The Chemical Goldilocks Challenge for Transport and Storage of Hydrogen

SAND2020-11101PE

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

Mark D. Allendorf, Sandia National Laboratories

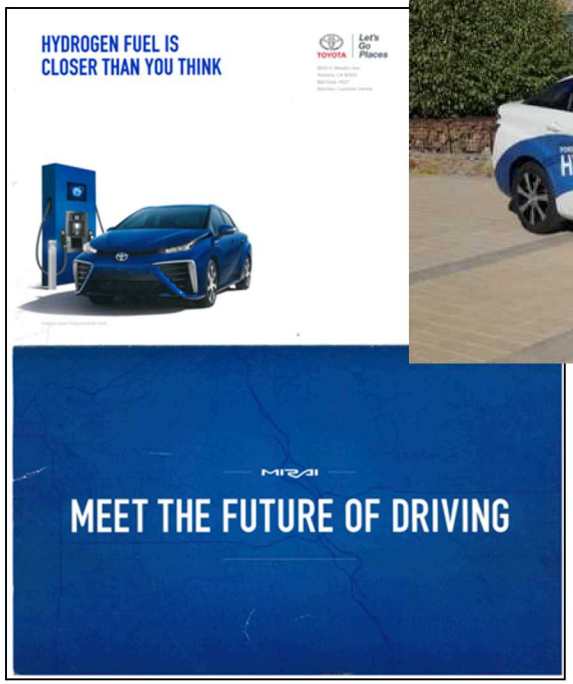
NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · Lawrence Livermore National Laboratory · Berkeley Lab · Pacific Northwest National Laboratory · NIST · SLAC National Accelerator Laboratory

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

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND_____

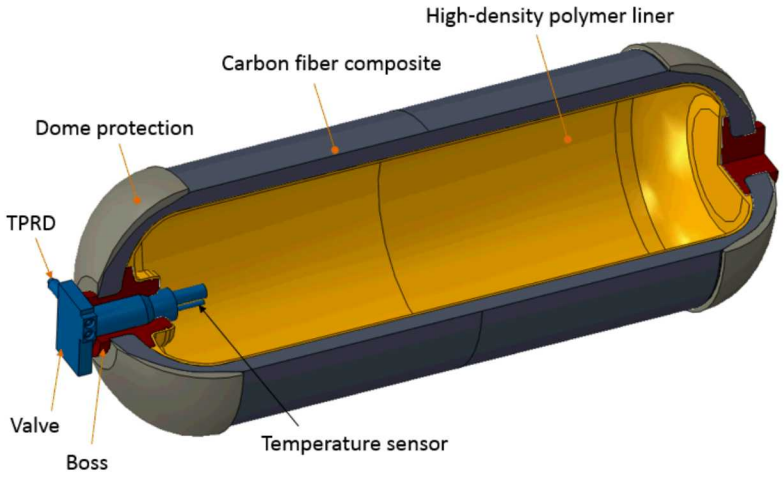
Hydrogen-powered cars are now commercially available



- 700 bar pressurized tanks
- 265 – 312 mile range
- Refueling stations being installed in some areas

