HyMARC: Hydrogen Storage Materials Advanced Research Consortium

2016 DOE Hydrogen Annual Merit Review

June 8, 2016

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Lawrence Livermore National Laboratory

Project ID# ST129

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LLNL-PRES-XXXXXX

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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 Planned DOE Funding: $735K
Total Funds Received: $985K

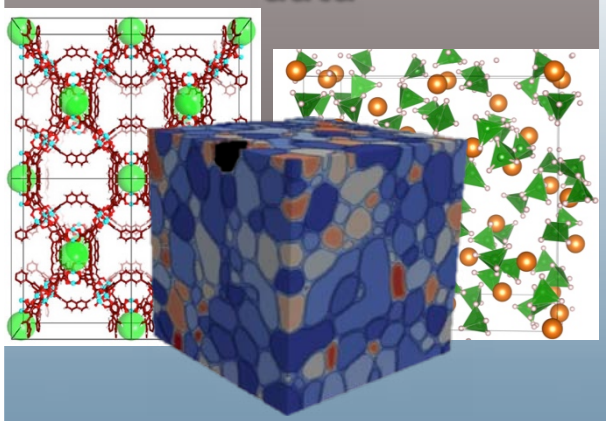
Team

Funded Partners:
Sandia National Laboratories (lead)
Lawrence Berkeley National Laboratory

Relevance & objective

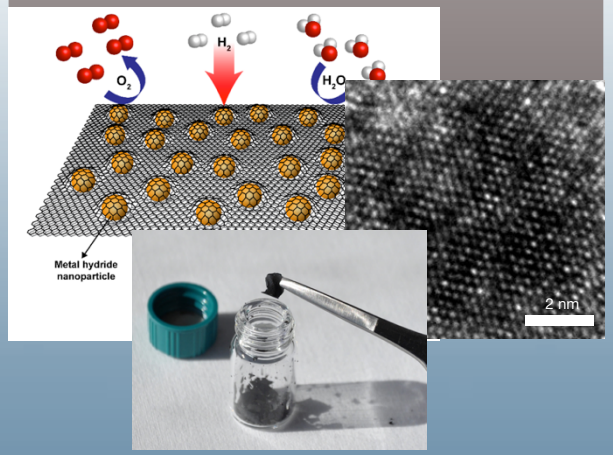
HyMARC will provide **community tools** and **foundational understanding** of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials

Theory, simulation, & data



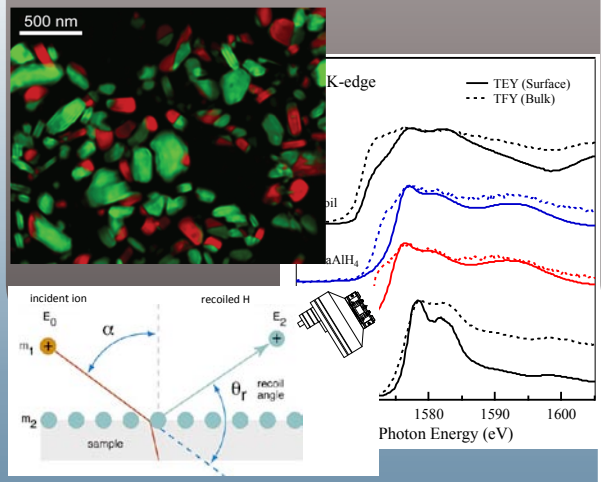
- **Quantum Monte Carlo for sorbents**
- **DFT/*ab initio* molecular dynamics for bulk/surface/interface chemistry**
- Classical MD & **kinetic Monte Carlo for non-equilibrium transport**
- **Phase-field modeling for solid-state phase transformation kinetics**
- **Computational spectroscopy**
- **Community software & databases**

Controlled synthesis



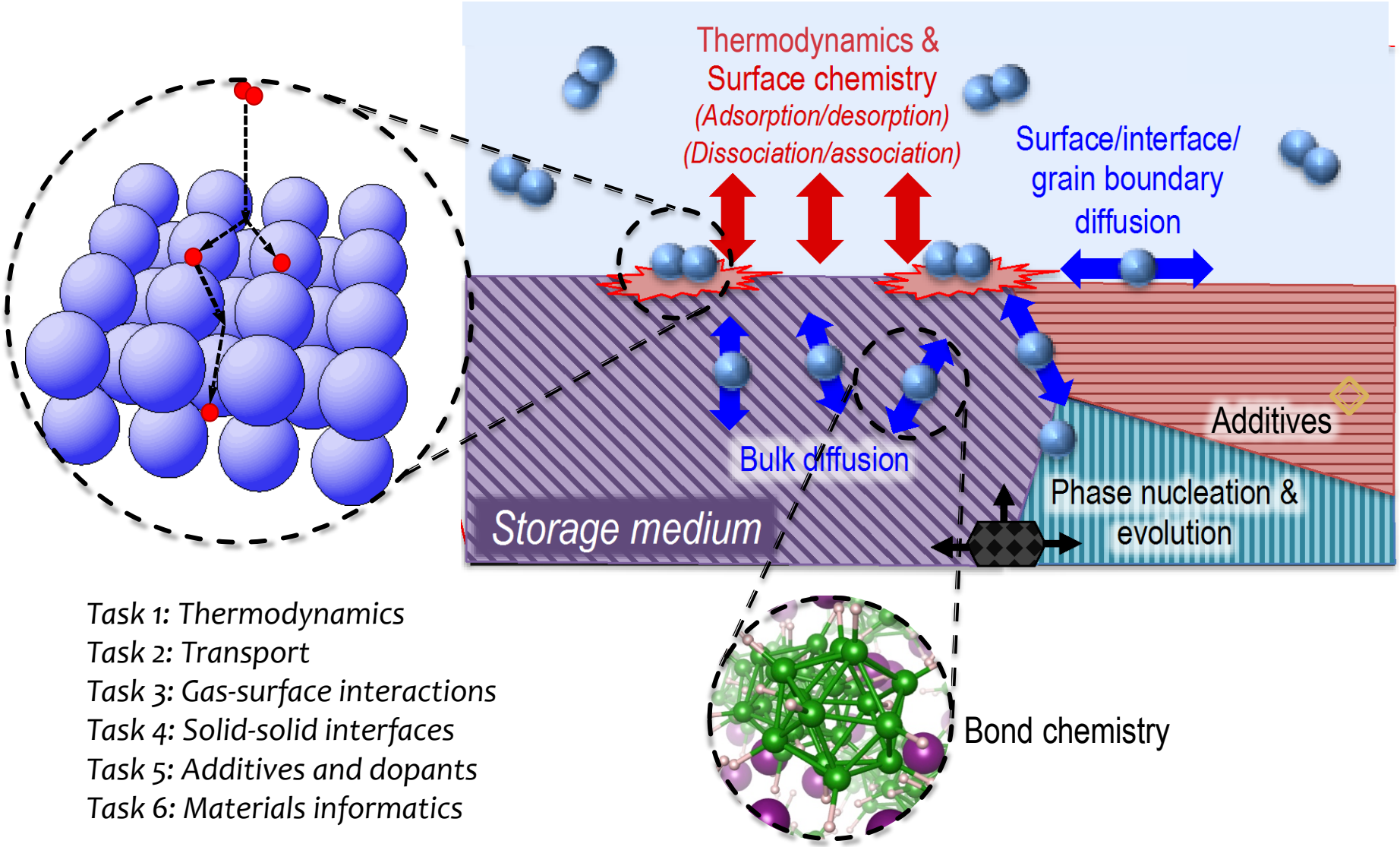
- Metal organic frameworks (MOFs)
- Hierarchical integrated bulk and nanoscale metal hydrides
- High-pressure synthesis
- Functionalized carbon encapsulants and **porous nanoconfining media**
- Sorbent suite for model testing and validation

In situ characterization



- Ambient-pressure XPS for gas-surface interactions
- **Soft X-ray absorption and emission spectroscopy**
- Electron microscopy and X-ray spectromicroscopy
- Low-energy ion scattering for surface hydrogen detection

