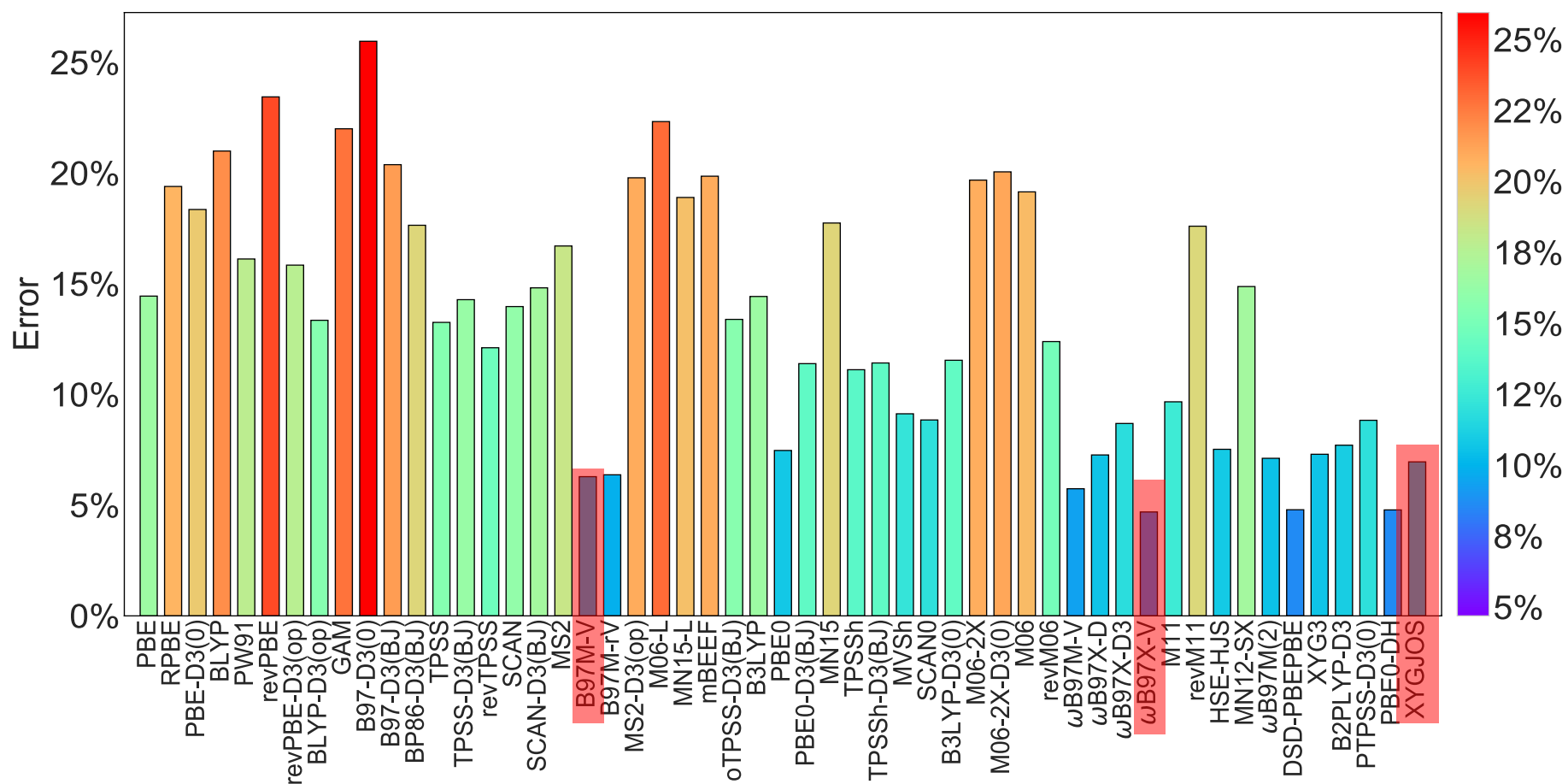
- *Existing hydride database was catalogued and machine learning classifiers were applied; new complex hydride free energy calculations were completed*

FY20Q4: Demonstrate confinement stress as an engineering strategy (50%)

- *Implemented new extensions of confinement stress prediction and initiated validation strategy through strategic partnership with KAIST (Korea)*

Sorbents: Performance of density functionals for H₂ physisorption

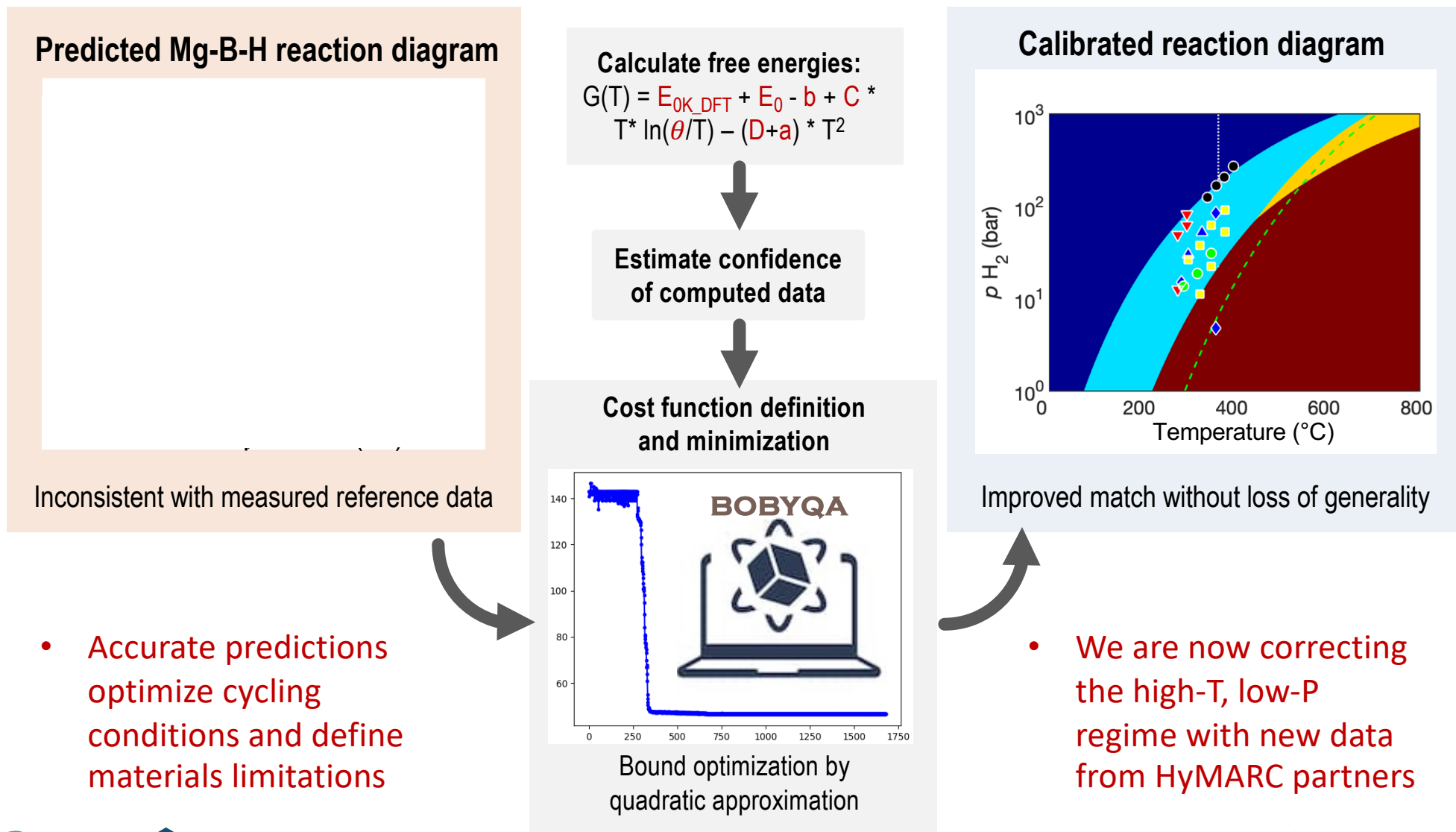
Performed comprehensive assessment of density functionals for H₂ physisorption by comparing with “gold standard” coupled-cluster calculations on a large data set



- ω B97X-V and PBE0-DH are the best performers but with high cost
- B97M-V provides the best compromise between accuracy and cost

Metal hydrides: Data science approach improves thermodynamic predictions by calibrating against reference values

Computed Mg-B-H free energies were corrected against experimental thermodynamics data using a new constrained optimization approach that retains underlying physics



