# HyMARC Core Activity: Computational Modeling

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

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**Project ID #: ST207**

# *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

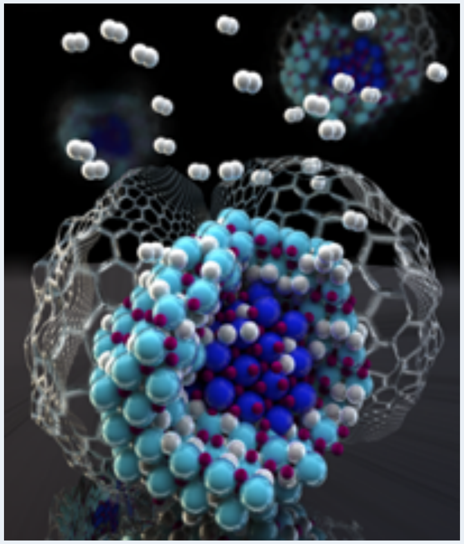
## Partners

Sandia (lead)
NREL (lead)
PNNL
LBNL
NIST
SLAC
ORNL
LLNL

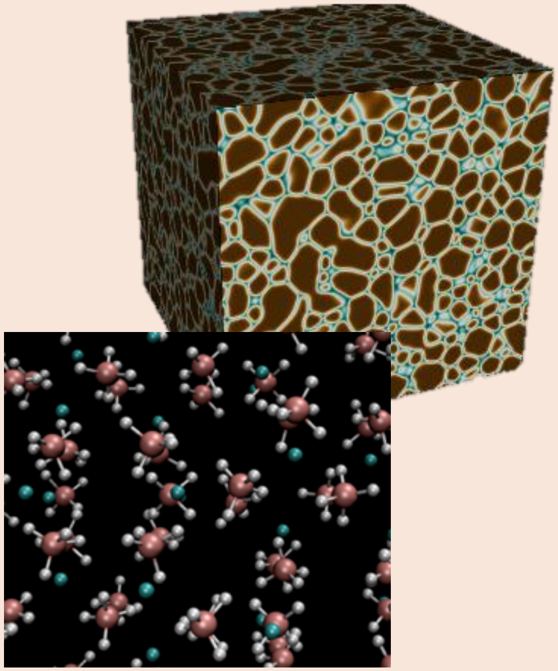
**Project continuation determined annually by DOE*

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

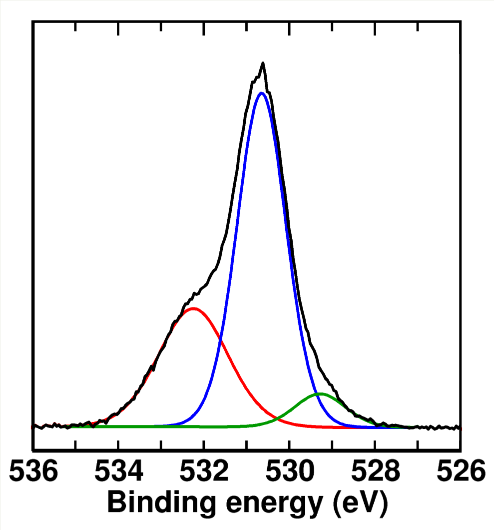
### Real materials under real conditions



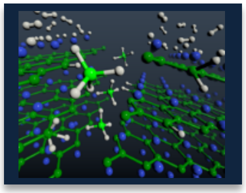
### Multiscale modeling



### Experiment-theory integration

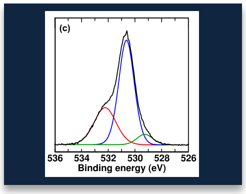


# *Relevance:* How is theory helping with progress towards targets?



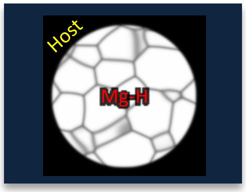
## Assess

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



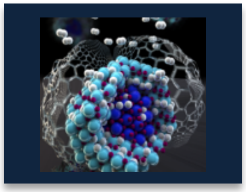
## Interpret

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



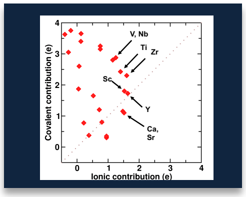
## Model

- 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”

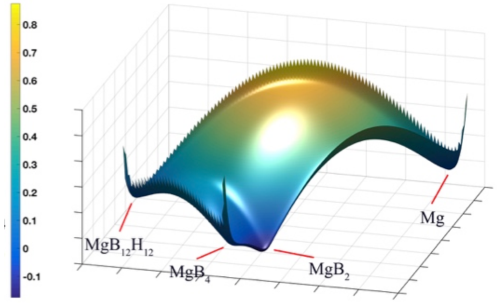


## Design

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

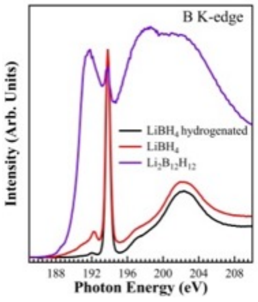
# *Approach:* Capabilities address key HyMARC priorities

- 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

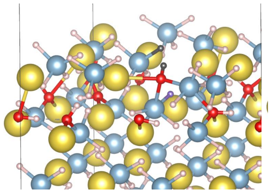
### Atomic/molecular
### (0 – 1 nm)

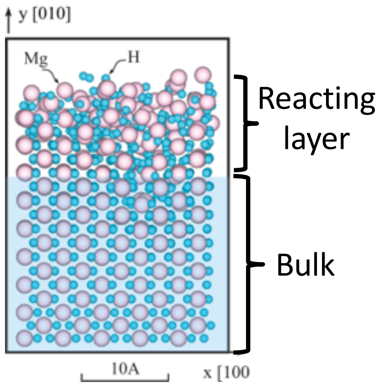


Computational Spectroscopy

Hydrogen chemisorption & physisorption

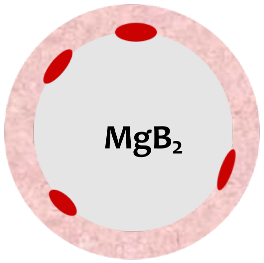
### Molecular/micro
### (0.5 – 2 nm)

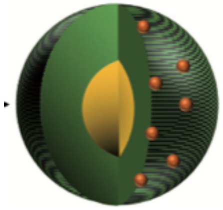




Surface/interface chemistry

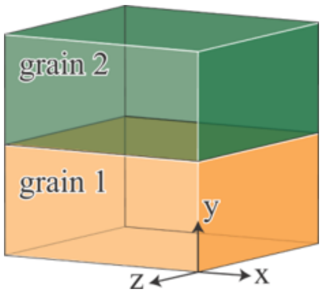
### Mesoscale
### (2 - 100 nm)





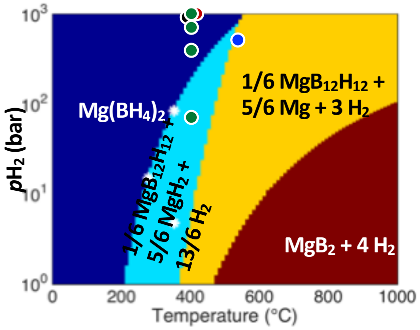
Nucleation kinetics
Phase microstructures

### Grains
### (≤ 10 μm)



Grain boundaries
Particle size effects
Stress/strain

### Macroscale/Bulk



Thermodynamics
Mixing

| | | | |
|---|---|---|---|
| *Density functional theory & ab initio molecular dynamics* | *Classical molecular dynamics & microkinetic modeling* | *Phase-field modeling & microelasticity* | *Ab initio thermodynamics* |

$10^{-10}$ $10^{-8}$ $10^{-6}$ $10^{-4}$ $10^{-2}$

Length (m)

# *Accomplishments and progress towards modeling milestones*

**FY19Q3: Develop computational approach for screening additives to activate B-B bonds in $MgB_2$ (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%)**