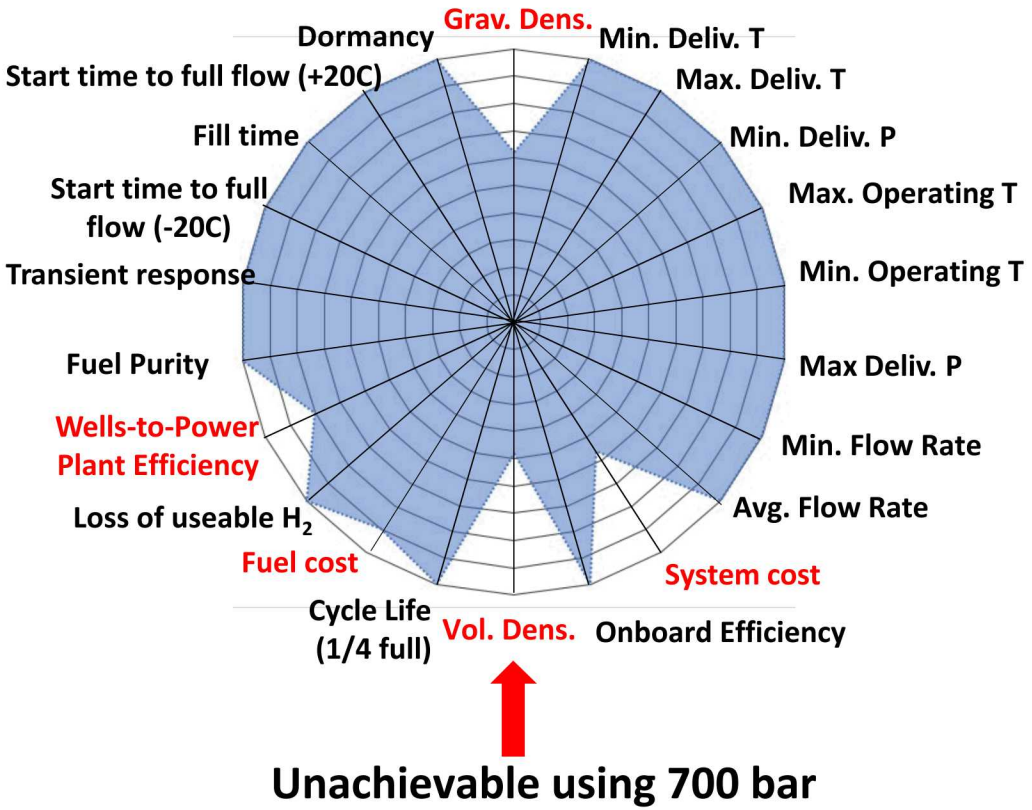
Although fuel cell vehicles are now commercially available, compressed H_2 storage falls short of several DOE targets

700 Bar Compressed Gas (2015 record) vs. revised DOE Ultimate Targets



TPRD = Thermally Activated Pressure Relief Device

Credit: Process Modeling Group, Nuclear Engineering Division. Argonne National Laboratory (ANL)



Unachievable using 700 bar

https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles

Efficient transport of hydrogen from point of production to fueling station is not possible using compressed gas

- 1 kg H_2 = 1 gallon of gasoline (~4 L)
- Steel tubes: 280 kg per tanker
- Somewhat better: Composite tanks: 550 kg of hydrogen at 250 bar
- Typical gas station stores 75,000 – 230,000 L (20,000 – 60,000 gallons)

Limitations of variable power inputs: the “duck chart”