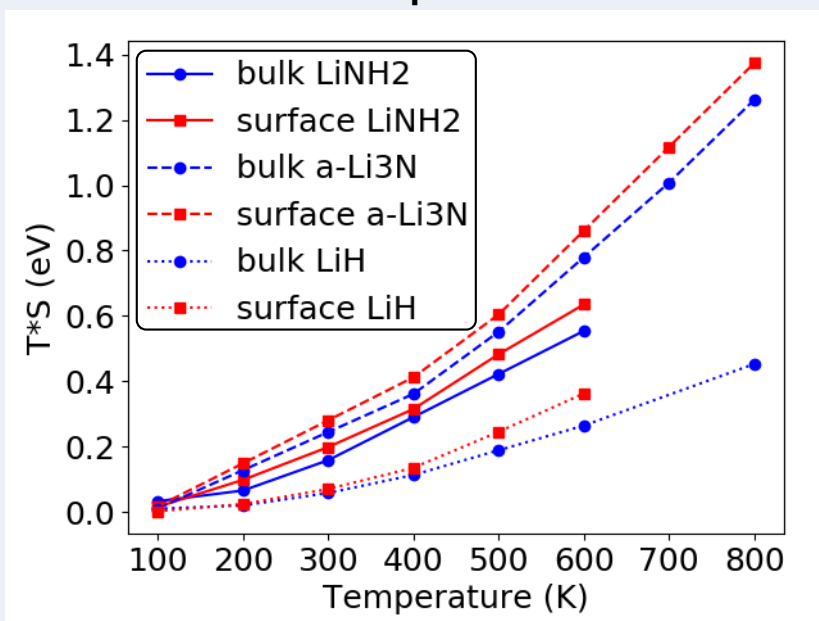
- Accurate predictions optimize cycling conditions and define materials limitations

- We are now correcting the high-T, low-P regime with new data from HyMARC partners

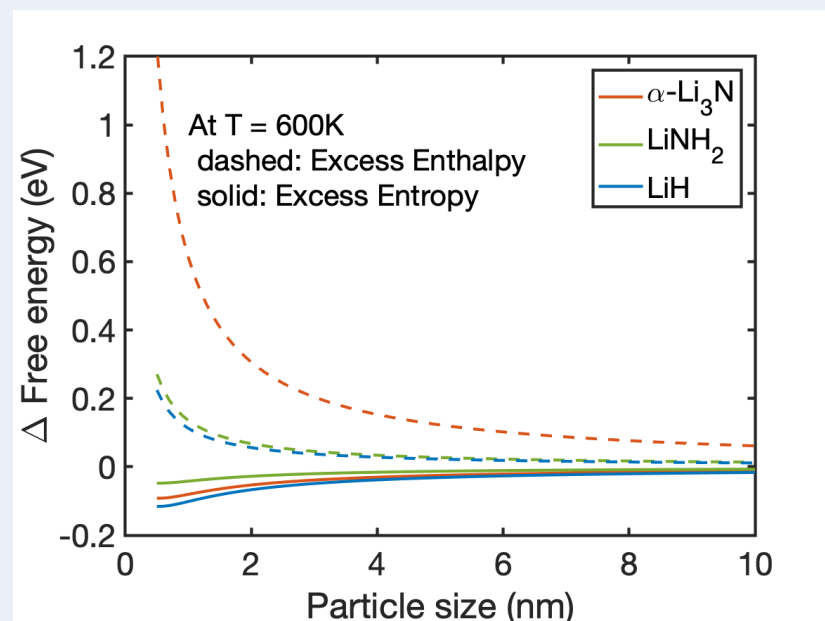
Metal hydrides: Thermodynamics of nanoscale metal hydrides

We successfully demonstrated our method for determining tunability limits of nanoscaling due to enthalpy-entropy compensation

Increased surface entropy for nanoparticles



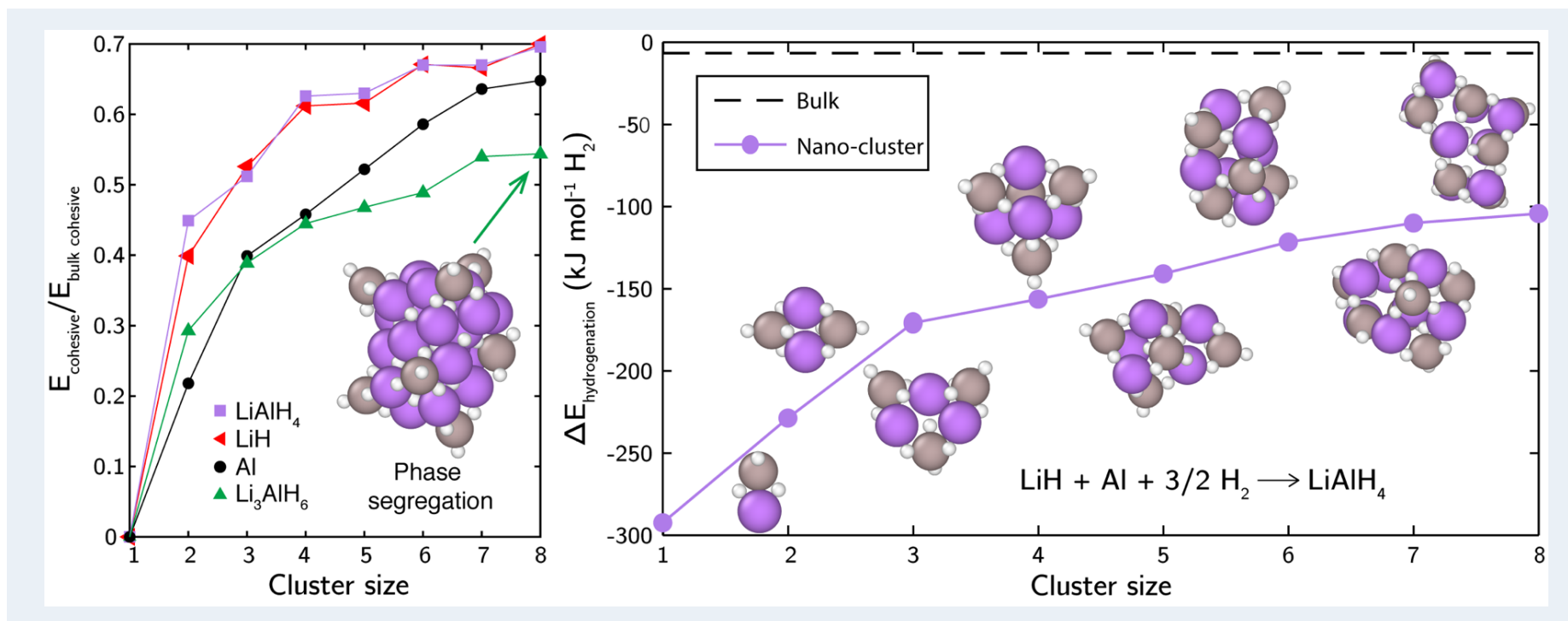
Enthalpy and entropy competition



- Enthalpy-entropy tradeoffs can be predicted to determine which hydride reaction pathways can be favorably altered by nanosizing
- Entropy for nanoparticle surfaces is up to twice that of bulk

Metal hydrides: Enabling reversibility via nanoconfinement

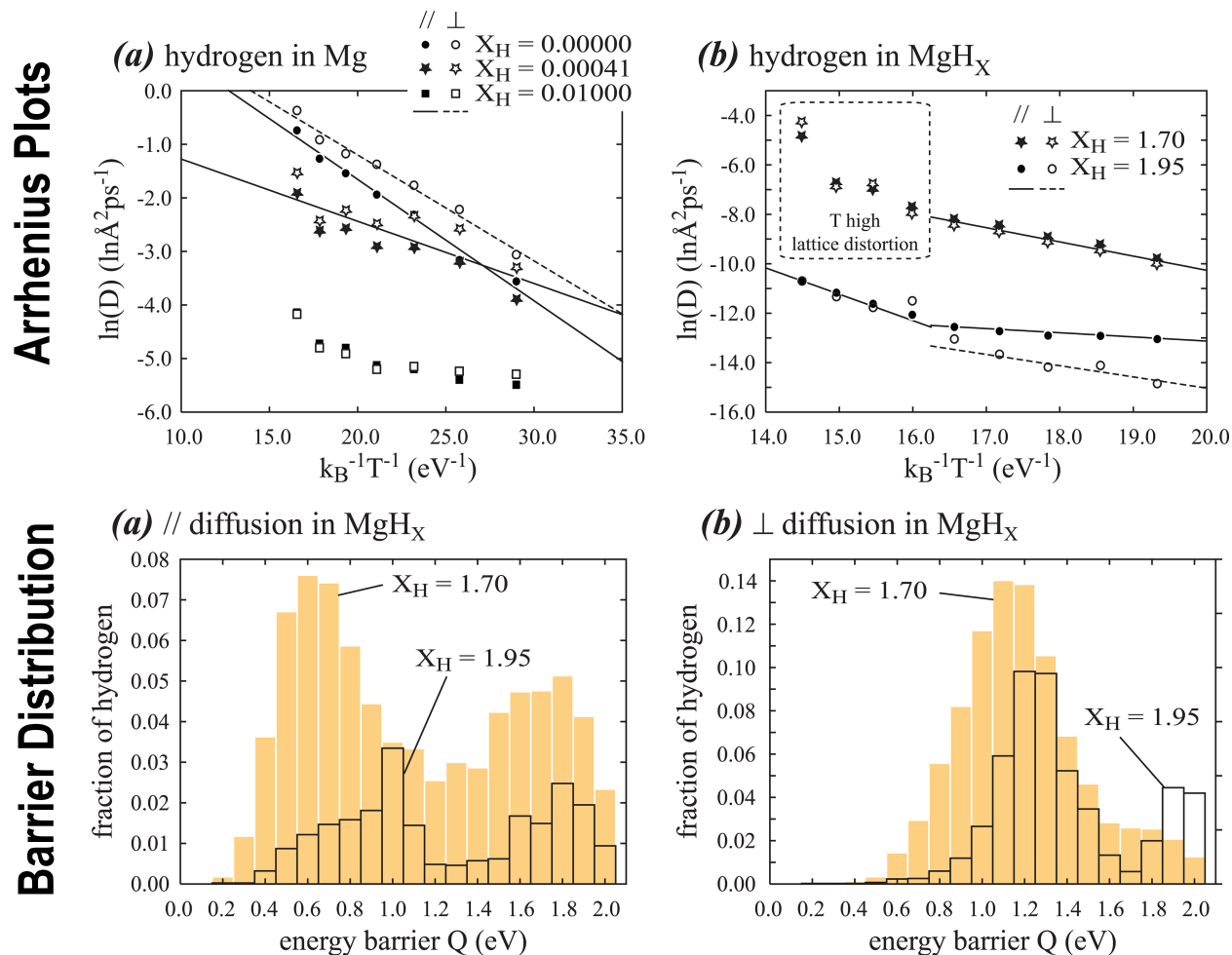
Toolkit for predicting size-dependent reactions was used to assess changes in reaction landscape for reversibility of nanoconfined LiAlH_4 in porous carbon