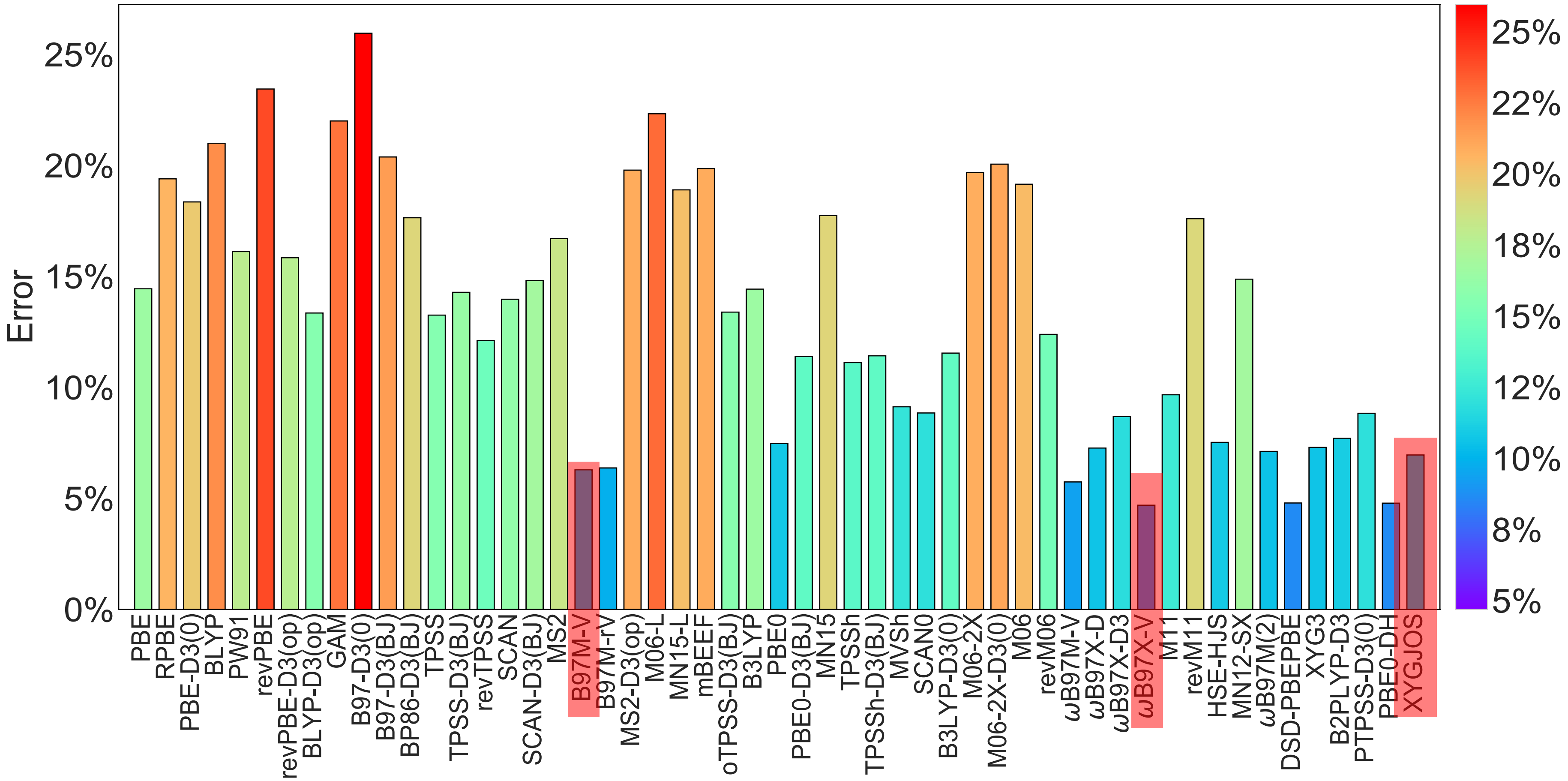
- *Existing hydride database was catalogued and machine learning classifiers were applied; new complex hydride free energy calculations were completed*

**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 $H_2$ physisorption

*Performed comprehensive assessment of density functionals for $H_2$ physisorption by comparing with "gold standard" coupled-cluster calculations on a large data set*



- ωB97X-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*

**Predicted Mg-B-H reaction diagram**

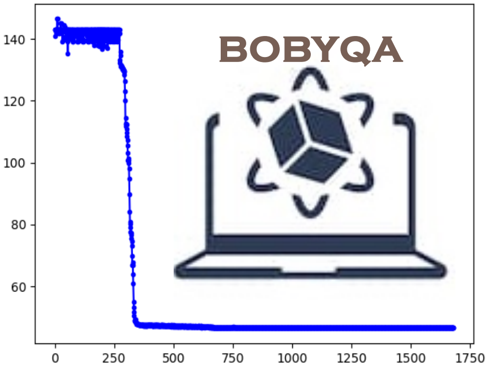
Inconsistent with measured reference data

**Calculate free energies:**

$G(T) = E_{0K\_DFT} + E_0 - b + C * T * \ln(\theta/T) - (D+a) * T^2$

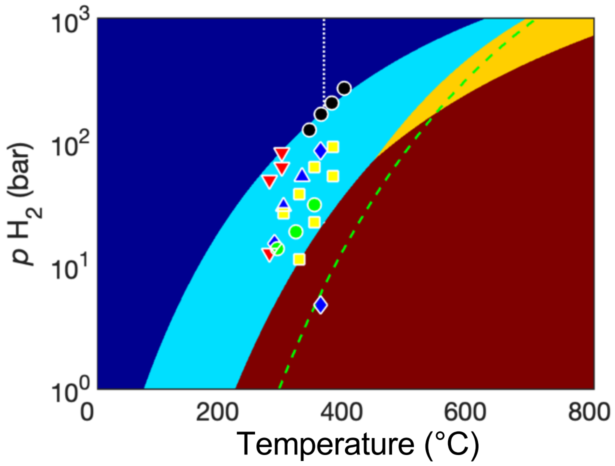
**Estimate confidence of computed data**

**Cost function definition and minimization**



Bound optimization by quadratic approximation

**Calibrated reaction diagram**



Improved match without loss of generality

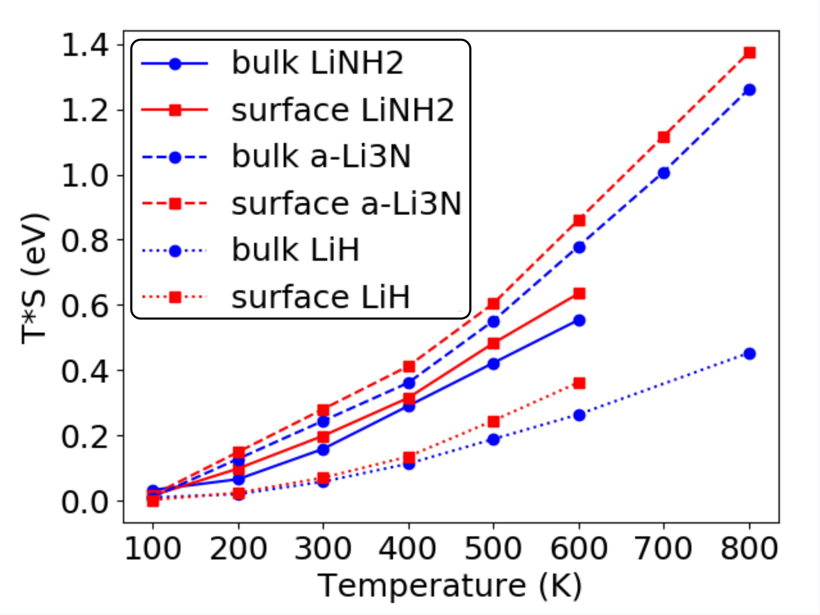
- Accurate predictions optimize cycling conditions and define materials limitations

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

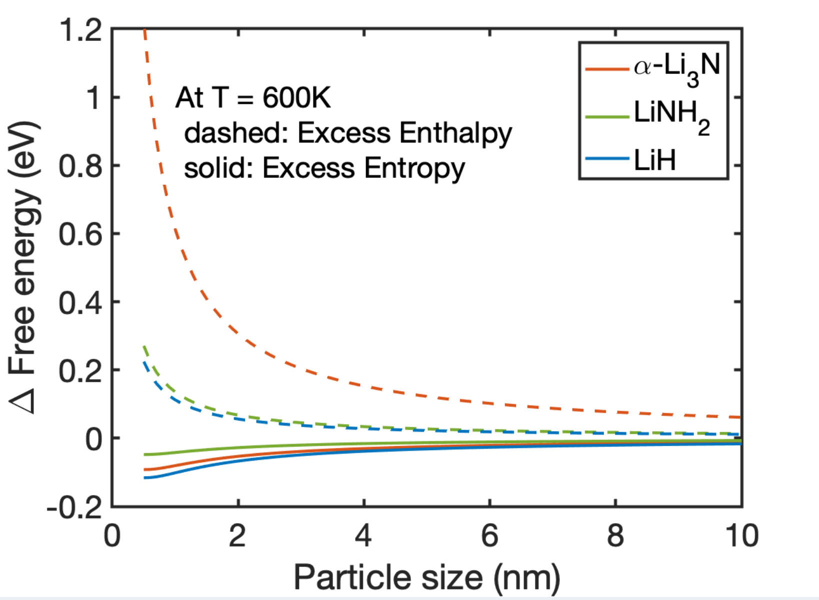
# *Metal hydrides:* Thermodynamics of nanoscale metal hydrides