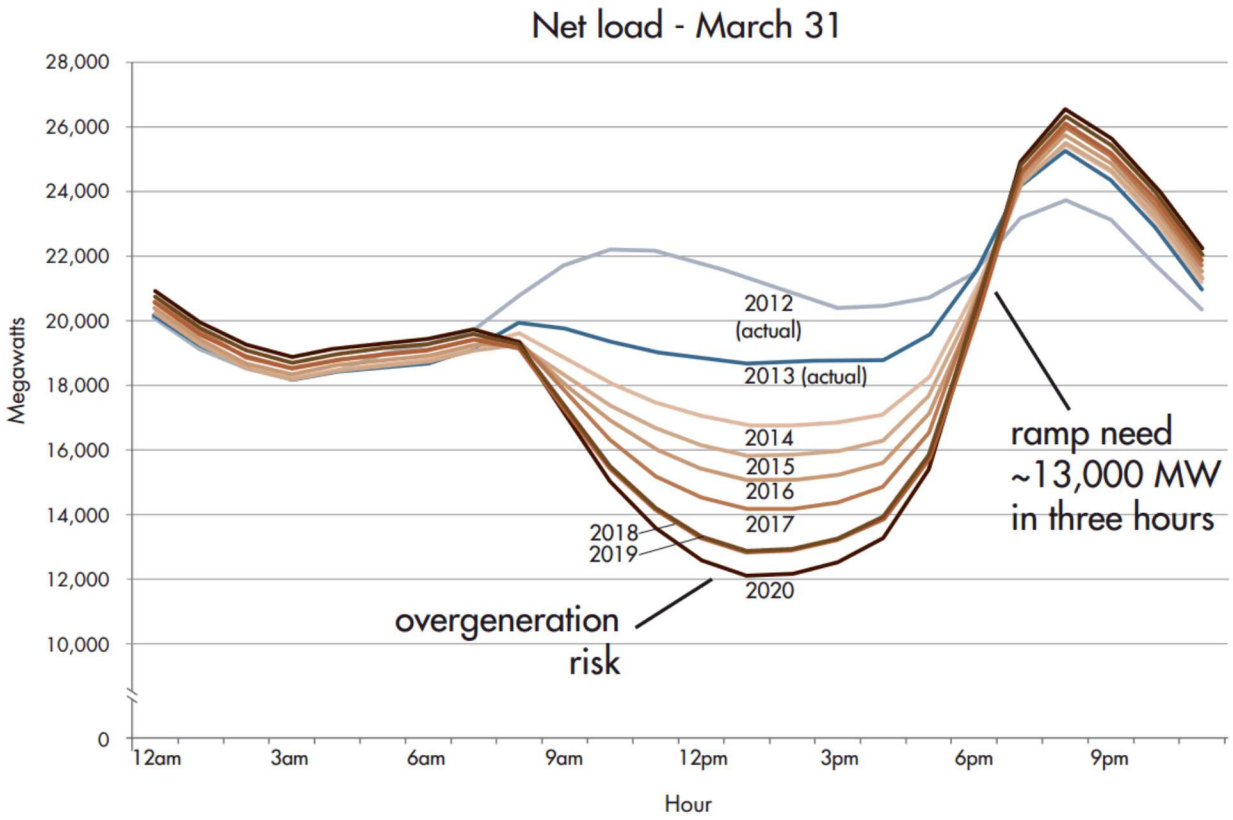


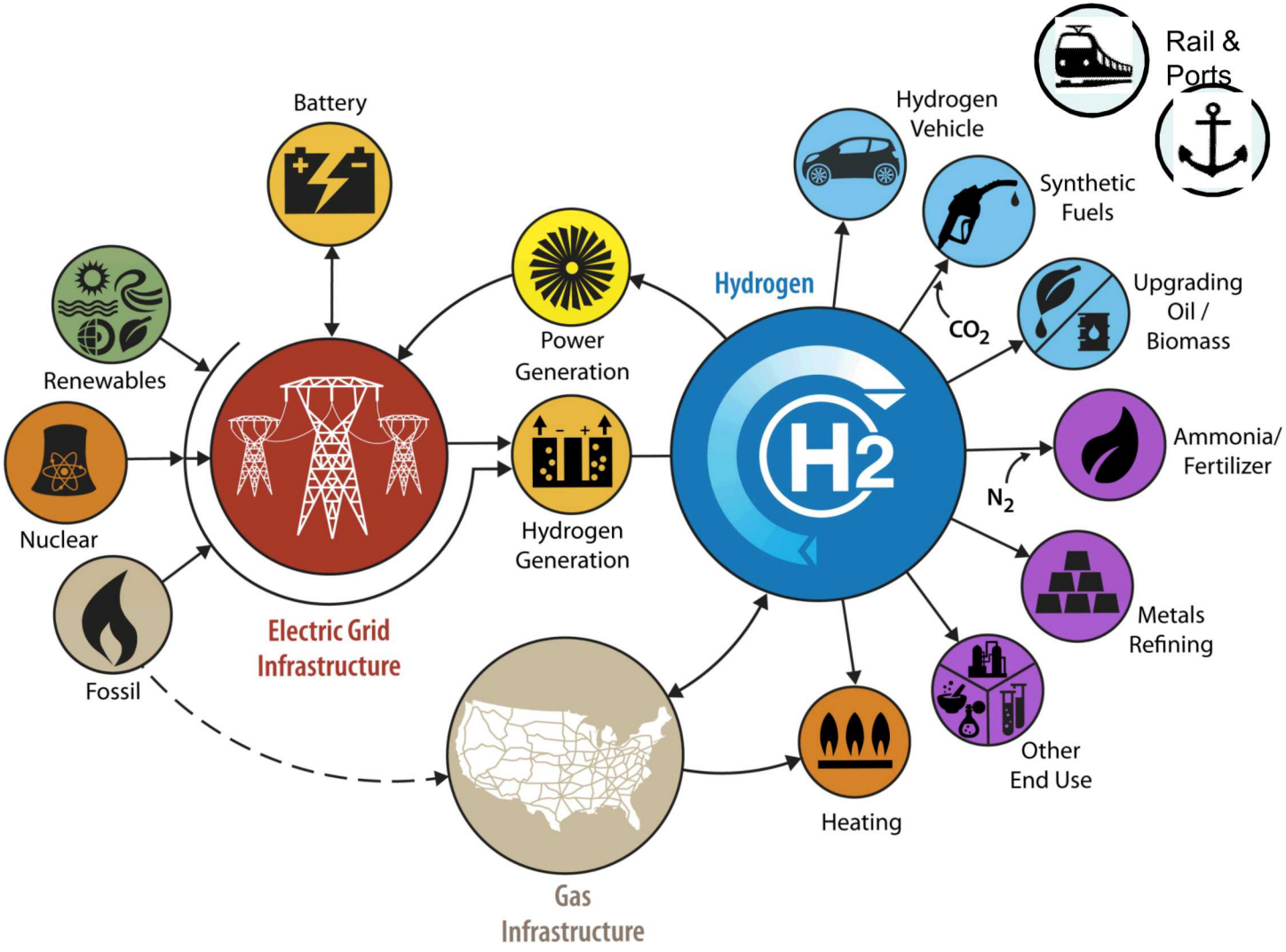
Figure 1. The CAISO duck chart

Source: CAISO 2013

Curtailment will lead to an abundance of low value electrons, and we need solutions