- Nanosizing destabilizes Li_3AlH_6 intermediate, consistent with ^{27}Al NMR
- Nanoconfinement and interaction with N-doped carbon shifts thermodynamics to enable reversibility of LiAlH_4 for the first time

Metal hydrides: Dynamics simulations of hydrogen diffusion

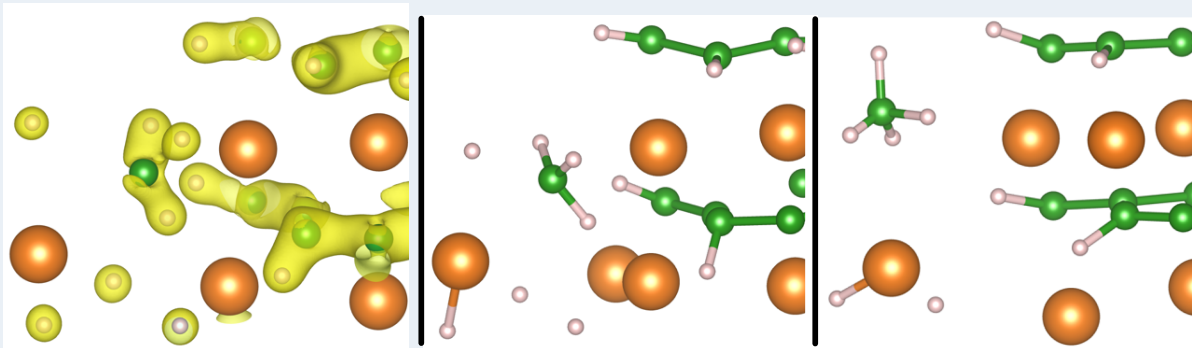
Molecular dynamics calculations help to assess mass transport limitations in MgH_2



- Diffusion rates change with concentration and structure
- Analytical fits link atomic-scale diffusion to continuum models that can guide microstructural design for optimized kinetics

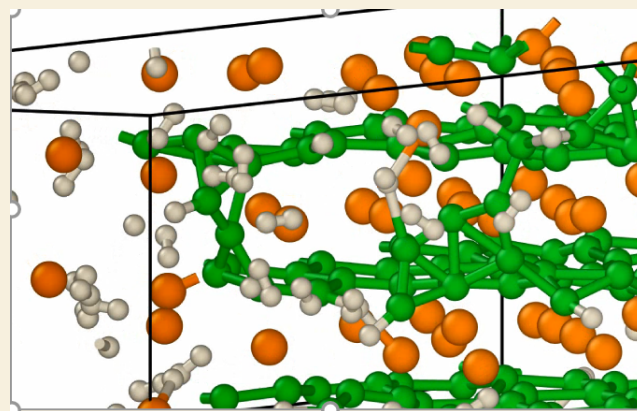
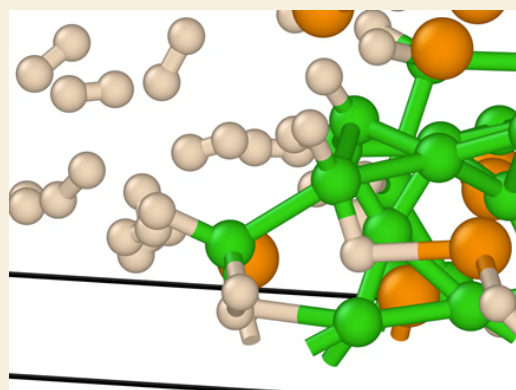
Metal hydrides: Direct simulations provide guidance for activating chemical bonds

Ab initio molecular dynamics simulations reveal how local substoichiometry mediates charge fluctuations to induce chemistry for faster reversibility of MgB_2



Mg-rich edges facilitate BH_4^- formation

Excess negative charge on B dissociates H_2 and facilitates B-H formation



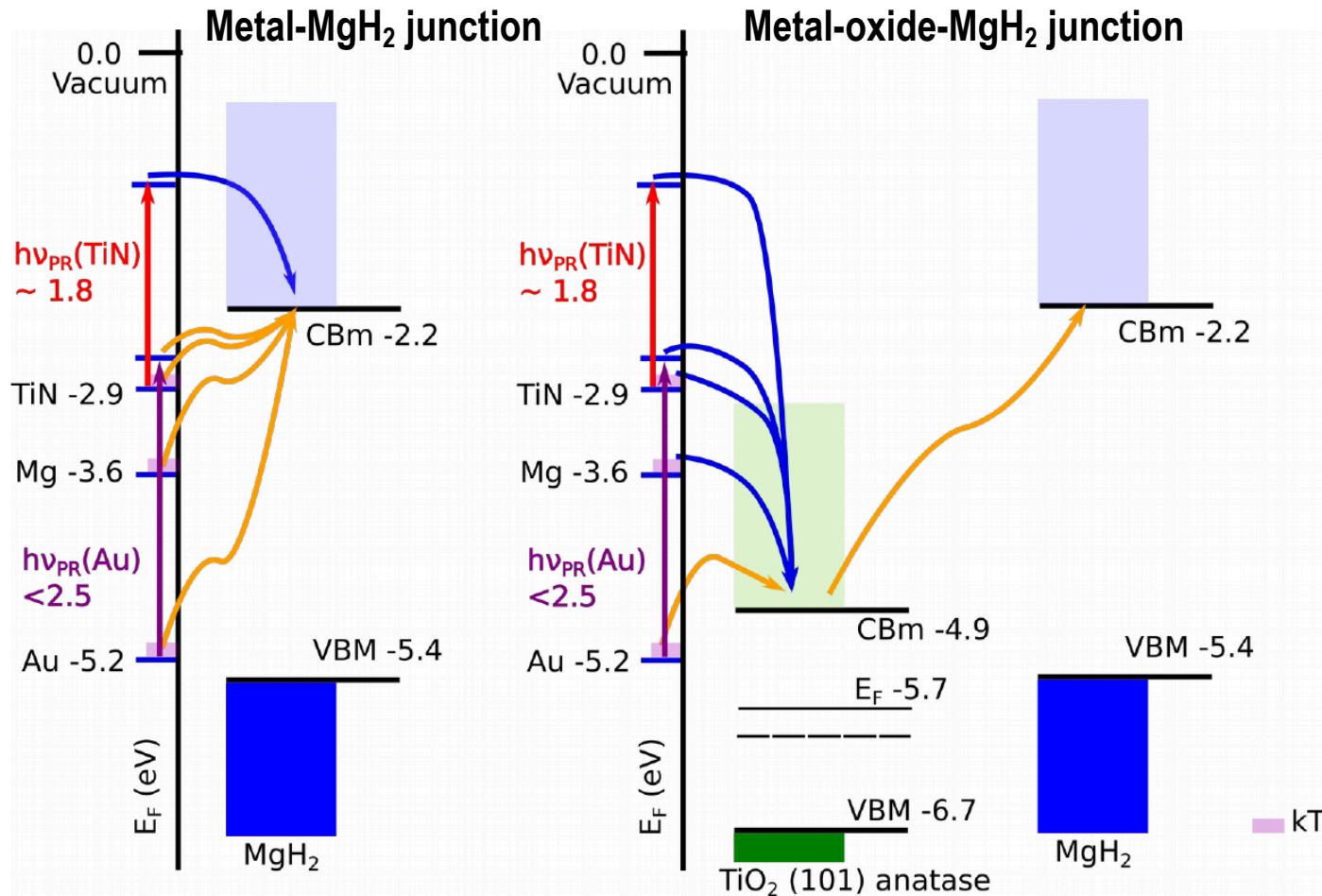
B-rich edges facilitate B-B bond breaking