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

**Increased surface entropy for nanoparticles**



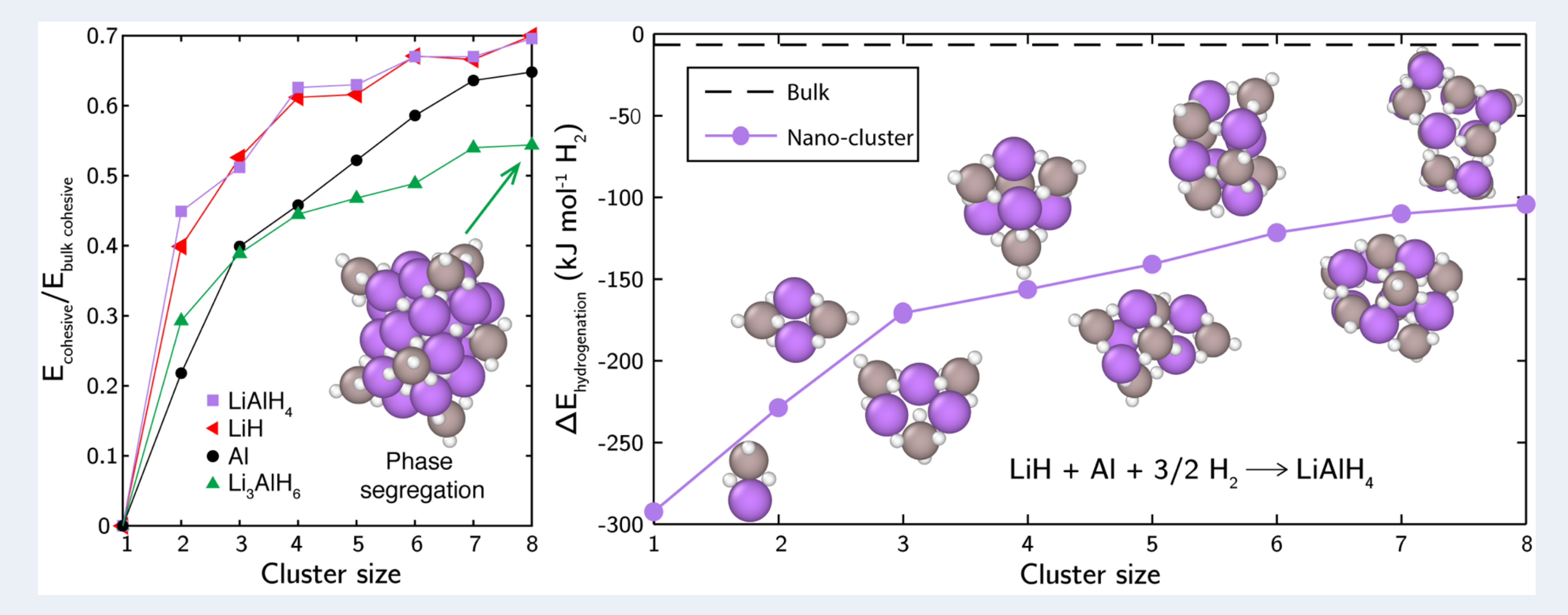
**Enthalpy and entropy competition**



- 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*

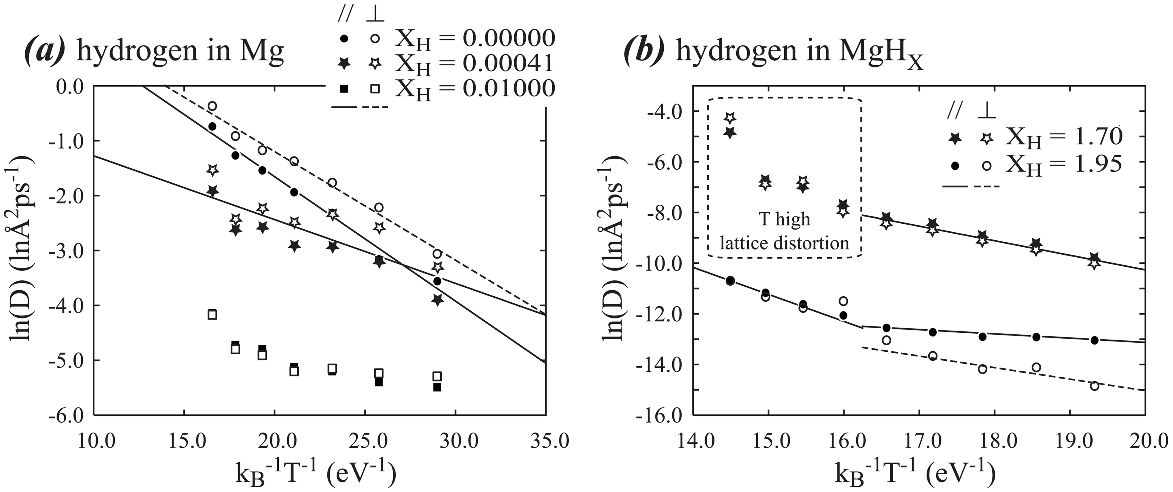


- Nanosizing destabilizes $Li_3AlH_6$ intermediate, consistent with $^{27}$Al NMR
- Nanoconfinement and interaction with N-doped carbon shifts thermodynamics to enable reversibility of $LiAlH_4$ for the first time

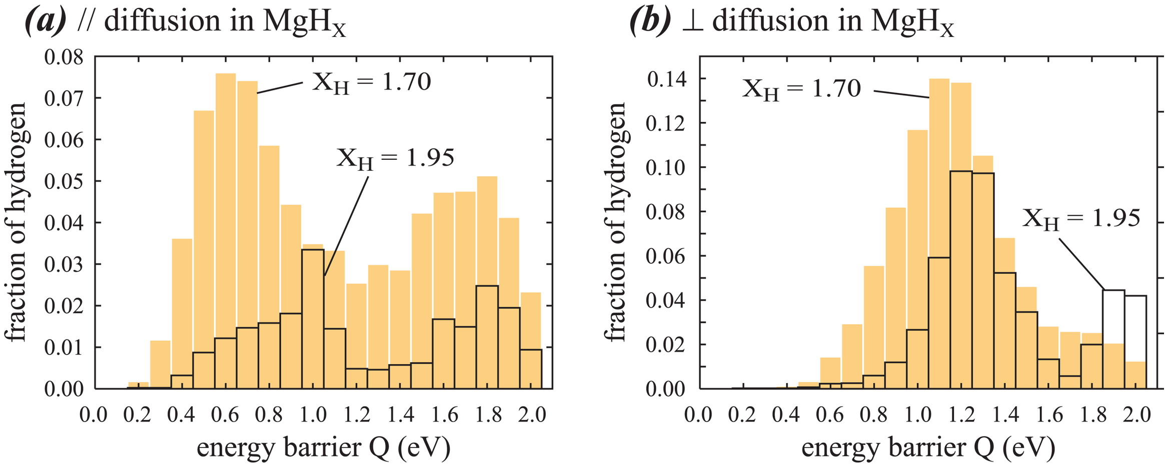
# *Metal hydrides:* Dynamics simulations of hydrogen diffusion

*Molecular dynamics calculations help to assess mass transport limitations in $MgH_2$*

**Arrhenius Plots**



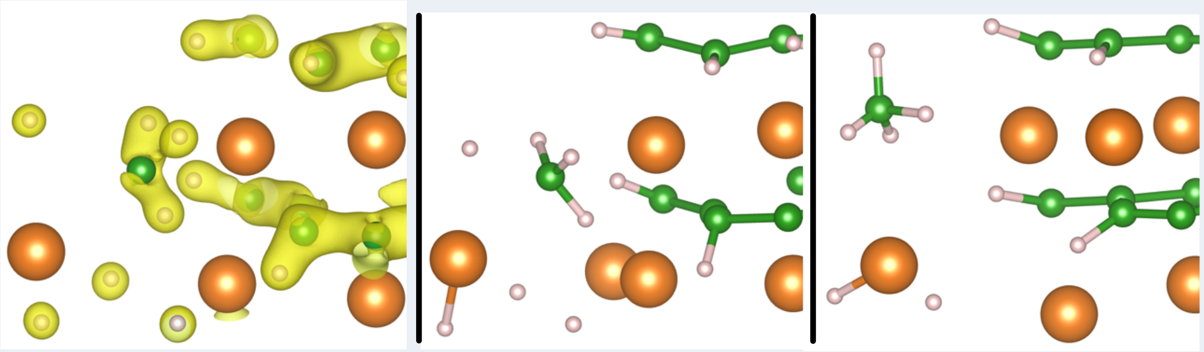
**Barrier Distribution**



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

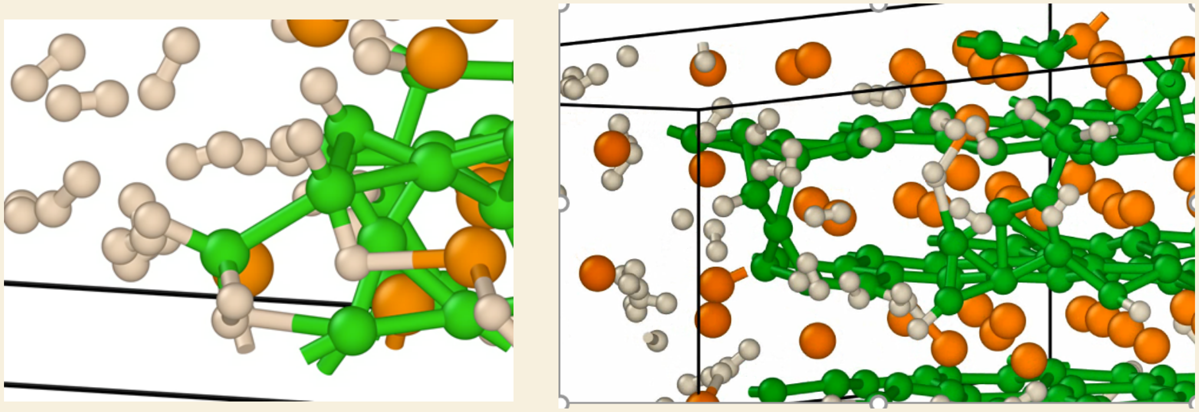
# *Metal hydrides:* Direct simulations provide guidance for activating chemical bonds