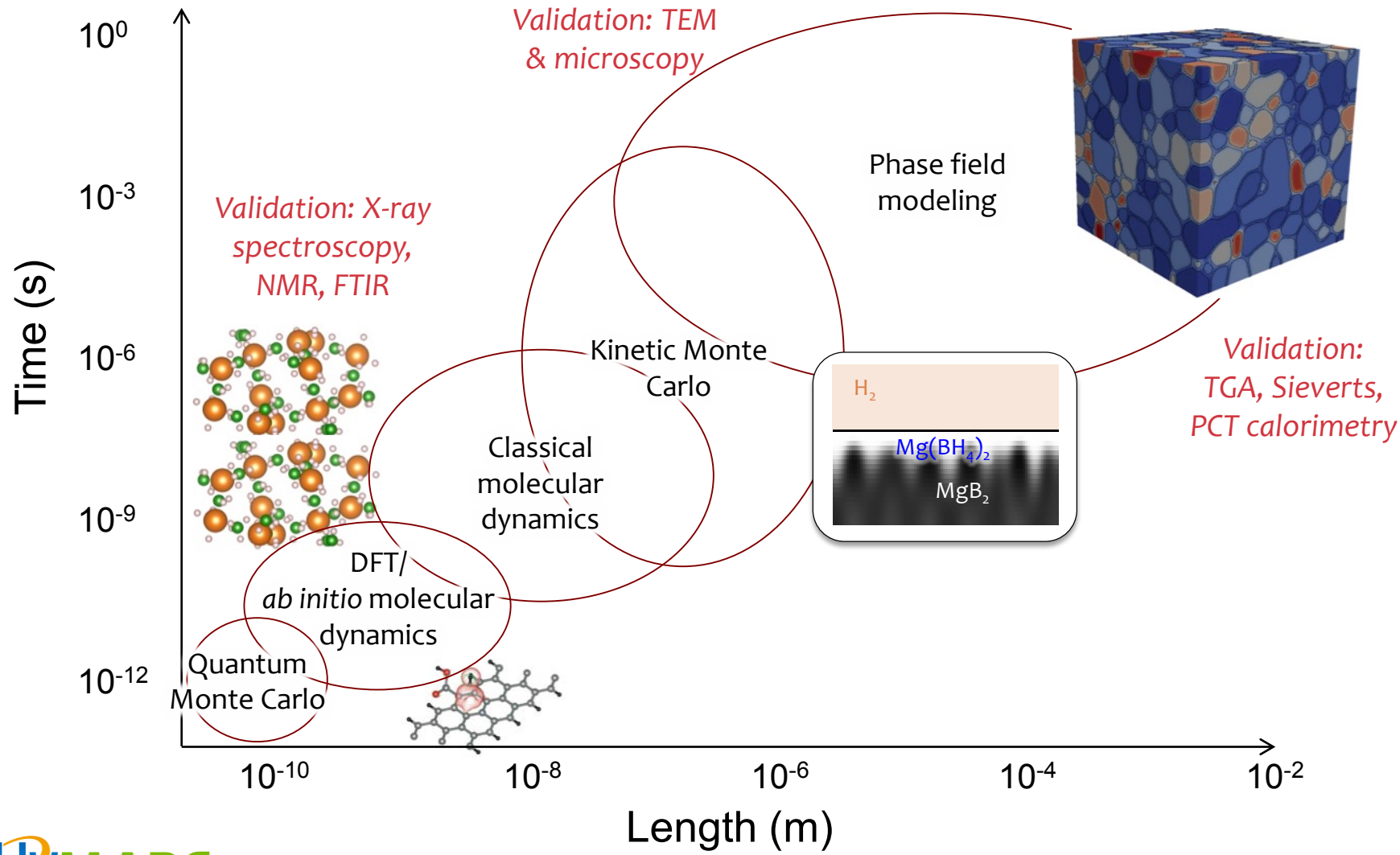
Approach: HyMARC tasks target thermodynamics and kinetics



Task 1: Thermodynamics
Task 2: Transport
Task 3: Gas-surface interactions
Task 4: Solid-solid interfaces
Task 5: Additives and dopants
Task 6: Materials informatics

Approach: Validated multiscale modeling

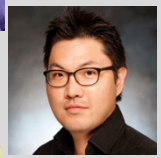
Modeling approach focuses on integrating techniques at multiple scales to tackle complexities of **"real" (beyond-ideal) materials**



LLNL contributions to HyMARC

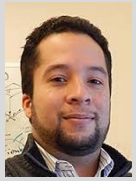
Multiscale modeling

DFT & ab initio molecular dynamics: Brandon Wood



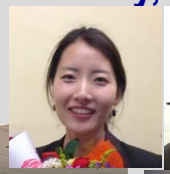
Phase-field mesoscale kinetic modeling: Tae Wook Heo

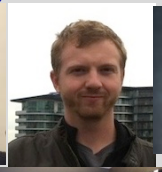
Kinetic Monte Carlo: Stanimir Bonev

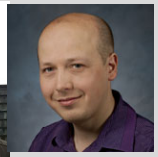


Quantum Monte Carlo: Miguel Morales

Postdocs: ShinYoung Kang, Keith Ray, Roman Nazarov, Patrick Shea



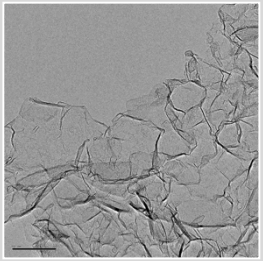




Porous carbon synthesis

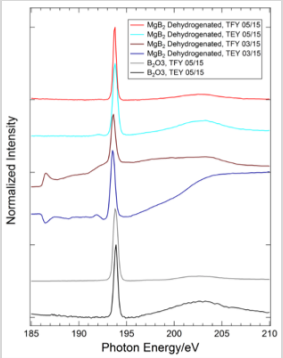
Ted Baumann

Pat Campell



X-ray absorption/emission

Jon Lee



Progress towards milestones with key LLNL FY16 activities

Q1: (S) Synthesize library of bulk-phase model storage systems for T1-T5
Task 1: Synthesize and characterize high-surface area carbon frameworks with pore sizes < 2 nm (100%)

Q2: (S) Demonstrate size control method for one prototype complex hydride nanostructure
Task 1: Perform sensitivity studies to determine design rules for nanoconfined metal hydrides (50%)

Q3: (C) Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating
Tasks 3 & 5: Performed XAS spectroscopy of hydrides and dopants at LBL/ALS, SLAC, and Canadian Light Source (75%)

Q4: (C+T) Identify hydride mobile species and diffusion pathways
Task 2: Perform ab initio molecular dynamics of surface and bulk model hydrides (80%)
Task 2: Gather defect formation energies and migration barriers for model materials (70%)
Task 2: Construct initial KMC framework for interface/amorphous transport (100%)
Task 3: Compute H_2 dissociation energetics on model surfaces (75%)
Task 3: Construct initial microkinetic model for surface reactions (100%)
Task 4: Construct initial phase-field modeling code for solid-solid interface kinetics (100%)

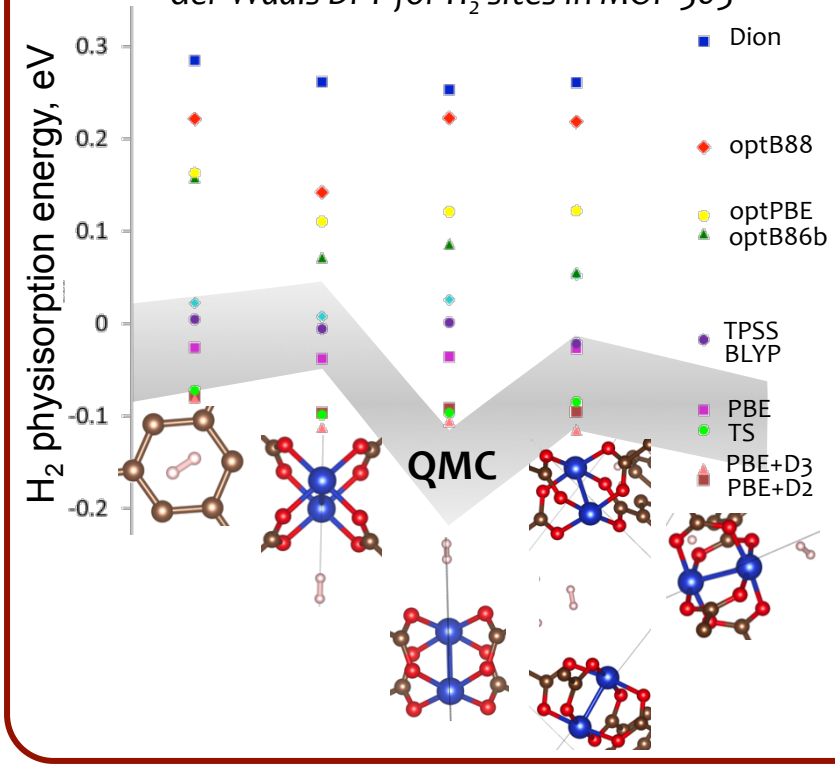
Q4: (S+C) Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, > 10 nm for one prototype hydride
Tasks 1-5: Select model materials for facilitating experiment-theory feedback within each Task (100%)