Weakened pi bonding from charge depletion causes bond rearrangement

- Different MgB_2 edge chemistries lead to very different bond activation character, guiding strategies for design of proper additives

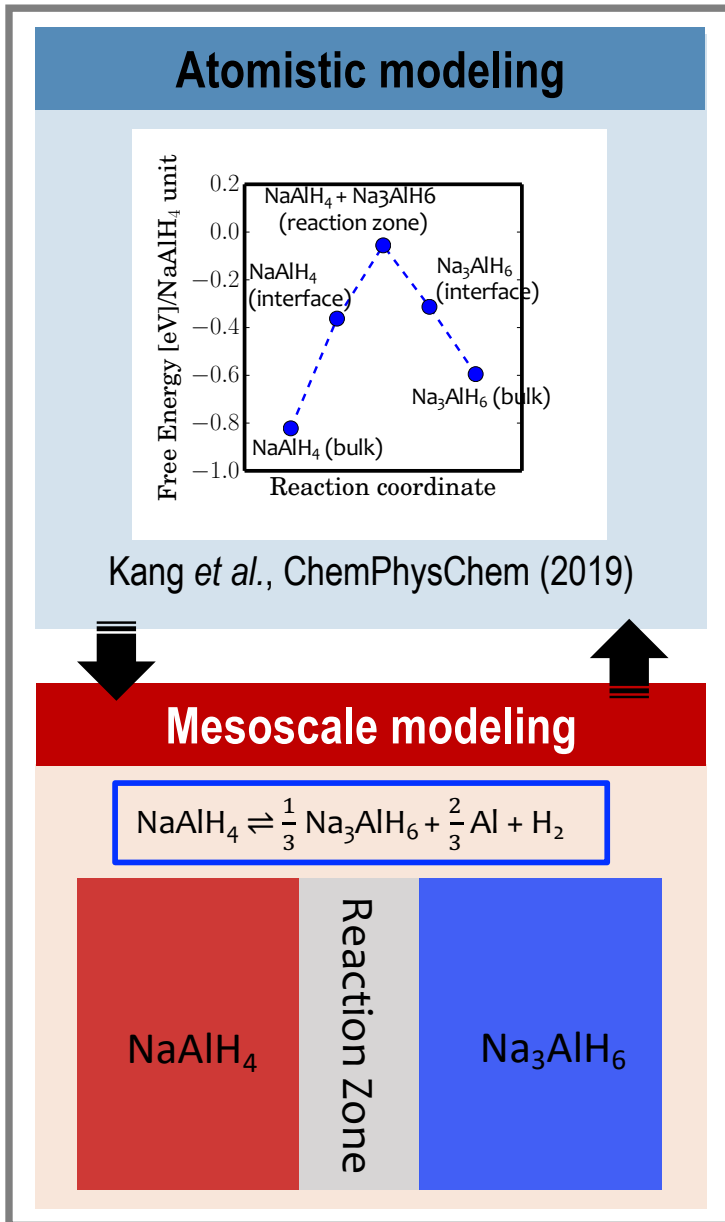
Metal hydrides: Plasmonics as a novel method for faster H₂ release

Ongoing band alignment calculations provide insight into plasmonic interactions for pristine and oxidized MgH₂ on plasmonically active TiN for rapid H₂ release

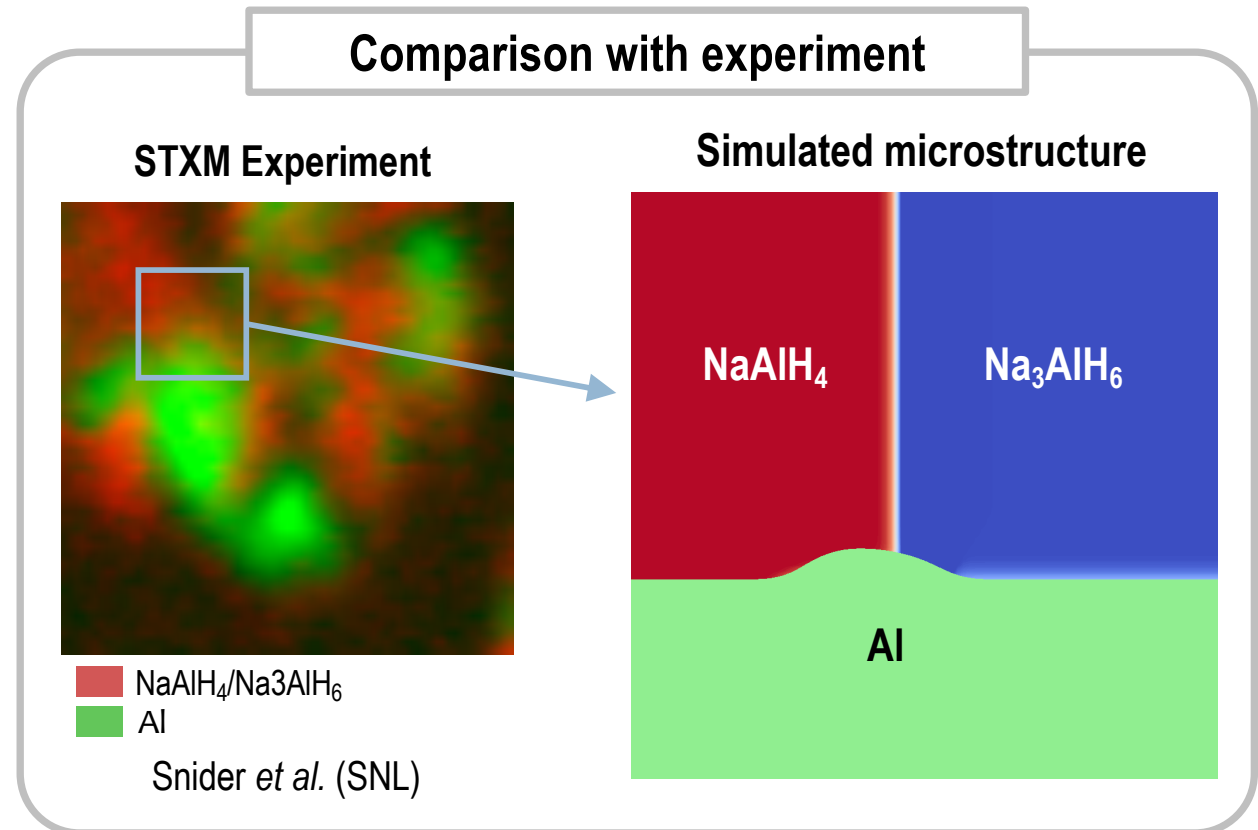


- Plasmonically activated electrons are predicted to accelerate H₂ release, but surface oxidation or formation of Mg at the interface frustrates charge transfer

Metal hydrides: Improved description of interfacial reaction within the DRINK (de)hydrogenation model framework