*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*



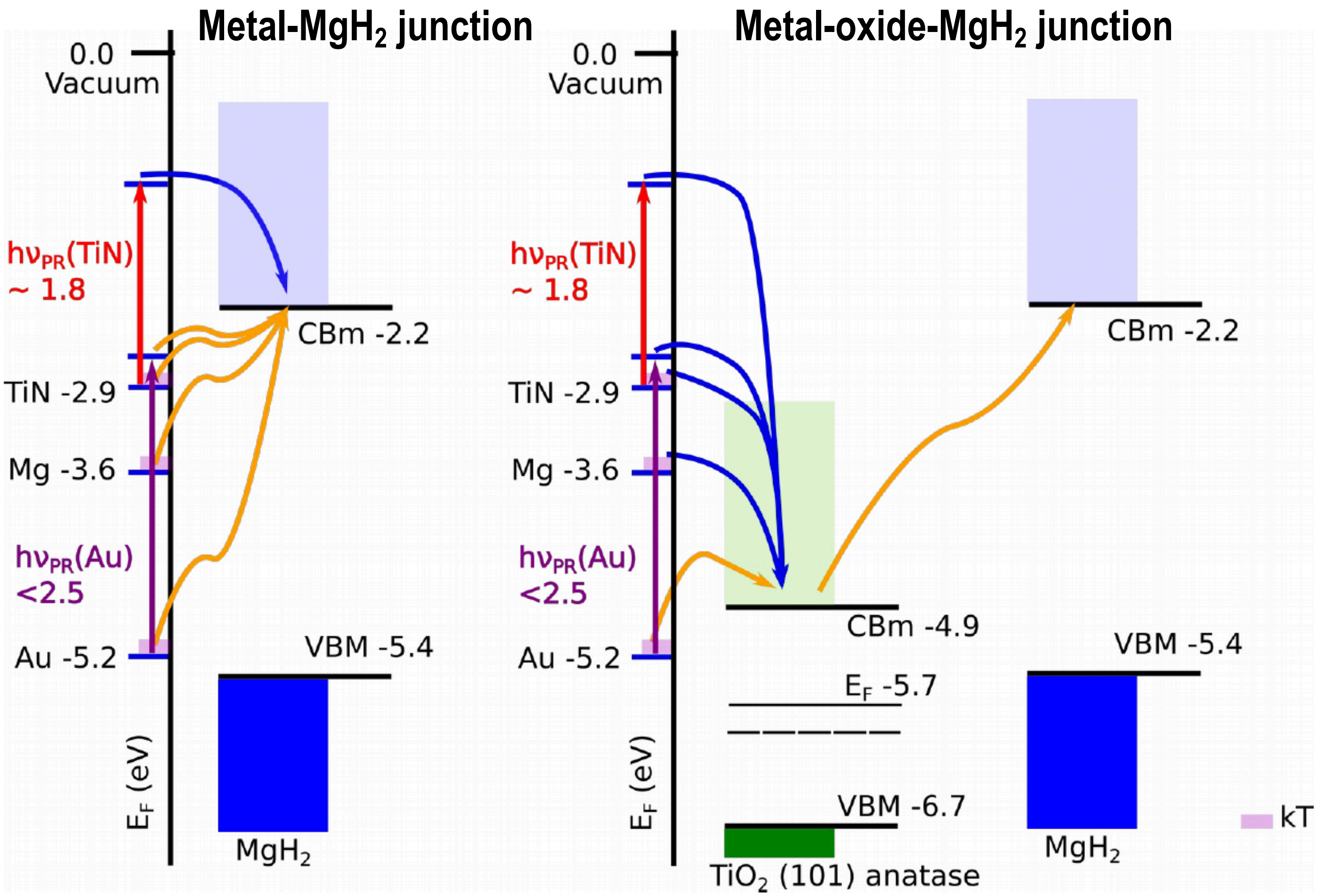
**B-rich edges facilitate B-B bond breaking**

*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 $H_2$ release

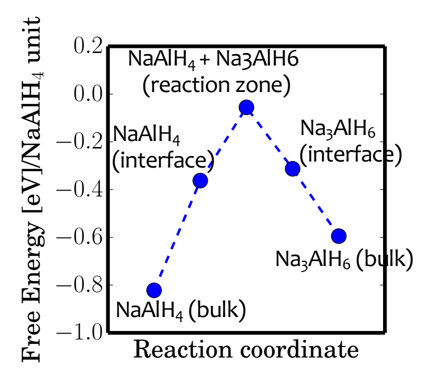
*Ongoing band alignment calculations provide insight into plasmonic interactions for pristine and oxidized $MgH_2$ on plasmonically active TiN for rapid $H_2$ release*



- Plasmonically activated electrons are predicted to accelerate $H_2$ 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

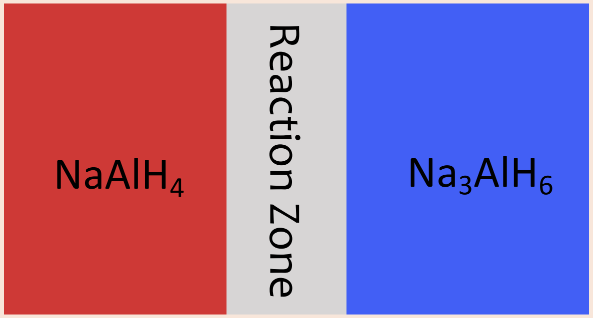
## Atomistic modeling



Kang *et al.*, ChemPhysChem (2019)

## Mesoscale modeling

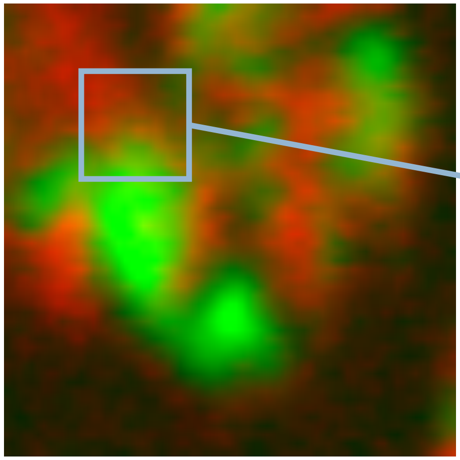
$$NaAlH_4 \rightleftharpoons \frac{1}{3} Na_3AlH_6 + \frac{2}{3} Al + H_2$$



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

## Comparison with experiment

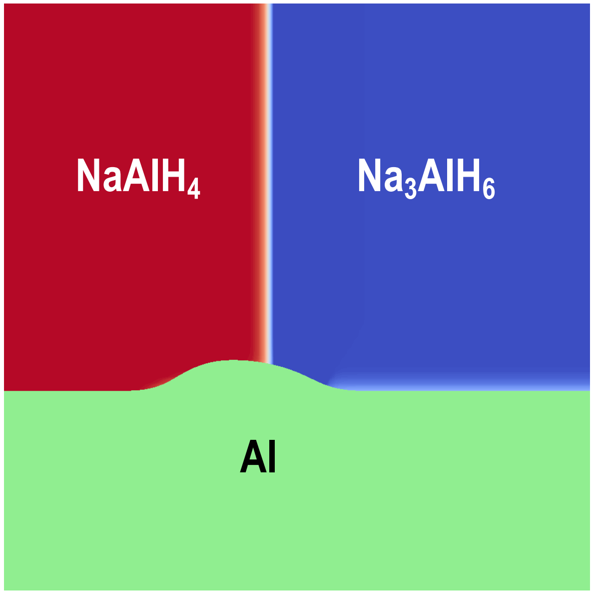
**STXM Experiment**



🟥 NaAlH$_4$/Na3AlH$_6$
🟩 Al

Snider *et al.* (SNL)