that will service our multi-sector demands

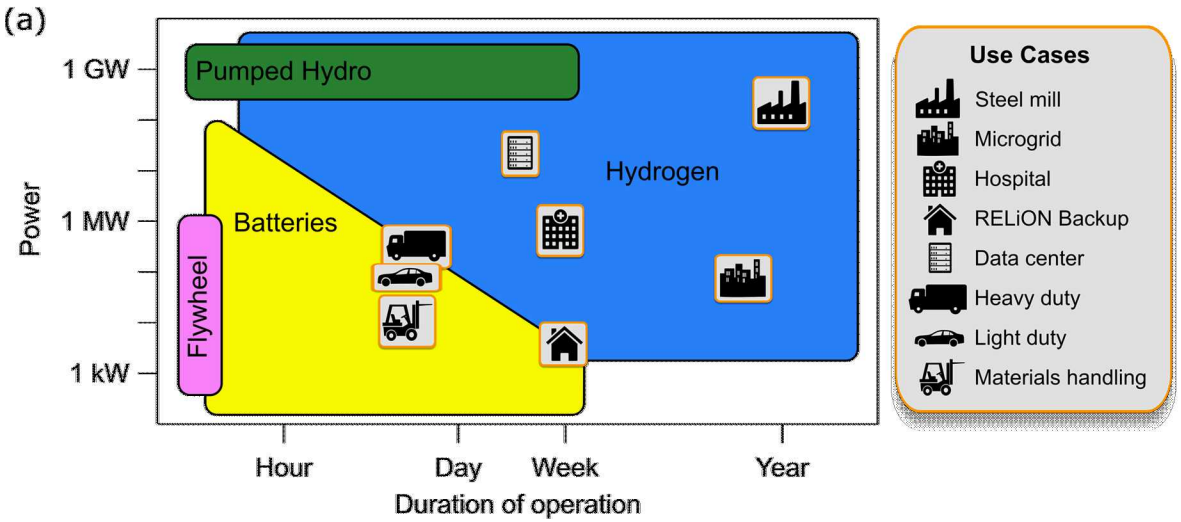
P. Denholm, P. et al. (2015) *Overgeneration from Solar Energy in California: A Field Guide to the Duck Chart* NREL/TP-6A20-65023