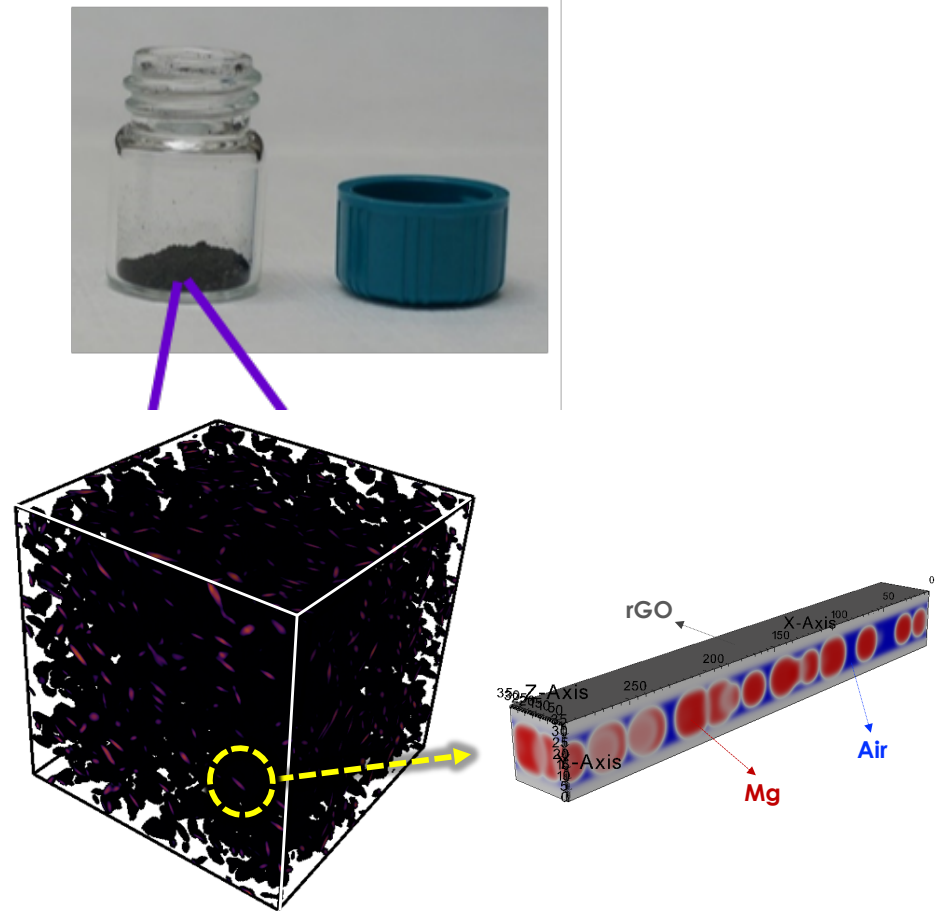
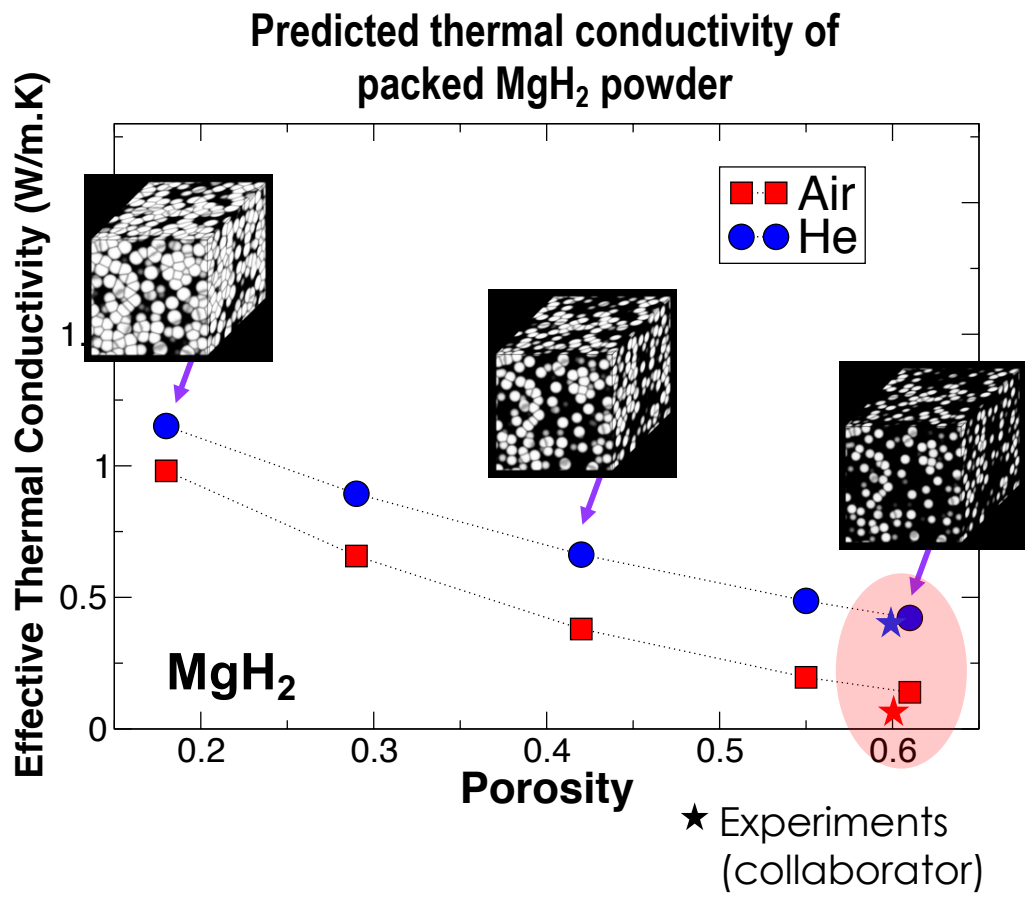
Our (de)hydrogenation kinetics model was improved to include interfacial chemical reactions in complex hydrides



- We are comparing simulations with STXM experiments for validation on NaAlH₄ as a model material
- Our model will enable broad parametric studies to determine rate-limiting steps for complex hydrides

Metal hydrides: Impact of microstructure on thermal transport

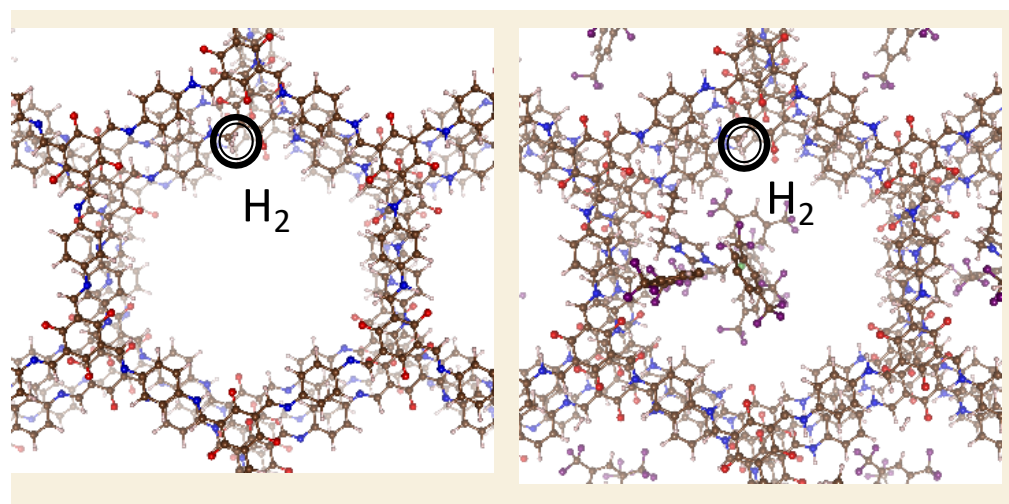
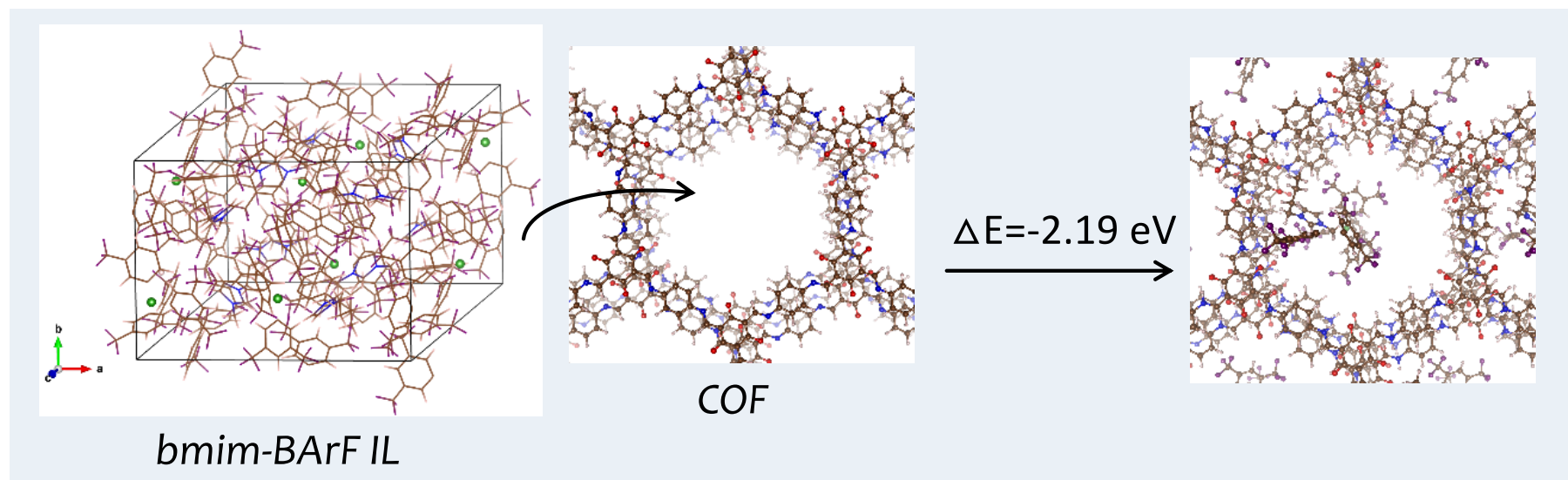
A possible rate limitation in metal hydrides is poor heat distribution, so we established an efficient model for investigating the microstructure-thermal transport relationship



- Simulated thermal conductivities are consistent with experimental measurements from KAIST-HyMARC collaboration
- Validated model is being applied to investigate more practical composites

H_2 carriers: Determining binding sites for porous liquid carrier design

Simulations clarify how bmim-BArF ionic liquid may incorporate into a TpPa-1 COF to provide binding sites for H_2 in the composite structure