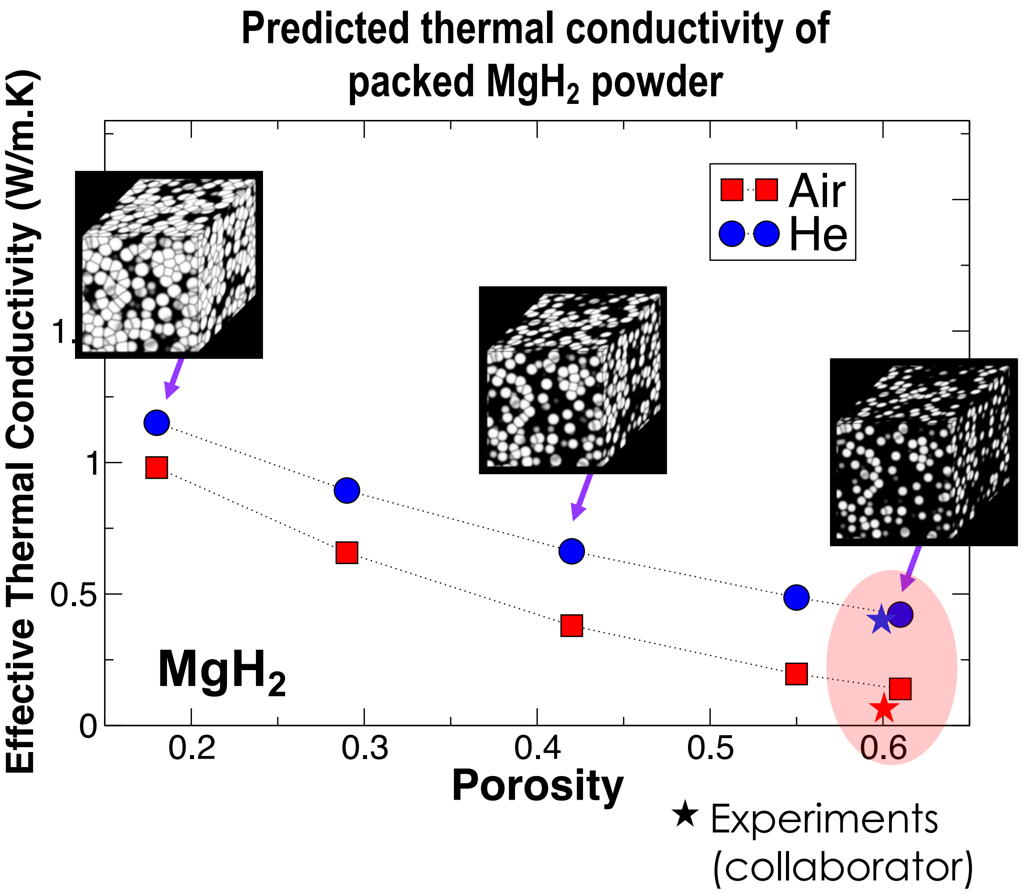
**Simulated microstructure**

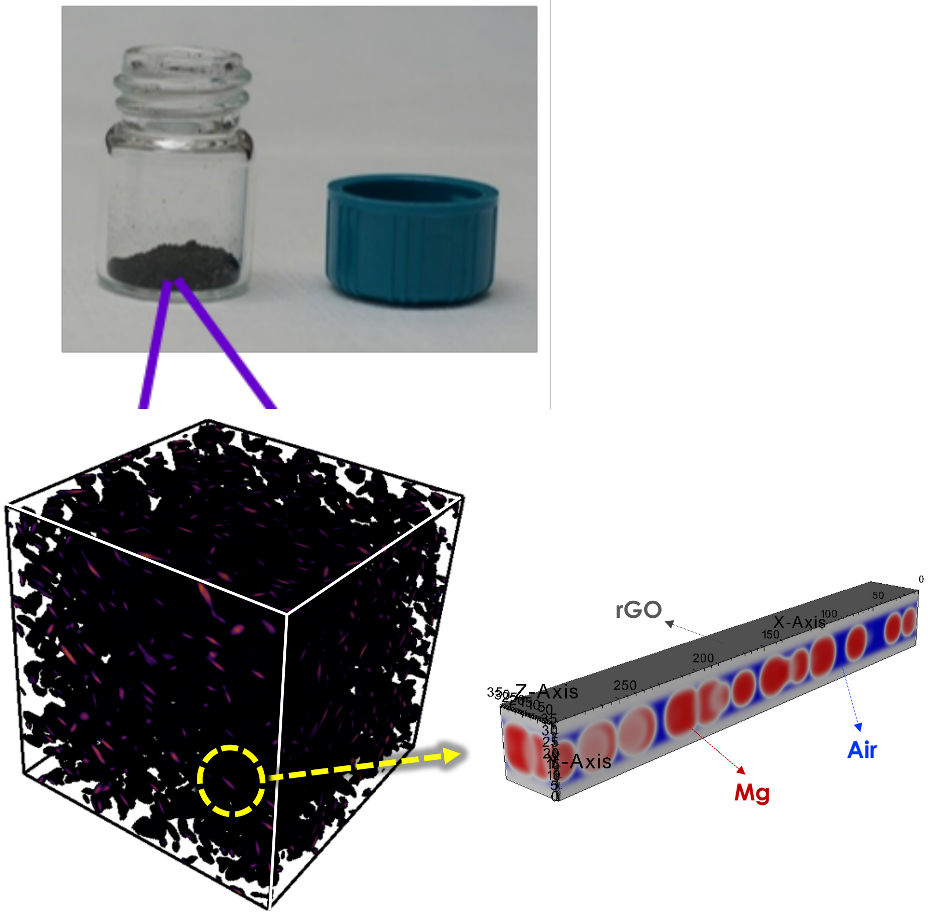


- We are comparing simulations with STXM experiments for validation on NaAlH$_4$ as a model material
- Our model will enable broad parametric studies to determine rate-limiting steps for complex hydrides

# *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*

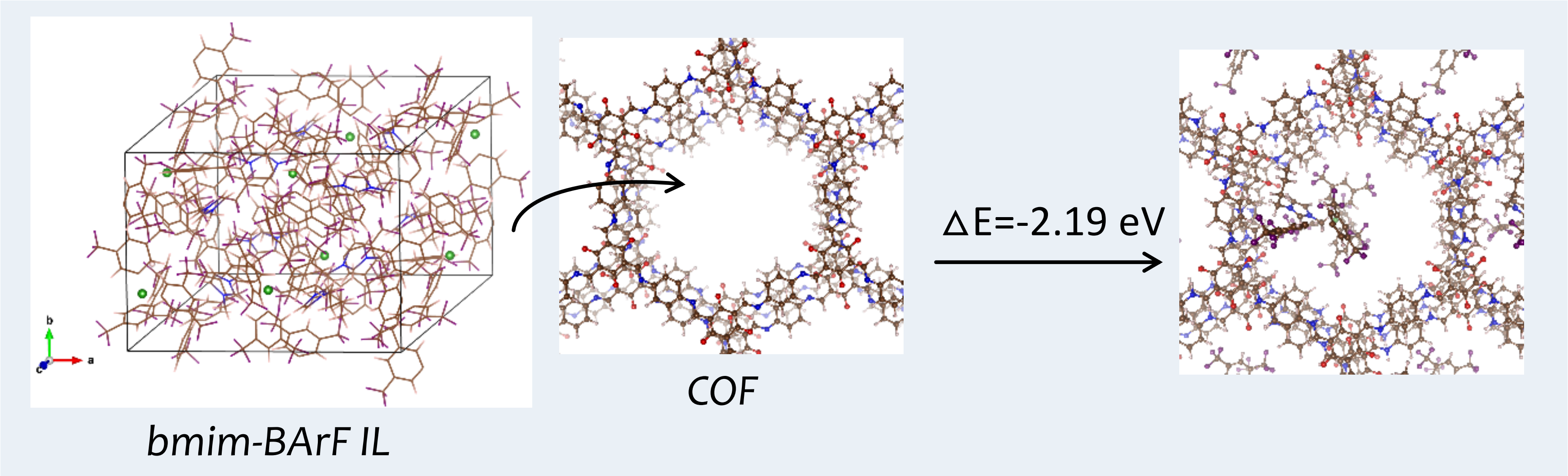


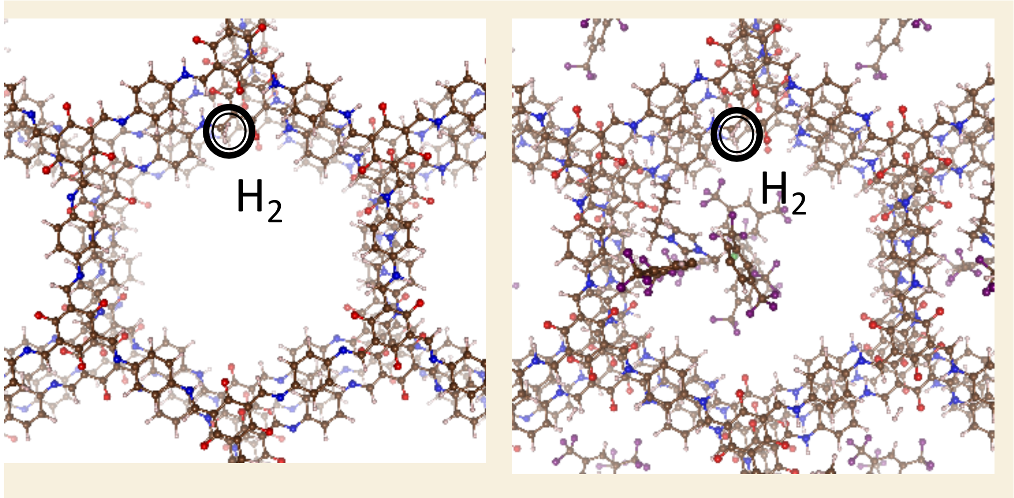


- Simulated thermal conductivities are consistent with experimental measurements from KAIST-HyMARC collaboration
- Validated model is being applied to investigate more practical composites