Task 1 Accomplishment: Accurate sorbent energetics

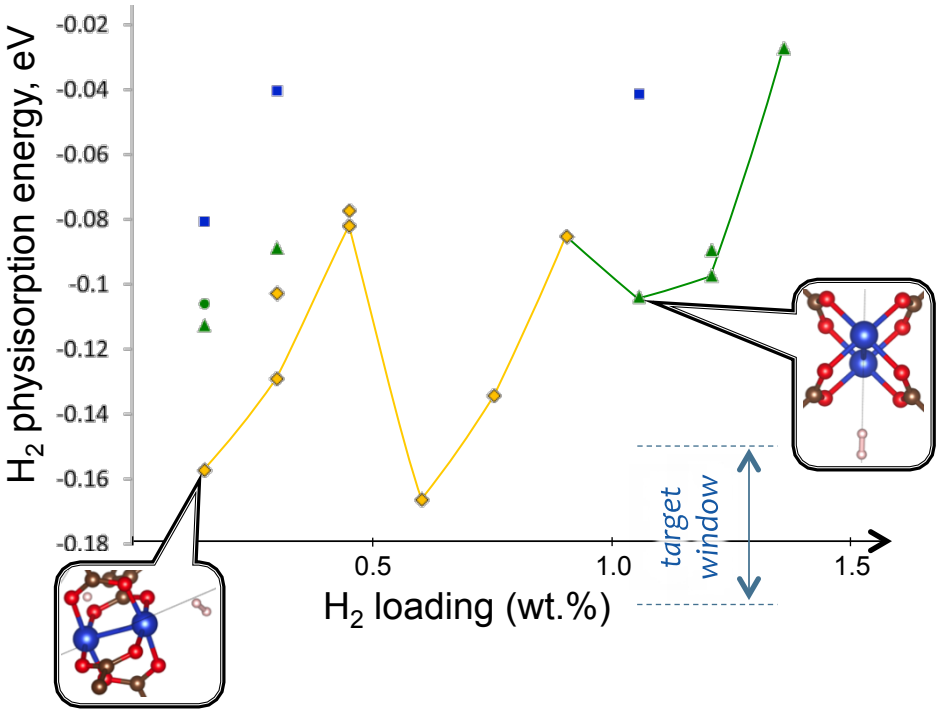
Quantum Monte Carlo (QMC) has been demonstrated as a viable approach for improving and bechmarking the accuracy of predicted H_2 sorption on model MOFs

DFT functionals give very disparate energies, but geometries are reliable and can be used as QMC inputs

Benchmarking QMC vs. flavors of van der Waals DFT for H_2 sites in MOF-505



Selecting appropriate DFT approximations for higher-pressure loading with multiple H_2 adsorption sites



Will also be used to parameterize classical potentials for future materials screening (Task 6) and predict isotherms that can compare against Sandia measurements

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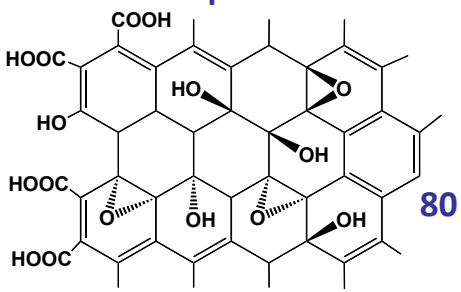
Task 1 Accomplishment: Porous carbon synthesis

Progress in reproducible synthesis pathways for carbons with tailored porosity & chemistry

Graphene oxide-derived synthesis procedure

GO suspension



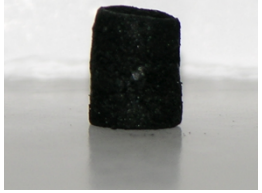
Catalyst

80 °C, 24-72 h

Drying

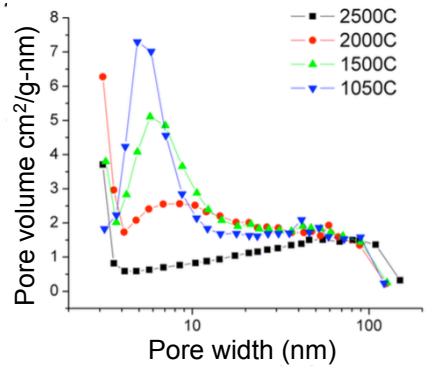
1050°C, N_2

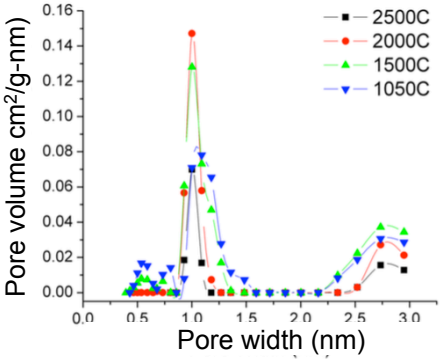
3D graphene macroassembly



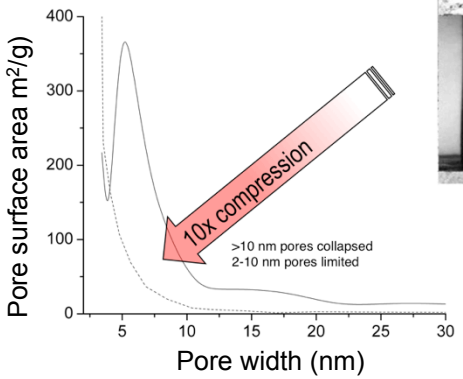
sp^2–C cross-linkers
Minimal O-functionality

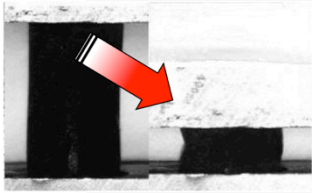
High-T heat treatment can reduce pore size and increase pore monodispersity while improving crystallinity





10X compression can remove larger pores without damage





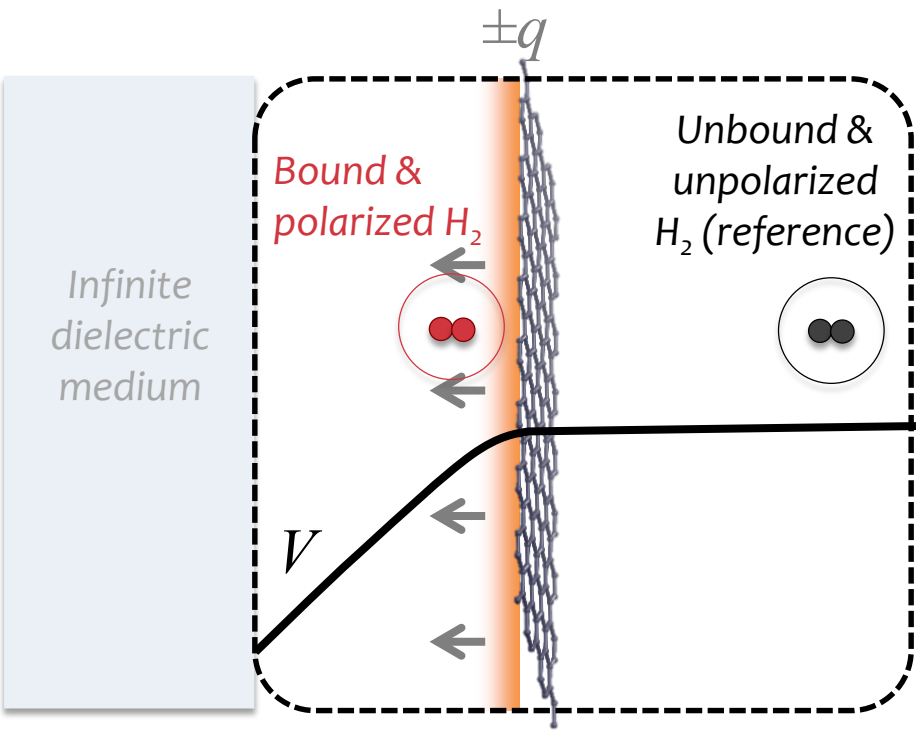
Heat-treated and compressed samples delivered to Sandia for high-pressure gas sorption measurements for benchmarking isotherm predictions