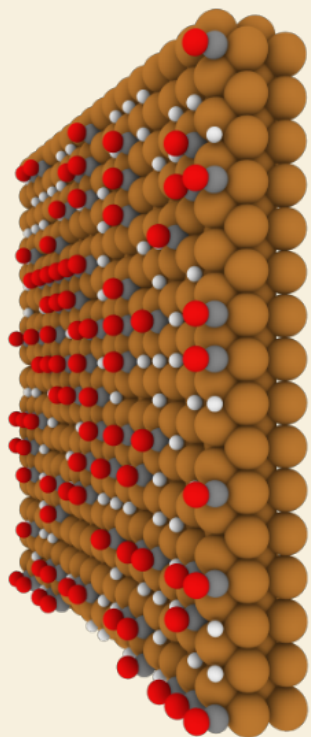


- Understanding can be used to guide co-design of ionic liquids and porous frameworks for optimizing H_2 capacity

H₂ carriers: Unified theory framework for thermal & electrocatalysis

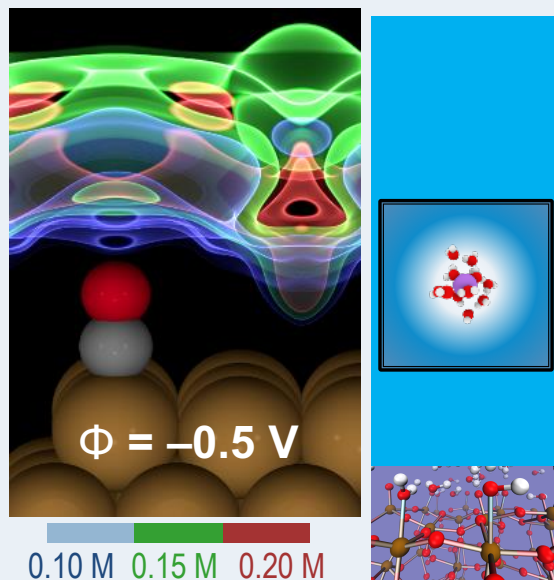
We treat systems at three different levels of approximation to understand energy landscape and predict efficiency, selectivity, and durability in different environments

Gas phase



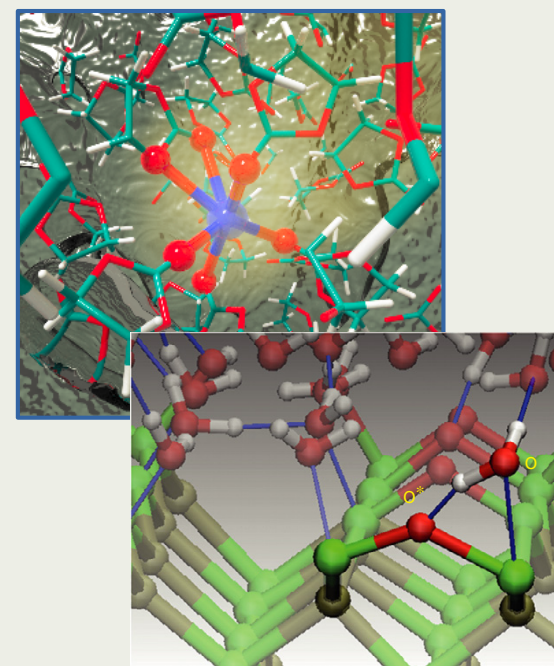
Thermal catalysis

Implicit environment



Thermal & electrocatalysis

Explicit environment

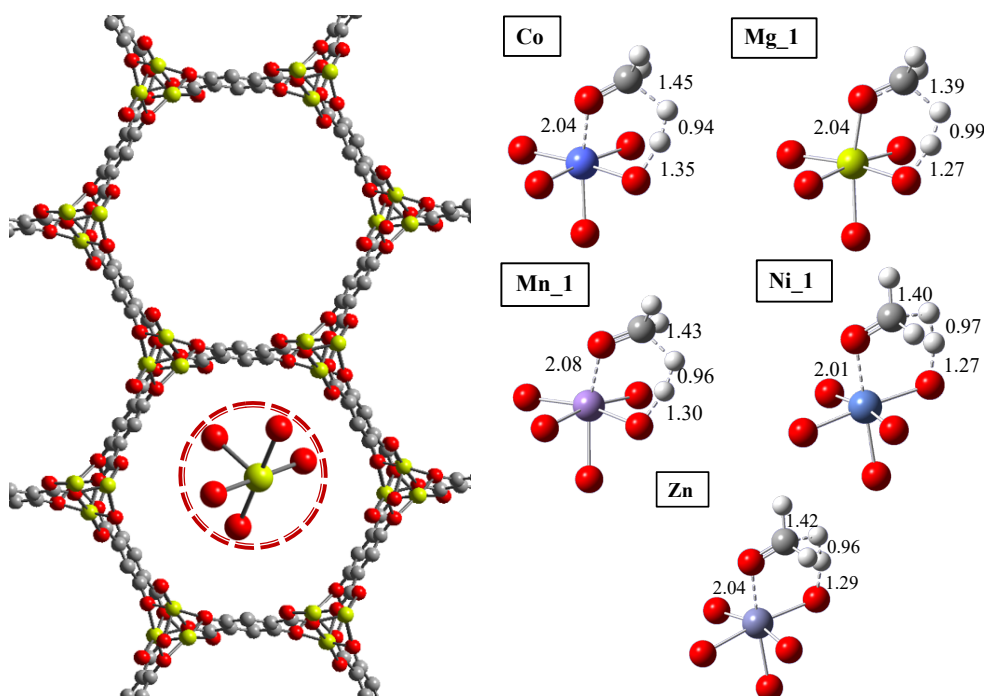


Thermal & electrocatalysis

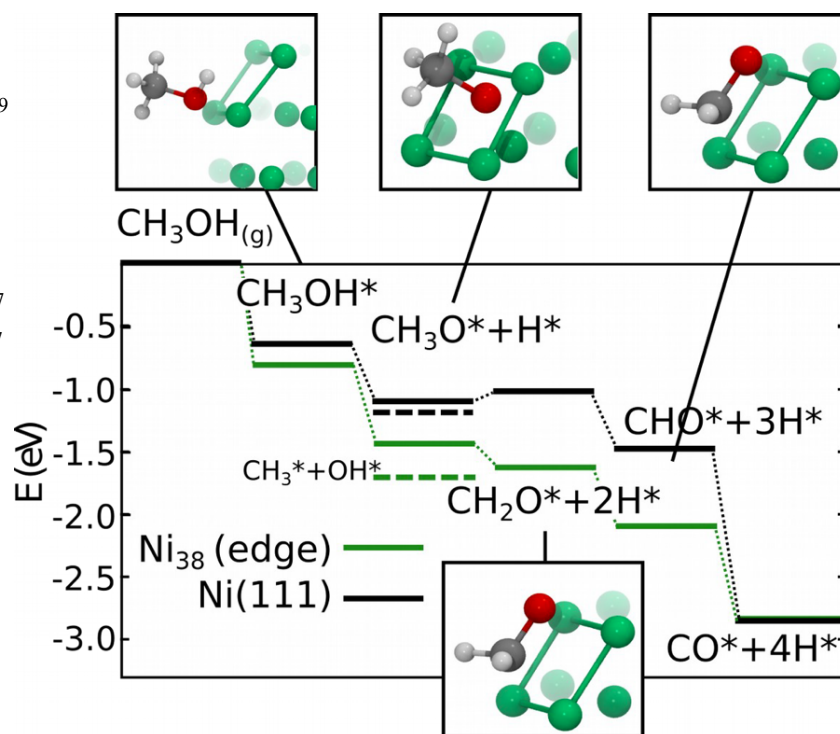
H₂ carriers: Investigating pathways for methanol decomposition

We are investigating the efficiency of methanol decomposition on supported Ni nanoparticle and metal MOF-74 catalysts

MOF-74 with different active metals



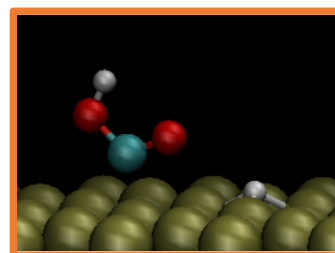
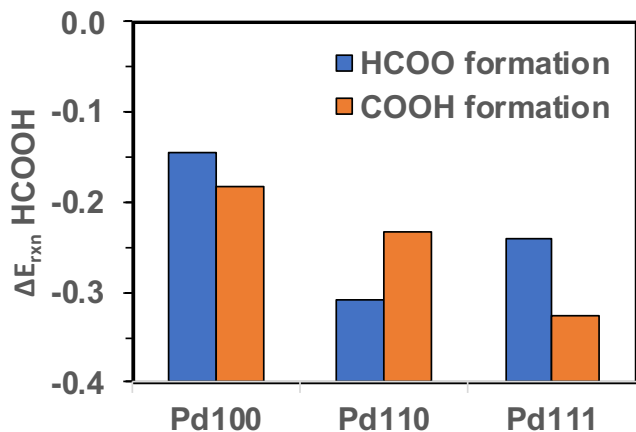
Computed reaction diagrams show dependence of energy landscape on Ni catalyst and hBN support