# *$H_2$ 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*



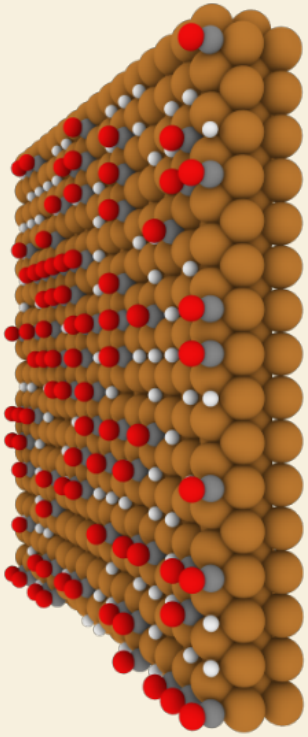


- Understanding can be used to guide co-design of ionic liquids and porous frameworks for optimizing $H_2$ capacity

# *$H_2$ carriers:* Unified theory framework for thermal & electrocatalysis

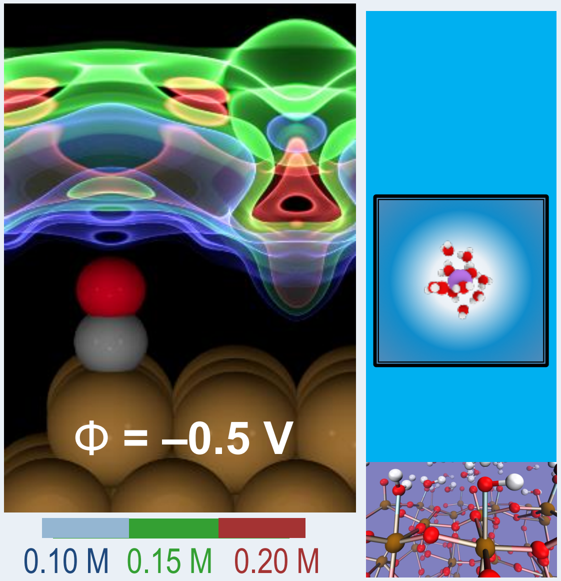
*We treat systems at three different levels of approximation to understand energy landscape and predict efficiency, selectivity, and durability in different environments*

**Gas phase**



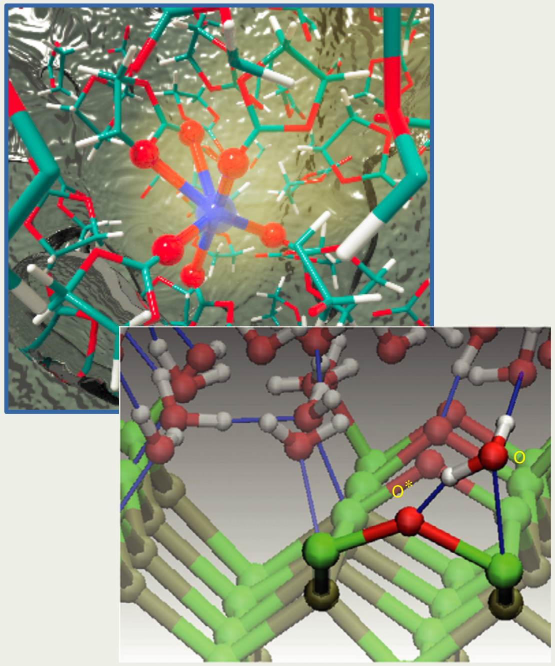
Thermal catalysis

**Implicit environment**



Thermal & electrocatalysis

**Explicit environment**

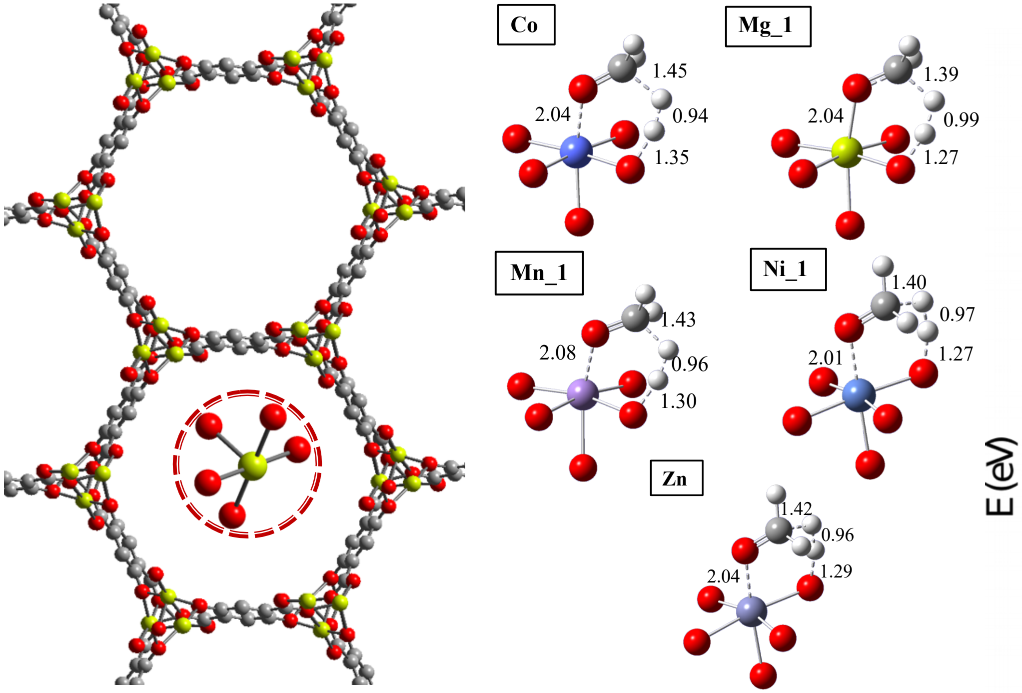


Thermal & electrocatalysis

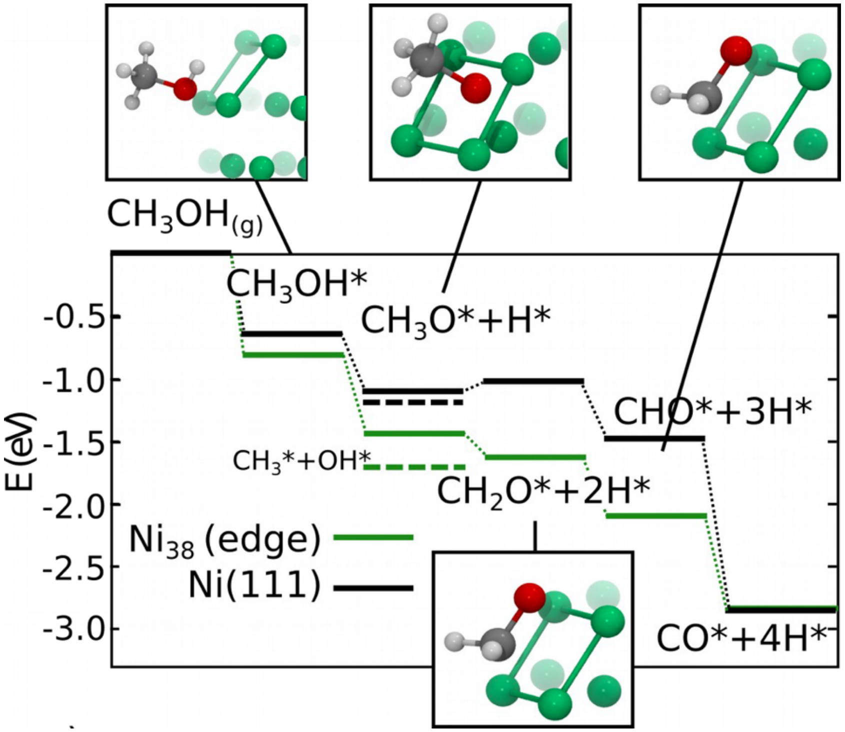
# *$H_2$ carriers:* Investigating pathways for methanol decomposition

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

MOF-74 with different active metals



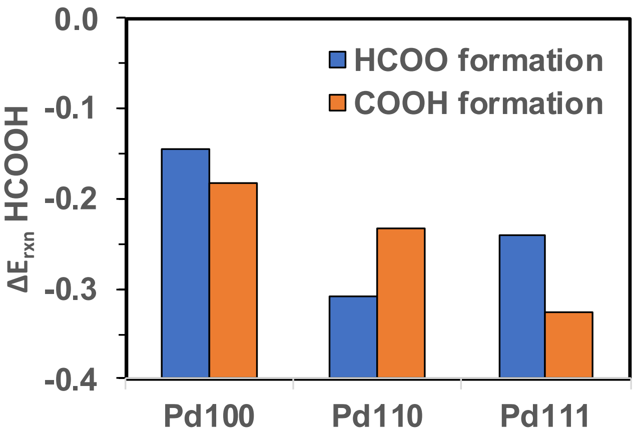
Computed reaction diagrams show dependence of energy landscape on Ni catalyst and hBN support