H_2@Scale: Hydrogen as an Energy Carrier



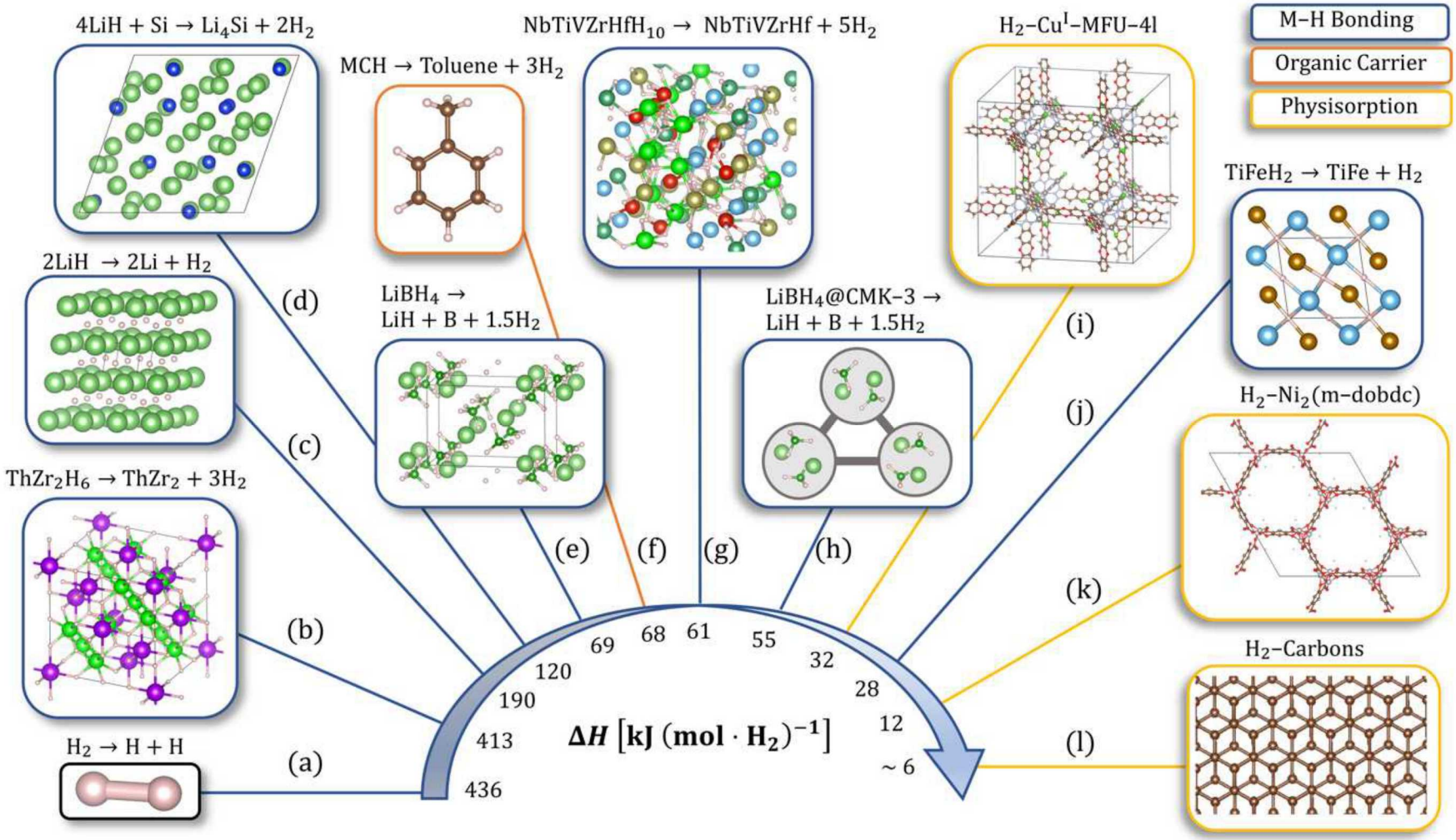
B. Pivovar et al. *Interface* 2018 **27**(1) 67

Hydrogen carriers illustrating a range of power and energy and hydrogen usage and storage requirements