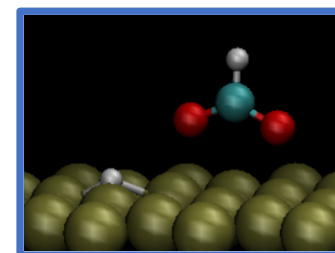
- Metal in MOF-74 significantly affects reaction energy and barrier height
- Interaction with substrate for Ni-supported catalyst crucially alters energy landscape
- Defective substrate immobilizes Ni nanoparticles to prevent sintering

H₂ carriers: Tuning selectivity in formic acid decomposition

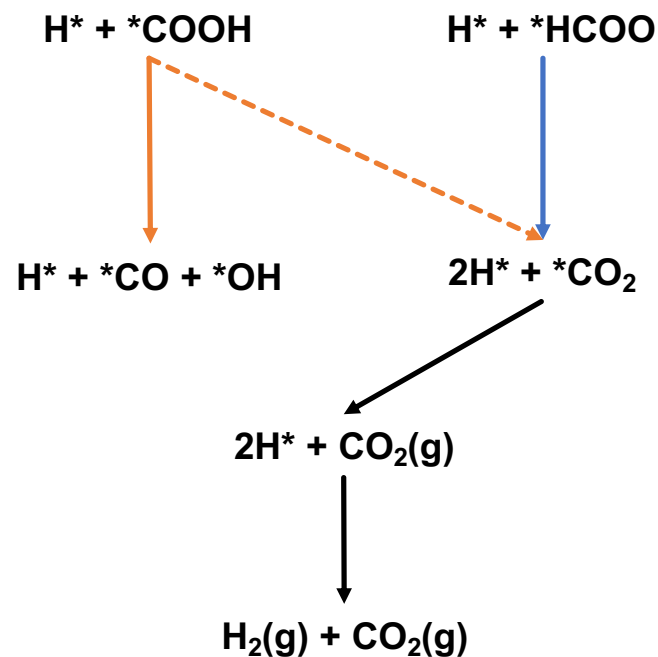
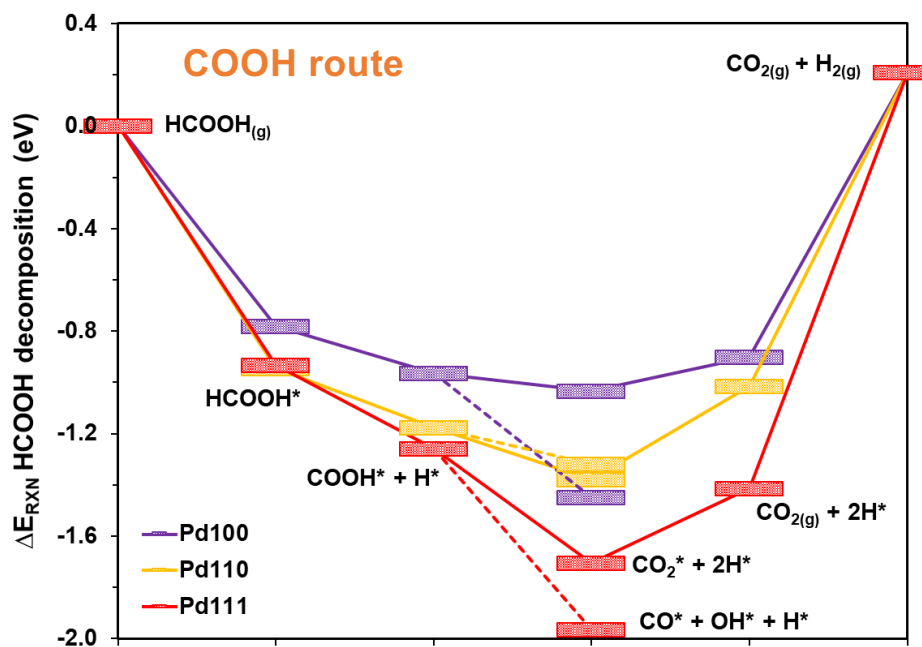
We are investigating the role of Pd catalyst facets on selectivity for formic acid decomposition



Carboxylic acid route



Formate route



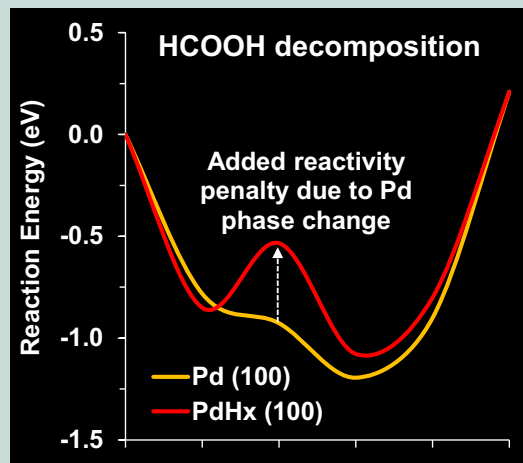
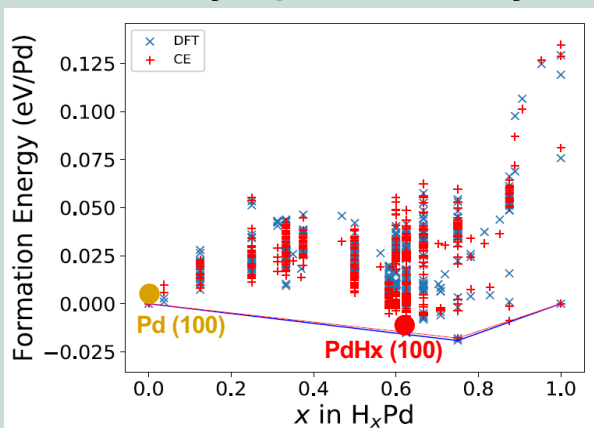
- Pd catalyst geometry and surface morphology can tune selectivity for desired formate decomposition route for higher-efficiency conversion

H₂ carriers: Predicting catalyst conformation & surface activity changes

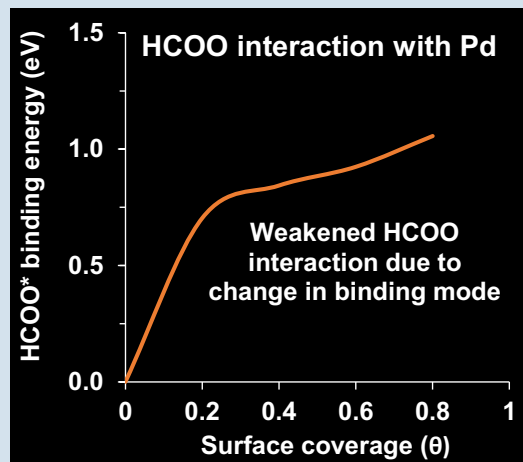
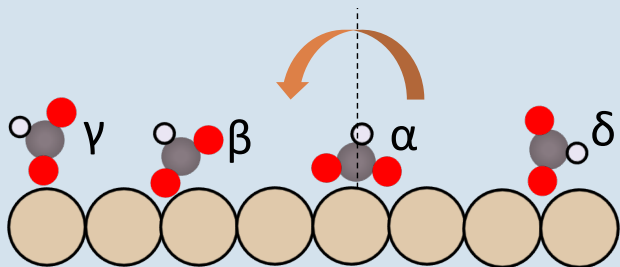
We are predicting the stability and reactivity of catalysts for generation of key H₂ carriers with different environments and energy sources (thermal vs. electrical)

Pd for formic acid decomposition

Catalyst phase stability



Catalyst site stability



Integrated stability prediction

Environment-driven phase stability

Realistic structure-performance prediction

Multiscale model

Surface activity

Collaboration & coordination

HyMARC collaborations

- *Multi-lab working group focus areas engage core laboratories*

Seedling support highlights

U. Hawaii (Godwin Severa)

- *Guidance on mechanisms of MgB_2 decomposition*

LiOx/Caltech (John Vajo)

- *Reaction diagram prediction for Mg-B-H*

Colorado School of Mines (Mike McGuirk)

- *Prediction of kinetics for opening and closing of framework structures*

U. South Carolina (Prof. Morgan Stefik)

- *Confinement stress effects on hydride thermodynamics*
- *NSF partnership with HyMARC*

External collaborations

KAIST, Korea (Profs. Eun Seon Cho, Seung Min Han, and Bong Jae Lee)

- *Microstrain and thermal transport in confined metal hydrides*
- *Multi-institutional partnership launched in September 2018*

Helmholtz Zentrum Geesthacht (Martin Dornheim)

- *Mixed metal hydride reactions and phase evolution*

AIST, Japan (Minoru Otani)

- *Hybrid quantum-classical simulations of catalytic interfaces for hydrogen carriers*

Future work: Materials co-design at multiple scales

Key future priority will connect individual materials properties to system-level understanding for highest-impact design guidelines



Individual materials properties

- Apply best functionals to enthalpy and entropy within new sorbent designs
- Construct validated database of hydride thermodynamics for nanoscale materials
- Use models to devise strategies for accelerating chemical bond activation and phase transformation kinetics
- Estimate thermodynamics and kinetics of catalyst efficiency, stability, and durability for screening H₂ carrier reactions