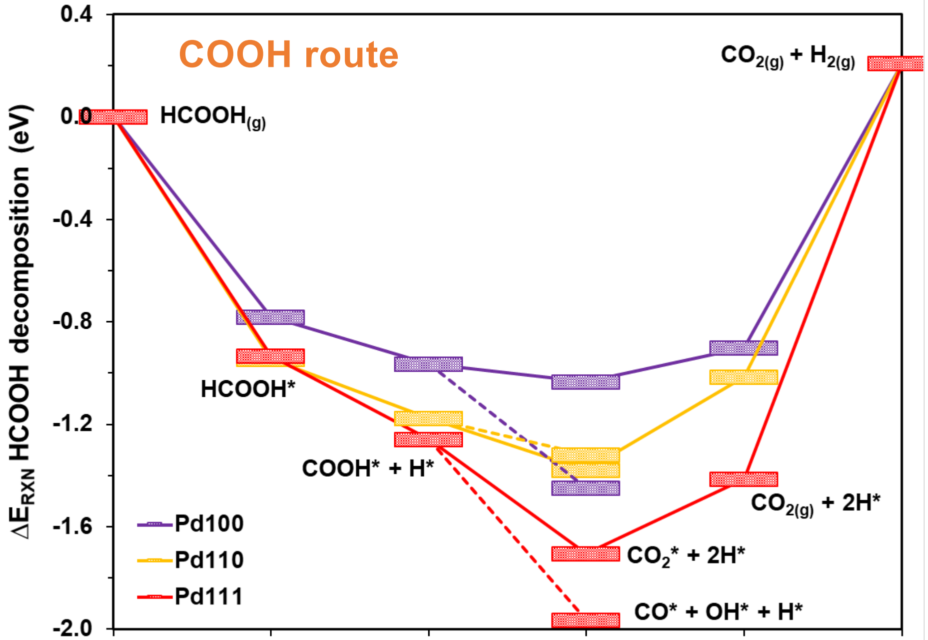


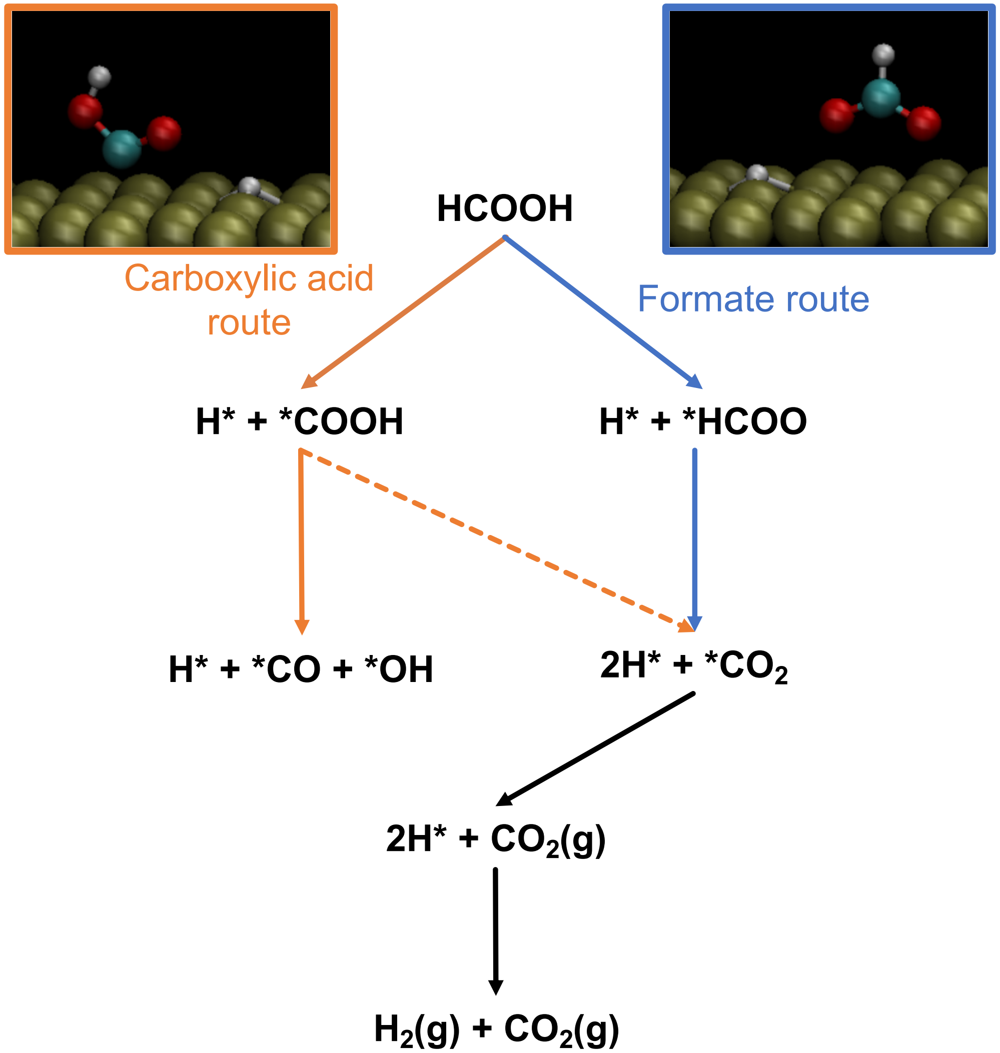
- Metal in MOF-74 significantly affects reaction energy and barrier height
- Interaction with substrate for Ni-supported catalyst crucially alters energy landscape
- Defective substrate immobilizes Ni nanoparticles to prevent sintering

# *$H_2$ carriers:* Tuning selectivity in formic acid decomposition

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







**HCOOH**

Carboxylic acid route

Formate route

**H* + *COOH**

**H* + *HCOO**

**H* + *CO + *OH**

**2H* + *$CO_2$**

**2H* + $CO_2$(g)**

**$H_2$(g) + $CO_2$(g)**

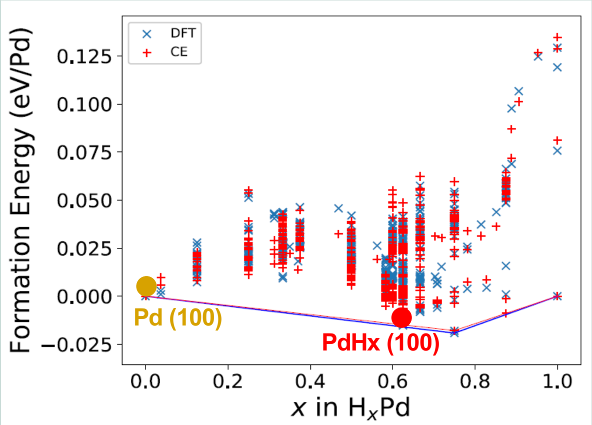
- Pd catalyst geometry and surface morphology can tune selectivity for desired formate decomposition route for higher-efficiency conversion

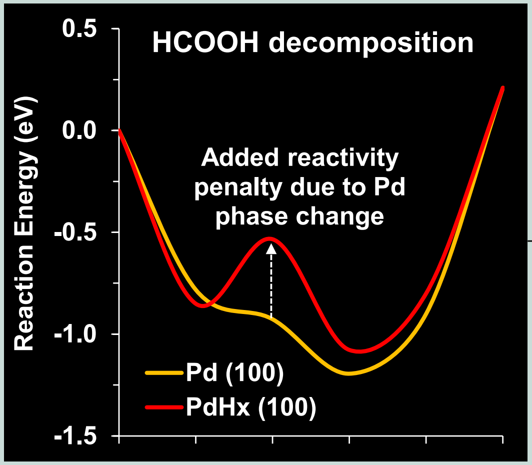
# *$H_2$ carriers:* Predicting catalyst conformation & surface activity changes

*We are predicting the stability and reactivity of catalysts for generation of key $H_2$ carriers with different environments and energy sources (thermal vs. electrical)*