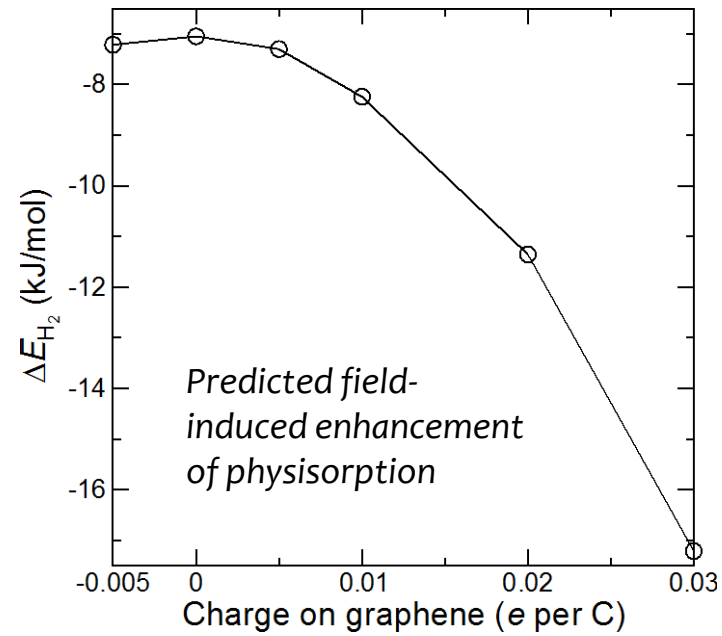
J. Am. Chem. Soc. **132**, 14067 (2010); *J. Phys. Chem. Lett.* **2**, 921 (2011); *ACS Nano*. **2014**, *8*, 11013–11022

Task 1 Accomplishment: Modeling sorbent charge/field effects

Developed first-principles modeling framework for simulating charge and field effects on H_2 physisorption on conductive sorbents for guiding synthesis

Uses Effective Screening Medium Method to compute physisorption as function of Fermi level*





Can be applied to functionalized materials and any 2D conductive sorbents, and will be used to assess polarization effects in HyMARC experiments

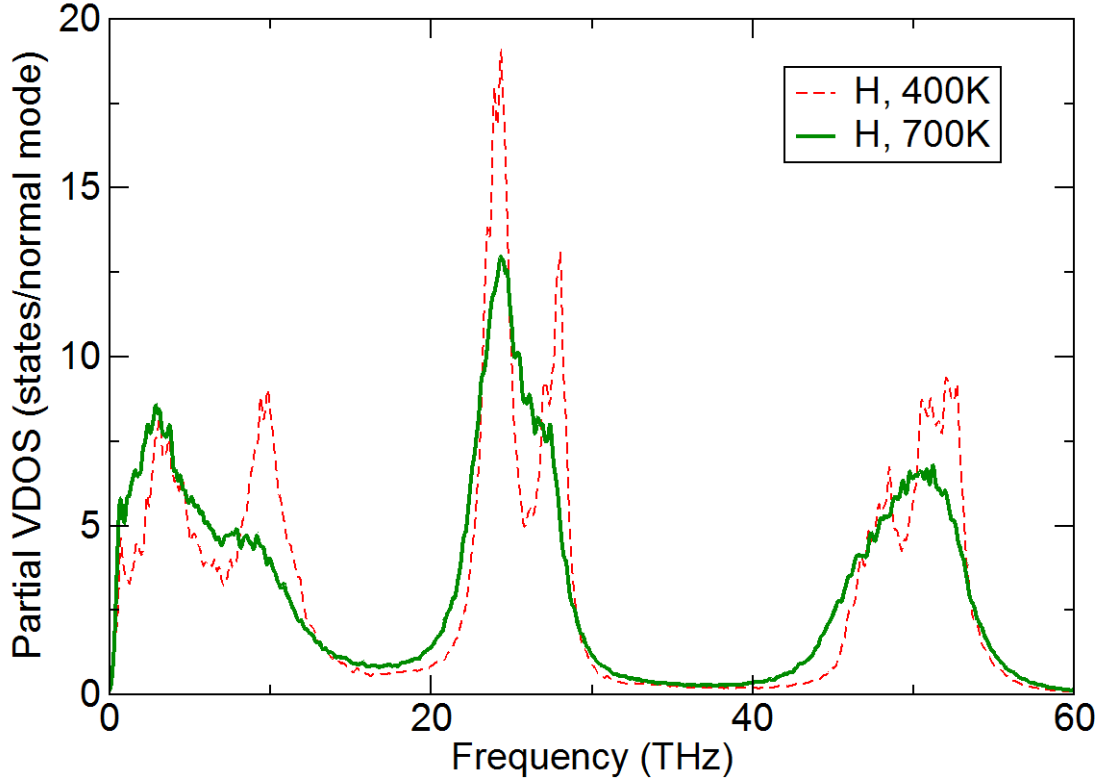
*Otani & Sugino, *Phys. Rev. B* **73**, 115407 (2006)

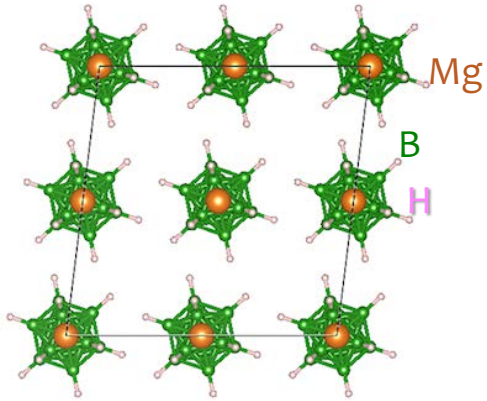
Task 1 Accomplishment: More accurate hydride thermodynamics

Established protocols for more accurate DFT computations of hydride thermodynamics that can improve predictive power beyond established methods by accounting for:

- *Dynamical (anharmonic) contributions to free energy via explicit finite-T simulations*
- *Microstructure, including phase coexistence and interface/surface contributions*
- *Phase morphology & nucleation: dispersed molecular defects vs. amorphous vs. crystalline*

Anharmonic molecular modes in I-m42 $(MgBH_4)_2$ from ab initio molecular dynamics