Emergent functional behavior

- Determine impacts of complex microstructures and packing geometries on effective mechanical, thermal, and transport properties
- Leverage competing kinetics to accelerate hydrogenation and carrier reactions
- Use data-driven approaches to establish structure-property-performance relationships for sorbent and hydride design



Connection to system-level models

- Inform system models with materials-level parameters
- Use system models to focus simulations on highest-impact factors

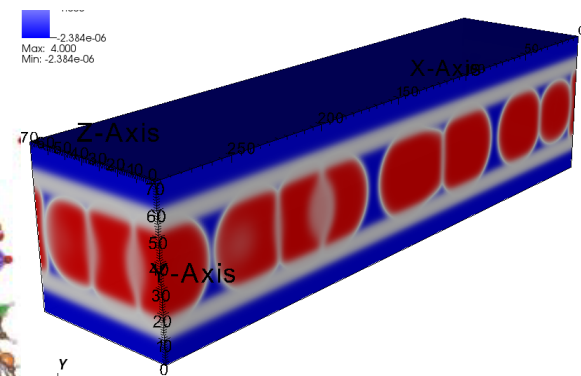
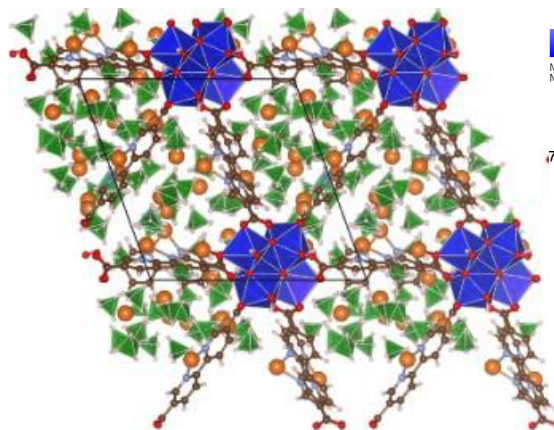
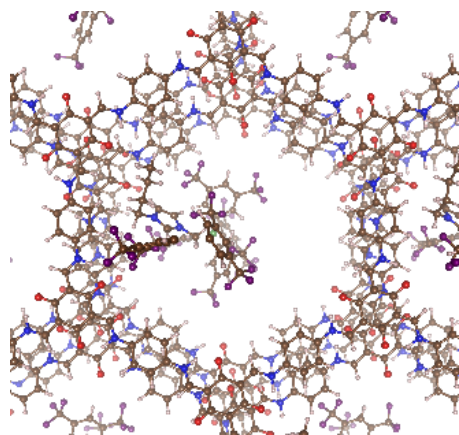
Summary: Modeling & simulation support key HyMARC missions

New foundational understanding of...

- Hydrogen interactions with interfaces and composites in sorbents and metal hydrides
- Nanosizing effects on metal hydrides thermodynamics and kinetics
- Chemical mechanisms for bond activation in metal hydrides
- Efficiency, selectivity, and durability of catalysts for key hydrogen carrier reactions

New capabilities for...

- Selecting proper methods for accurate physisorption predictions in sorbents
- Simulating kinetic regimes in complex metal hydrides (advanced DRINK model)
- Calibrating theory-experiment thermodynamic predictions using data science
- Incorporating effects of catalyst and environment chemistry in hydrogen carrier reactions



Technical backup slides

Metal hydrides: Confinement stress for destabilizing nano-hydrides

We assessed the reaction enthalpy changes of metal hydrides by “nanomechanics” modeling tool based on “quantum volume”

Modeling with “bulk” properties

	Molar volume [cm ³ /mol]	Bulk modulus K _{bulk} [GPa]
Mg	13.79	~36
MgH ₂	18.43	~53

Volumetric strain $\epsilon_V = -25\%$
Strain energy = 20.0 kJ/mol

This large compressive strain based on ideal materials properties is unrealistic

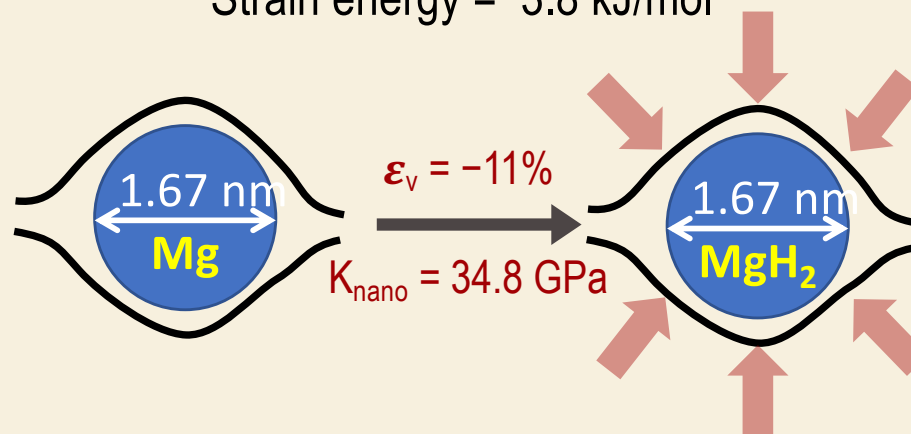
Mild reaction (T, p_{H₂}) conditions can be achieved by destabilizing hydrides. Compared to chemical and electronic interactions, impact of mechanical interactions between host and hydrides is not well understood.

More direct measurement of mechanical strain is under way in collaboration with KAIST

Modeling with “quantum volume” properties

132 Mg atom nanoparticle	Size [nm]	Bulk modulus K _{nano} [GPa]
Mg	~1.67	~24.6
MgH ₂	~1.74	~34.8

Volumetric strain $\epsilon_V = -11\%$
Strain energy = 3.8 kJ/mol



→ destabilizing MgH₂ by **3.8 kJ/mol H₂**
(vs. measured ΔH_{rxn} for 2 nm particles $\cong 8$ kJ/mol H₂)*

Workflow on DataHub – An Example

Expt.

- Experimental B K-edge XAS spectra of MgB_2 on the DataHub

Theory

- Simulate MgB_2 and related solid such as B_2O_3
- Download the expt. spectra and overlay with simulated spectra

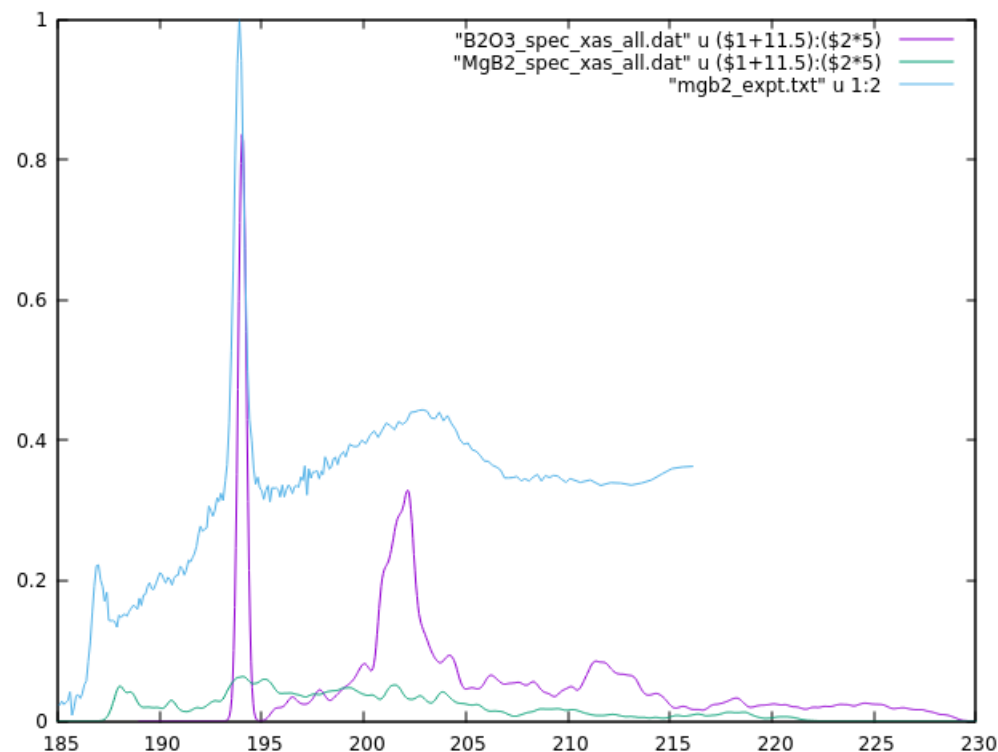
Theory

- Upload the overlaid spectra
- Match peaks between simulation and expt. to see if any in expt. correspond to B_2O_3

Expt.

- Indication of impurity or MgB_2 partially oxidized to B_2O_3
- Needs to be checked by experiments

Sample Spectra of MgB_2 and B_2O_3



Responses to previous year reviewer's comments

- Project was not reviewed last year in this format (reviews were by lab instead)