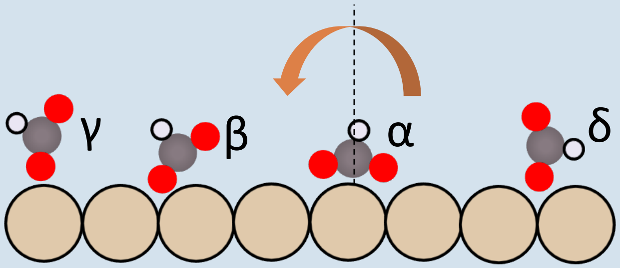
Pd for formic acid decomposition

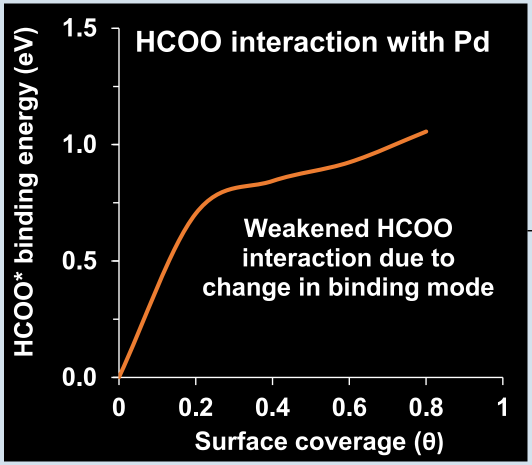
## Catalyst phase stability



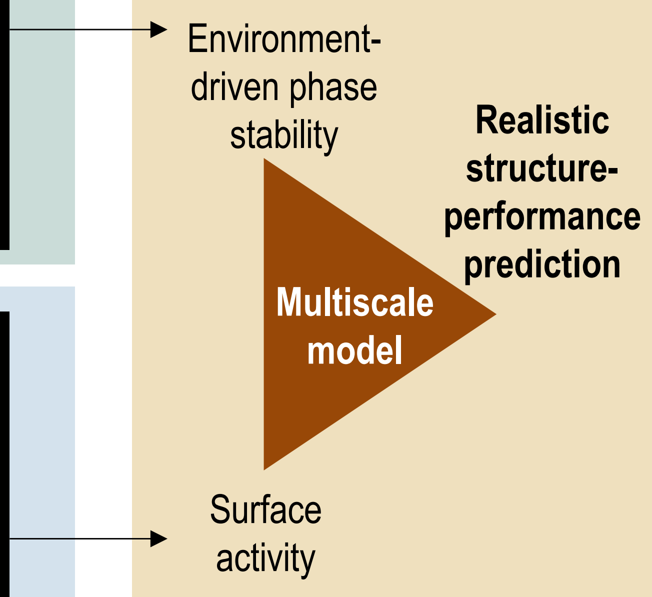


## Catalyst site stability





## Integrated stability prediction



Environment-driven phase stability

Surface activity

Multiscale model

Realistic structure-performance prediction

# *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 $H_2$ 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

HyMARC Hydrogen Materials Advanced Research Consortium

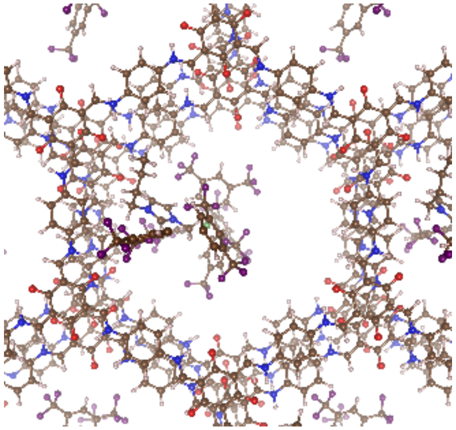
# *Summary:* Modeling & simulation support key HyMARC missions

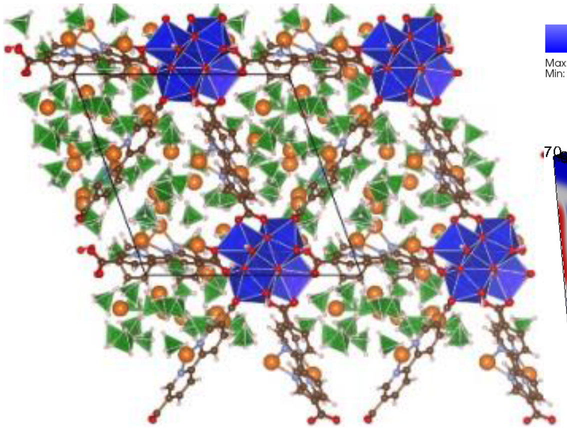
**New foundational understanding of…**

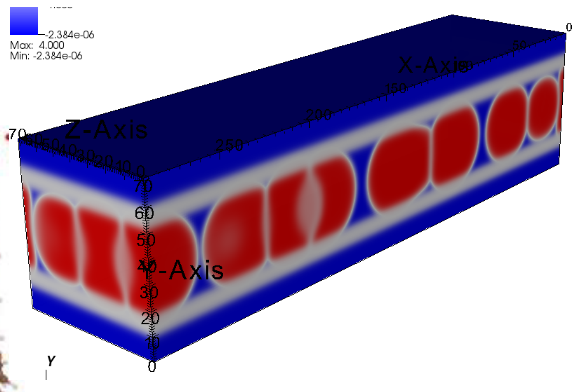
- Hydrogen interactions with interfaces and composites in sorbents and metal hydrides
- Nanosizing effects on metal hydrides thermodynamics and kinetics
- Chemical mechanisms for bond activation in metal hydrides
- Efficiency, selectivity, and durability of catalysts for key hydrogen carrier reactions

**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 $\boldsymbol{\varepsilon}_V = -25\%$
Strain energy = 20.0 kJ/mol

This large compressive strain based on ideal materials properties is unrealistic

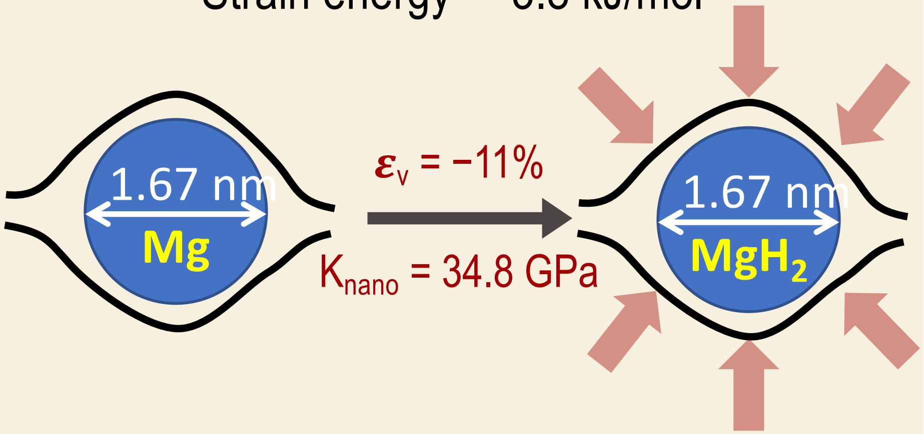
Mild reaction (T,$pH_2$) conditions can be achieved by destabilizing hydrides. Compared to chemical and electronic interactions, impact of mechanical interactions between host and hydrides is not well understood.

**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 $\boldsymbol{\varepsilon}_V = -11\%$
Strain energy = 3.8 kJ/mol



**→ destabilizing $MgH_2$ by 3.8 kJ/mol $H_2$**

(vs. measured $\Delta H_{rxn}$ for 2 nm particles ≅ 8 kJ/mol $H_2$)*

*Cho *et al.* Adv. Funct. Mater. **2017**, 27, 1704316

# 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

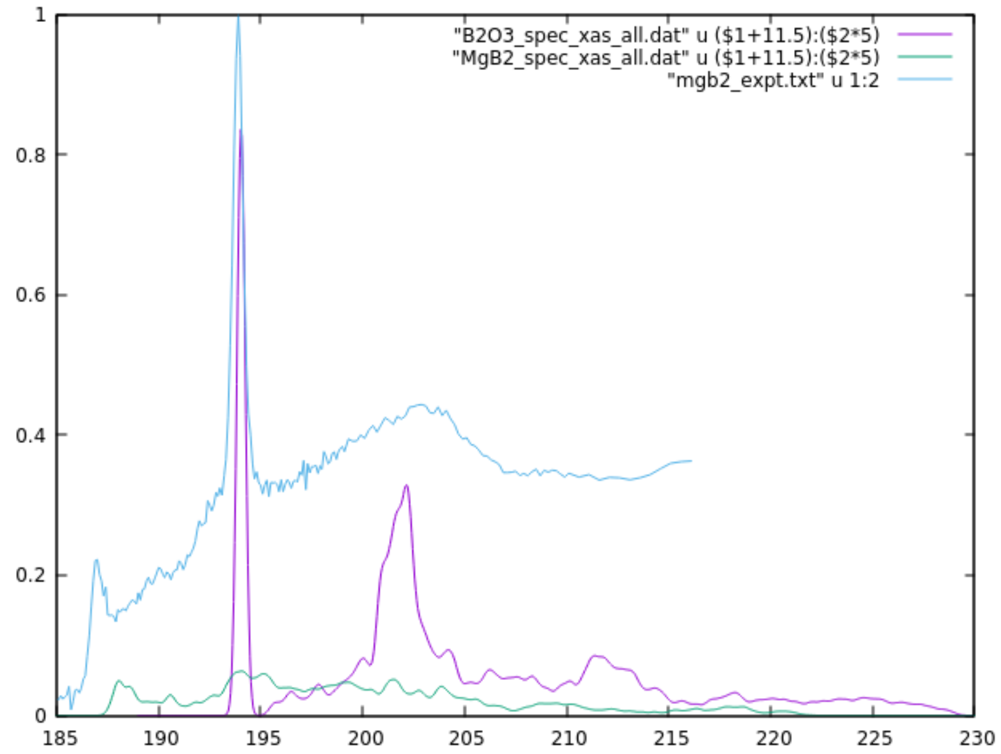
**Theory**

- Upload the overlayed 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)