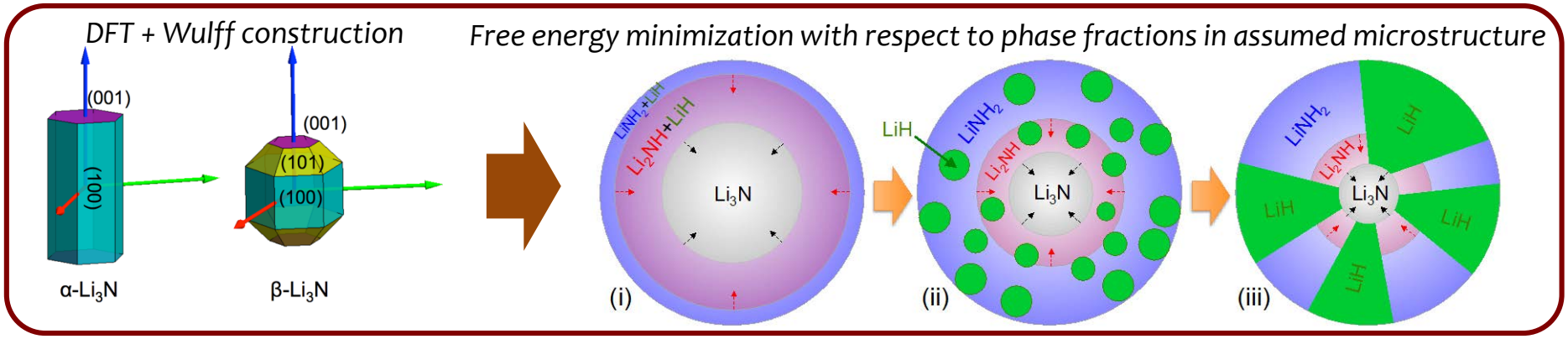




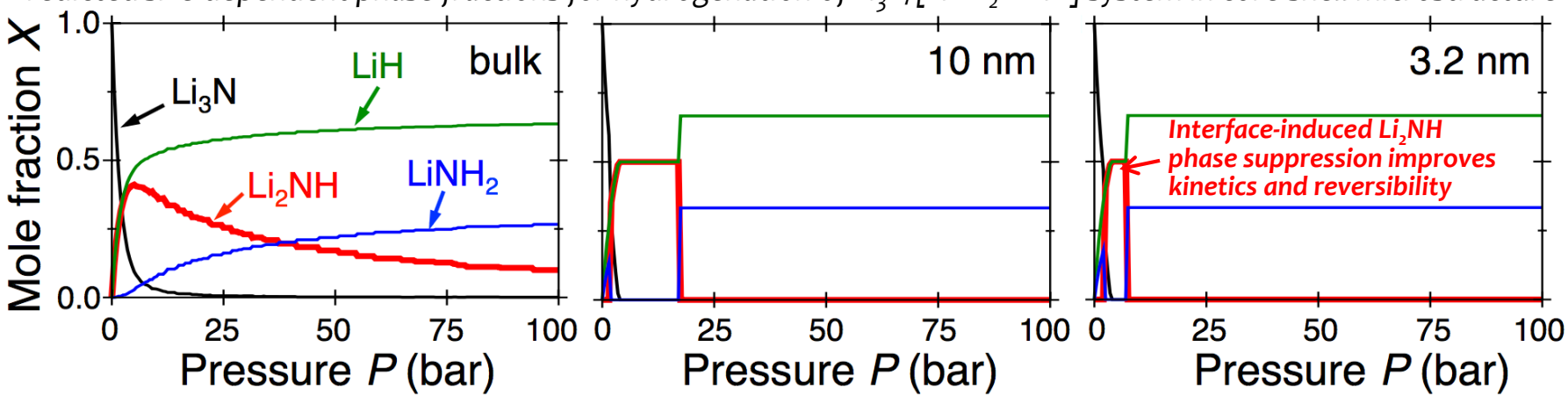
Results: Anharmonic modes can contribute as much as 12 kJ/mol in some predicted phases of $Mg(BH_4)_2$, which could alter phase stability

Task 1&4 Accomplishment: Hydride phase fraction predictions

*Demonstrated thermodynamic phase fraction prediction as a function of pressure, temperature, and size, accounting for **microstructure, phase coexistence**, and **nucleation***



Predicted size-dependent phase fractions for hydrogenation of $Li_3N/[LiNH_2+2LiH]$ system in core-shell microstructure



Successfully predicted Sandia-measured reaction pathway in nanoconfined Li-N-H and confirmed relevance of interfaces in determining phase stability

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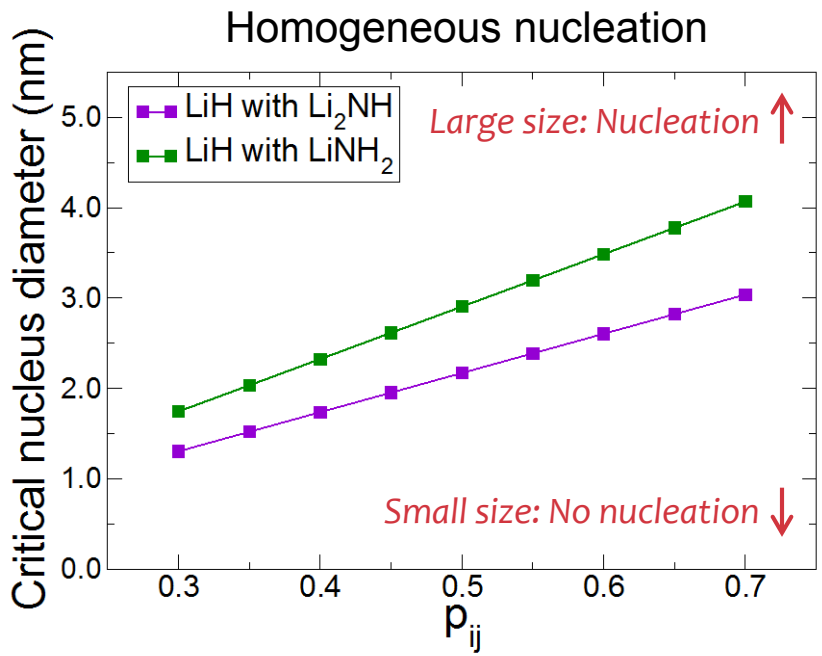
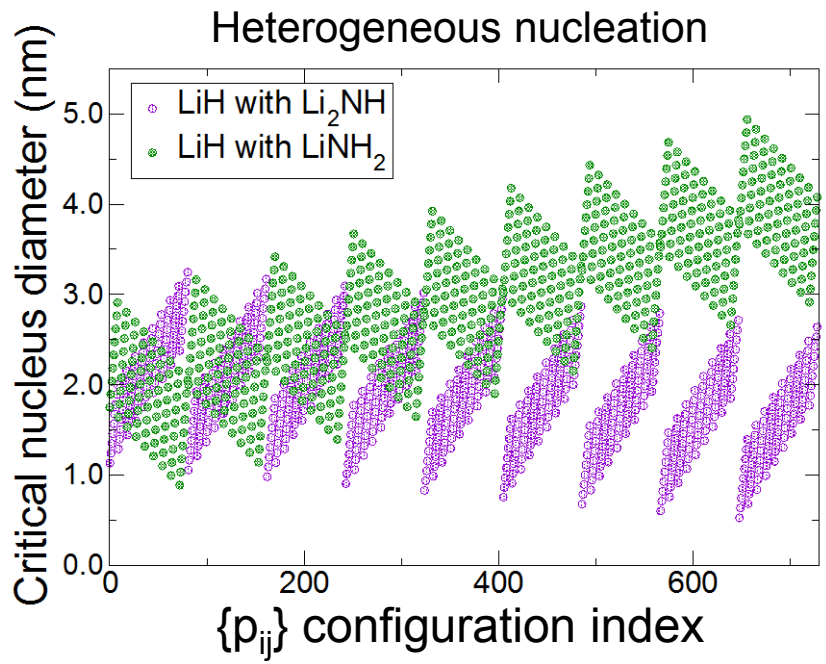
Task 1,4&5 Accomplishment: Phase nucleation in hydrides

Computed critical nucleus sizes for model hydrides to guide nanoscale synthesis as a means of kinetically suppressing undesirable intermediate phases

Interface energy approximation: $\gamma_{ij} = p_{ij} \cdot (\sigma_i + \sigma_j)$

LiH nucleation during hydrogenation of the $Li_3N/[LiNH_2+2LiH]$ system





Computed critical nucleus size for Li-N-H and Mg-B-H systems, including intermediates

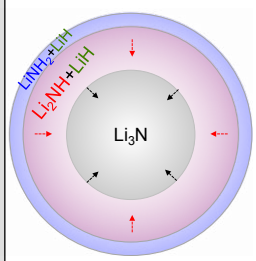
Task 1,4&5 Accomplishment: Statistical approach to interfaces

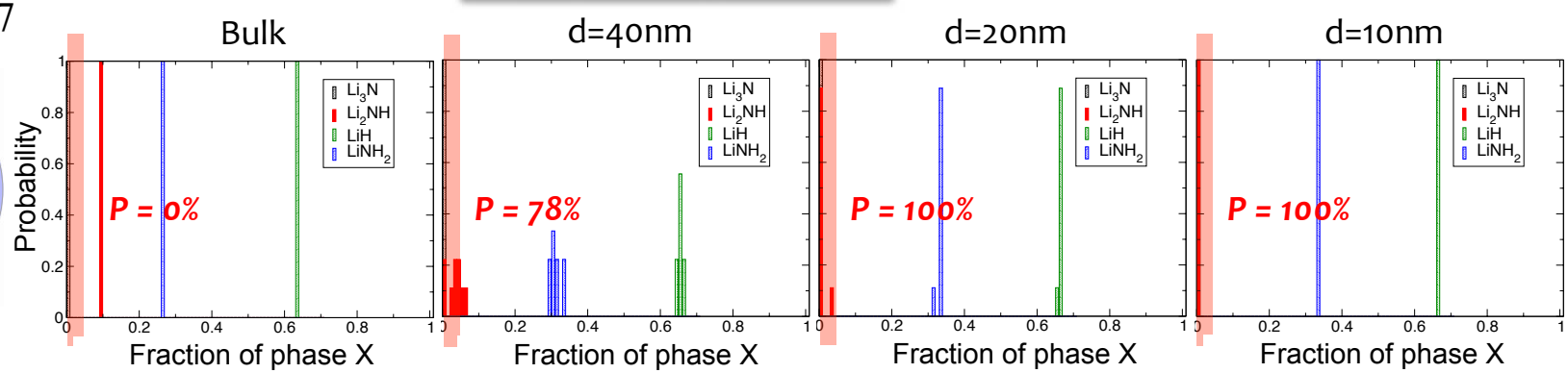
Demonstrated non-equilibrium statistical approach to quantify effects of non-ideal interfaces and additives on reaction pathways

Probability P of Li_2NH phase suppression in nanoscale $[LiNH_2+2LiH]/Li_3N$ sampled over interfacial energies

Hydrogenation (@P=100bar)

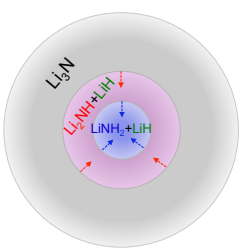
$0.3 \le p_{ij} \le 0.7$

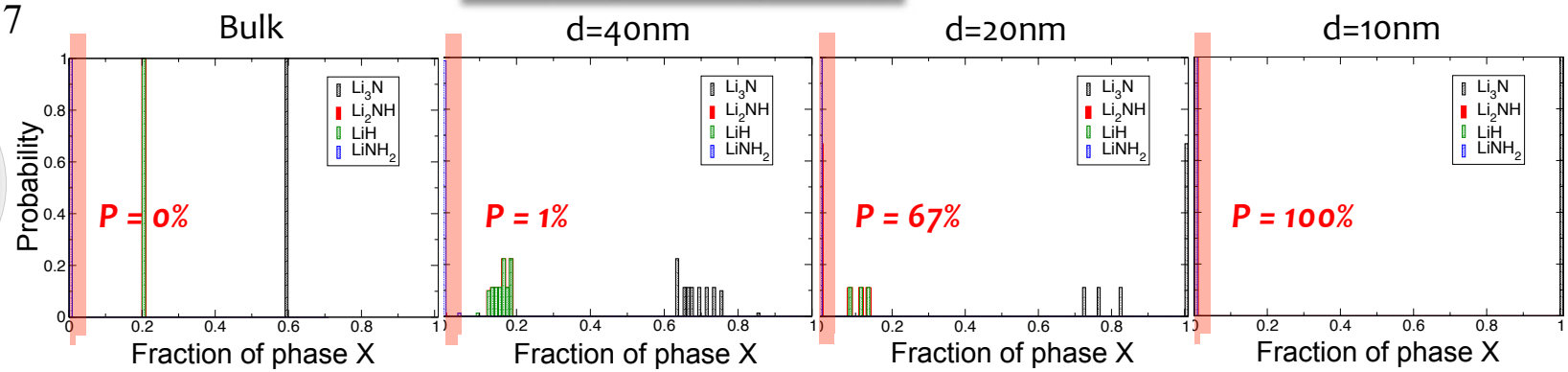




Dehydrogenation (@P=1bar)

$0.3 \le p_{ij} \le 0.7$





Sensitivity analysis can steer towards most promising engineering avenues

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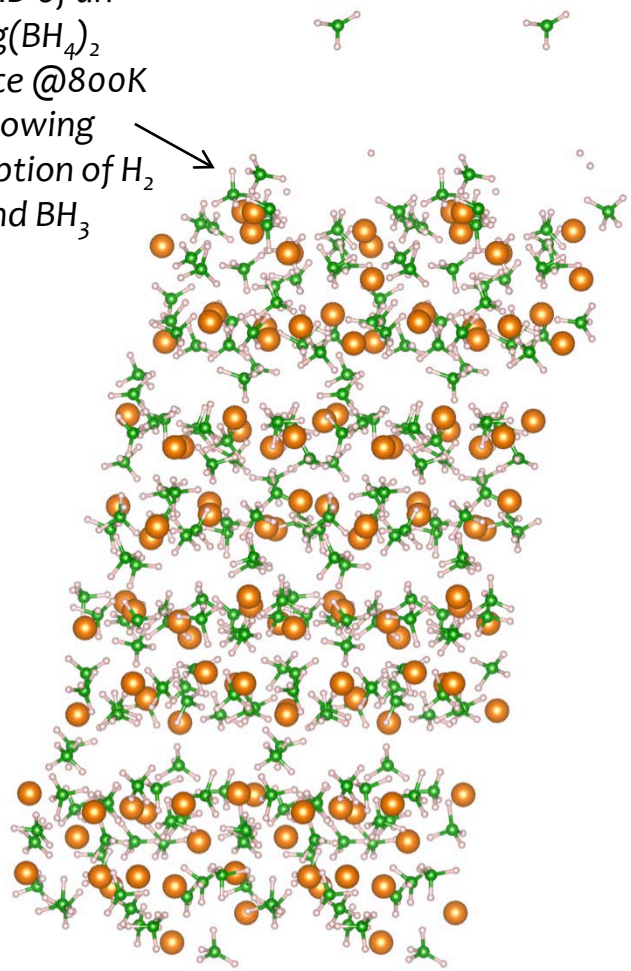
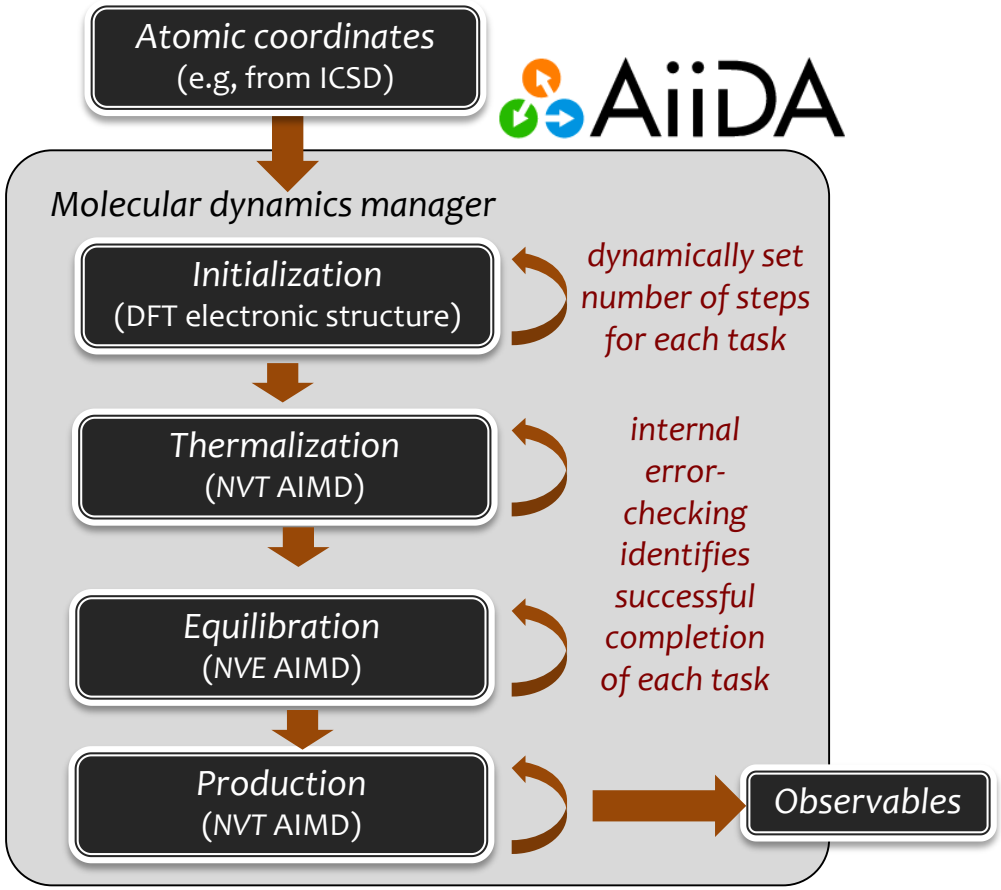
Task 2 Accomplishment: *Ab initio* molecular dynamics (AIMD)

AIMD is being used to elucidate transport/reaction pathways and enable finite-temperature calculations of thermodynamic and spectroscopic quantities

AIMD of an $Mg(BH_4)_2$ surface @800K showing desorption of H_2 and BH_3



Established software framework for automating AIMD, to be integrated within open-source AiiDA task management engine

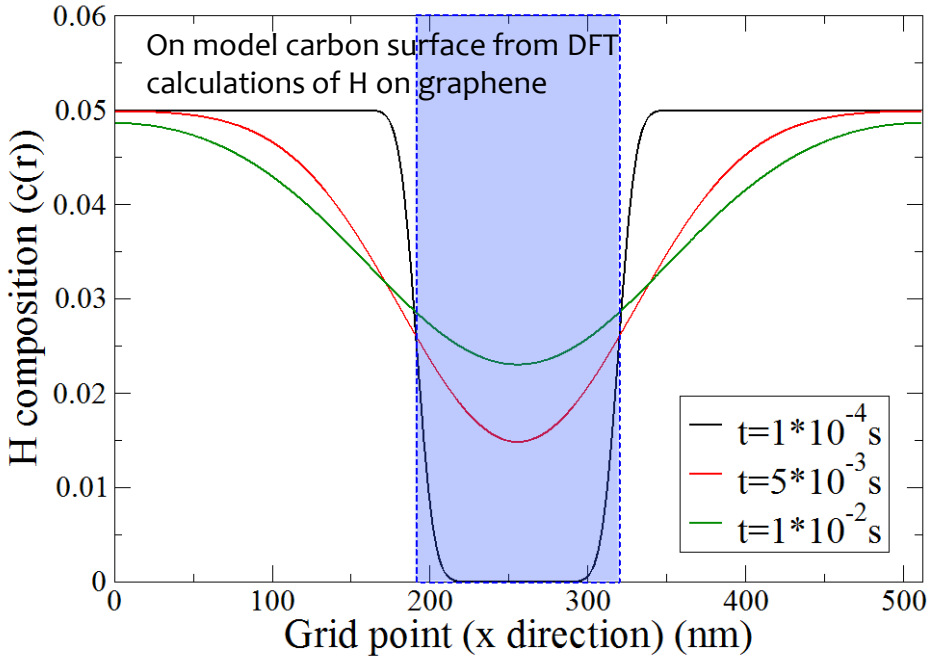


Task 2&3 Accomplishment: Multiscale surface hydrogen kinetics

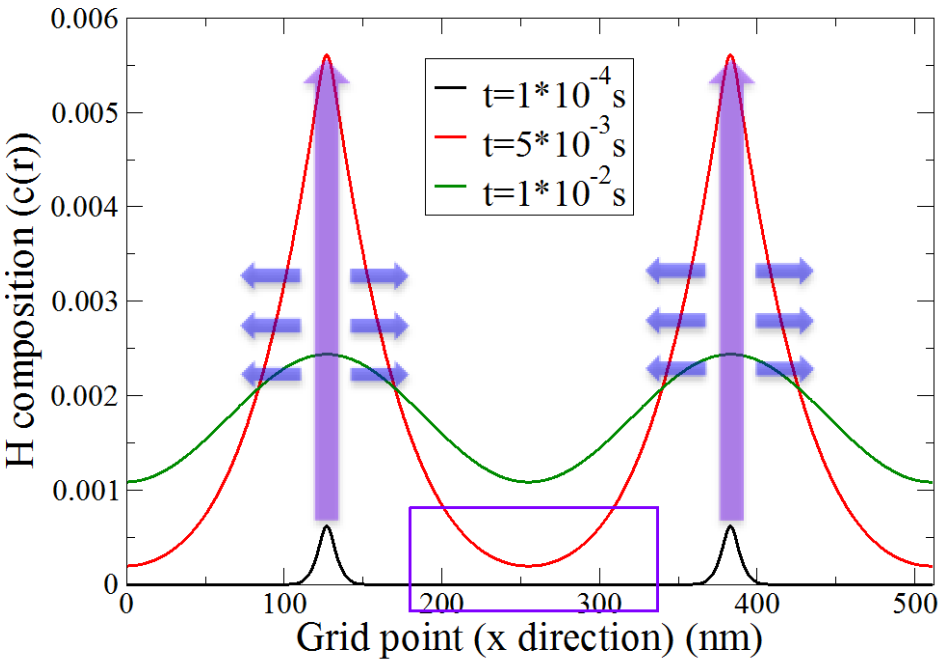
Demonstrated multiscale modeling of surface dissociation and diffusion of hydrogen by synthesizing DFT and continuum approaches

$$\frac{\partial c}{\partial t} = \vec{\nabla} \cdot D(r)\vec{\nabla} c + \psi(\vec{r}) j_0$$

Surface redistribution of atomic hydrogen



Surface dissociation + diffusion

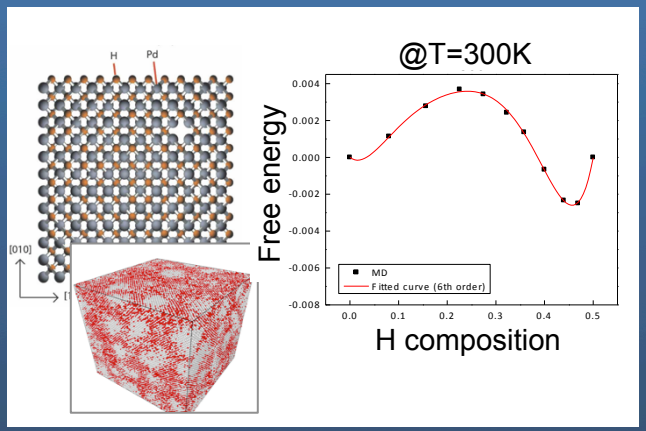


Combining with low-energy ion scattering (Sandia) to analyze surface diffusion

Task 4 Accomplishment: Solid phase transformation kinetics

Demonstrated coupled atomistic and mesoscale framework combining thermodynamics, mechanical stress, and phase nucleation/growth to model solid phase transition kinetics

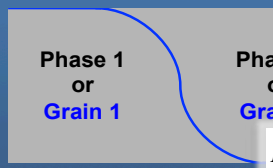
DFT (LLNL) + Molecular dynamics (Sandia)



Parameters

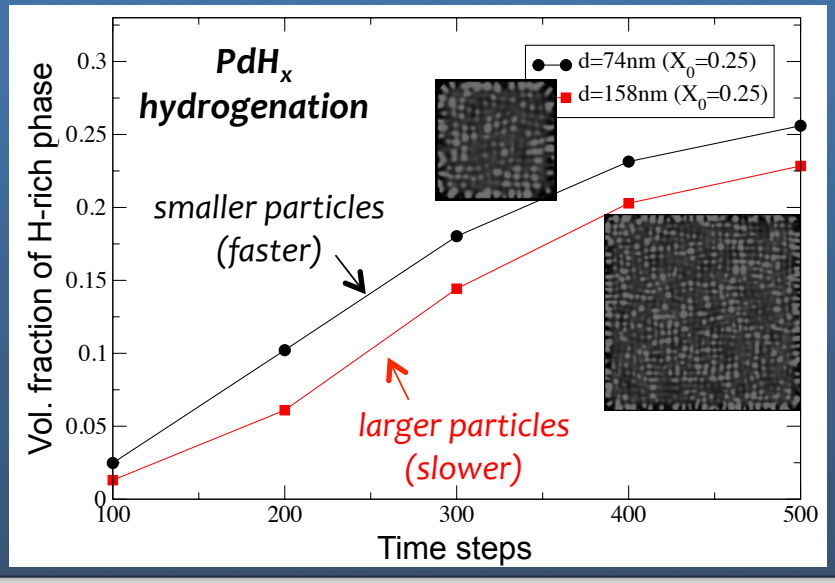
Bulk free energy, interfacial energy, elasticity, diffusivity

Phase-field modeling code (LLNL)



$$F = \int dV[f(\eta, X, \ldots) + (\text{gradient energy}) + (\text{elastic energy}) + \ldots]$$

Phase kinetics & comparison with LBNL experiments



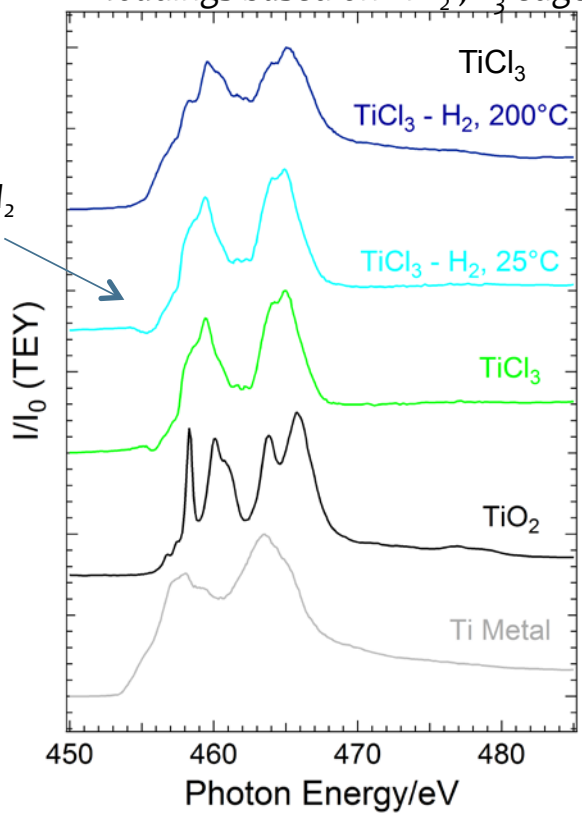
- *Successfully demonstrated application to model interstitial hydride (PdH_x); now adapting to MgH_2 based on DFT (LLNL) + classical MD (Sandia)*
- *Comparisons with LBNL experiments on encapsulated hydrides show predictions capture size-dependent kinetic behavior*

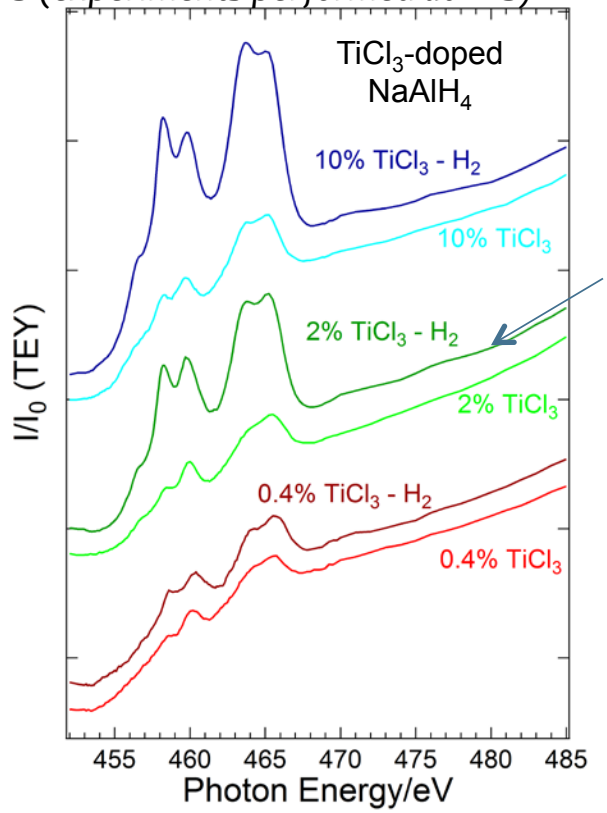
Task 3&5 Accomplishment: XAS spectroscopy of hydrides

Demonstrated X-ray absorption spectroscopy (XAS) for probing catalyst chemistry and surface vs. bulk hydrogenation effects on catalysts within doped hydrides

Hydrogenation effects of $TiCl_3$ and $TiCl_3$-doped $NaAlH_4$ with varying catalyst loadings based on Ti L_2-, L_3-edge XAS (experiments performed at ALS)

Pure $TiCl_3$ unaffected by H_2 exposure





H_2-induced chemical changes signaled by dramatic change in signal strength (i.e., surface conc.)

XAS results on Na-Al-H and Mg-B-H systems are used to devise more realistic surface hydrogenation models, which can be directly validated by computing XAS (LBNL)

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External collaborations

Collaborations are crucial for realizing HyMARC goals

- NMR and borohydride chemistry: T. Autrey, M. Bowden, B. Ginovska-Pangovska (PNNL; H_2 Storage Characterization Group)
  - *Several discussions, plus site visits in November 2015 and April 2016*
  - *HyMARC will focus on solid-state aspects and PNNL on borohydride chemistry*
- Neutron diffraction/spectroscopy: T. Udovic (NIST)
- DFT computations of H_2 physisorption on MOFs: M. Head-Gordon (LBNL; H_2 Storage Characterization Group)
- Li-N-H system: N. Poonyayant, N. Angboonpong, and P. Pakawatpanurut (Mahidol University, Thailand)
- Kinetic Monte-Carlo for solid-state diffusion: H. Kreuzer (Dalhousie U.)

Also extensive collaborations within HyMARC

Remaining challenges/barriers & mitigation strategies

- **Understanding internal microstructure evolution is challenging**
  - *Working with HyMARC team and collaborators to develop protocols for imaging low-Z materials with minimal beam damage*
  - *Focusing early efforts on materials (e.g., MgH_2) that can be more easily characterized*
- **Phase transformations of complex hydrides combine composition & phase changes, yet we are currently treating these separately**
  - *Separate treatment allows each to be independently validated, but integration of both will be explored in collaboration with the $Mg(BH_4)_2$ individual FOA project in FY17*
- **Need better validation of thermodynamics and transport for amorphous materials**
  - *Working with HyMARC team to synthesize amorphous materials for testing our amorphous transport and thermodynamics theory framework*
- **Improved interface energy estimates are desirable**
  - *HyMARC data will be used to benchmark new approaches for dealing with chemical and elastic contributions to the interface free energy*
  - *Statistical approach allows us to quantify robustness of predictions with respect to interface energy assumptions*
- **QMC needs reliable input geometries for sorbent energetics**
  - *HyMARC will collaborate with M. Head-Gordon (LBNL, part of NREL-led consortium) to use high-throughput DFT with corrected functionals on clusters to obtain geometries*

Proposed future work

Milestone	Description & LLNL subtask	% complete
Q3 FY16	**Demonstrate in situ soft X-ray AP-XPS, XAS, XES tools with sample heating** *Perform synchrotron XAS/XES of hydrogenation on catalyzed materials*	100
Q4 FY16	**Identify hydride mobile species and diffusion pathways** *Compute defect formation energies and ab initio dynamics of mobile species in model systems*	25
Q4 FY16 SMART	**Synthesize library of nanoparticles: 1-5 nm, 5-10 nm, > 10 nm for prototype hydride** *Demonstrate porous carbon nanoconfining medium synthesis with controlled pore sizes*	50
Q1 FY17	**Compute H_2 binding curves by QMC**	15
Q2 FY17	**Perform sensitivity analysis of local binding and second-sphere effects**	0
Q2 FY17 G/NG	**Rank improvement strategies: open metal sites, acid sites, polarization effects, phase change materials** *Perform analysis of potential of open metal sites (via QMC), acid sites/polarization (via DFT), and phase change materials (thermodynamic analysis)*	25

Summary

- Integrated **theory/synthesis/characterization** framework of HyMARC aims to provide foundational understanding and new tools for solid-state hydrogen storage
- FY16 LLNL modeling tasks focused on establishing framework for **multiscale integration** and approaches for **beyond-ideal materials modeling**
- FY16 LLNL synthesis tasks focused on establishing key **strategies for tailored porous carbon**
- FY16 LLNL characterization tasks focused on **spectroscopic changes upon hydrogenation** (complements LBNL activities)
- Early feedback between experiments and theory on the Pd-H and Mg-H systems demonstrates **feasibility of multiscale (de)hydrogenation kinetics simulation**
- Will be moving towards testing on complex hydrides and more complicated sorbents in FY17

- **Flexible modeling, synthesis, and characterization protocols** are being developed in preparation for application to upcoming FOA projects

Thank you for your attention!

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