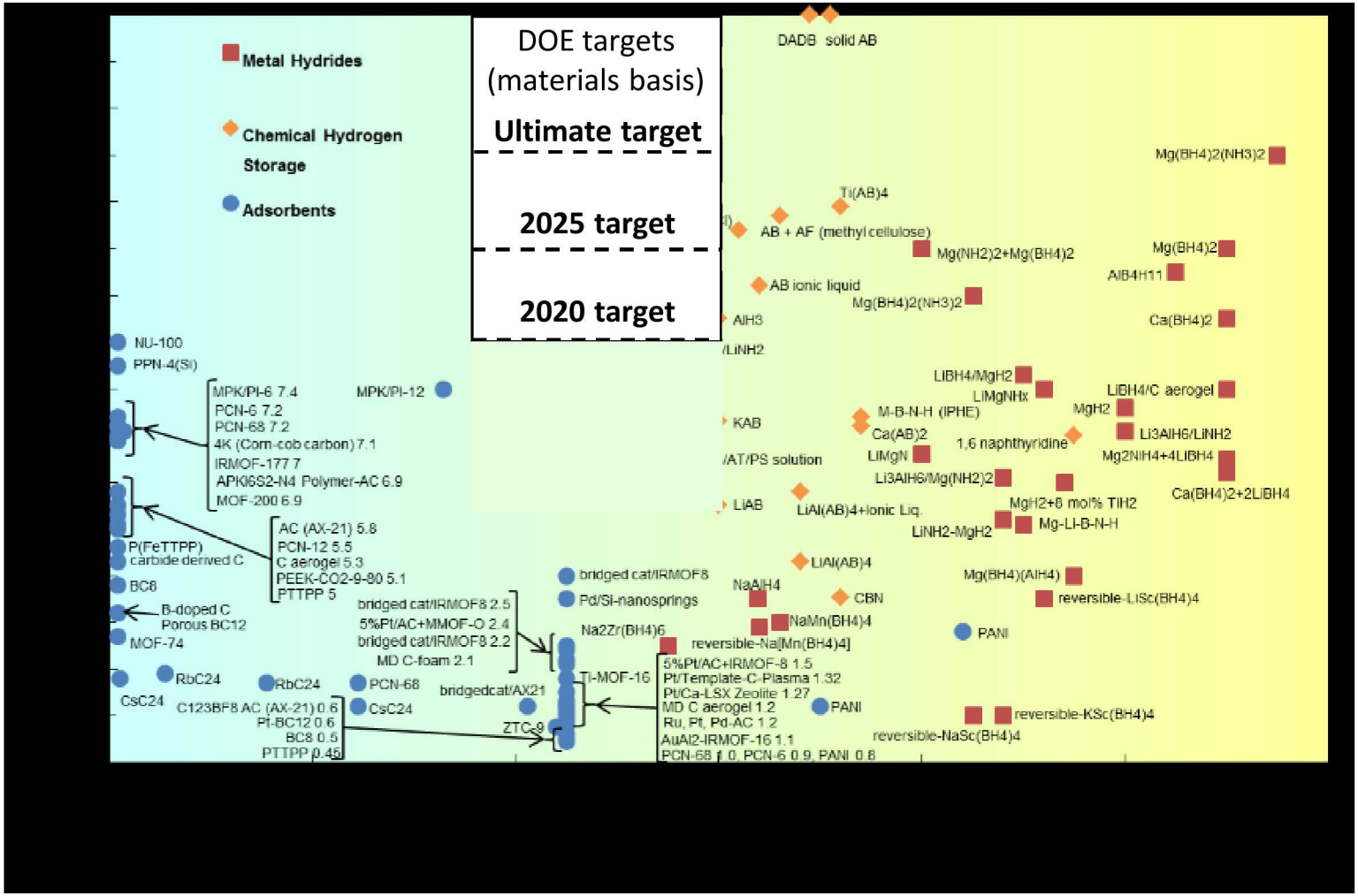
Use Case[a]	Relative Size	Power[b] (MW)	Energy[c] (MWh)	H_2 Usage[d] (kg/day)	Use Duration[e] (days)	H_2 Rate[f] (kg/hr)
Mobile Applications						
Light Duty Vehicle	Small	0.08	0.078	0.8	365	0.56
Long Haul Truck	Medium	0.24	0.83	60	365	5.4
High Speed Ferry	Large	4.9	17	2000	365	210
Regional Fuel Depot	Very Large	29	N/A	50 000	365	2000
Stationary Applications						
Telecom Backup	Small	0.003	0.2	4	3	0.17
Seasonal Microgrid Storage	Medium	0.027	85	39	130	1.6
Hospital Backup	Large	0.59	100	850	7	36
Data Center Backup	Very Large	20	1440	30 000	3	1250
Steel Mill DRI	Extreme	240	N/A	350 000	365	14 500

Activating hydrogen for storage or reaction: a continuum of length scales, morphologies, and reactivity



M. D. Allendorf et al. submitted for publication

2005-2013: 3 DOE/EERE-funded Centers of Excellence focused on materials discovery for light-duty vehicles

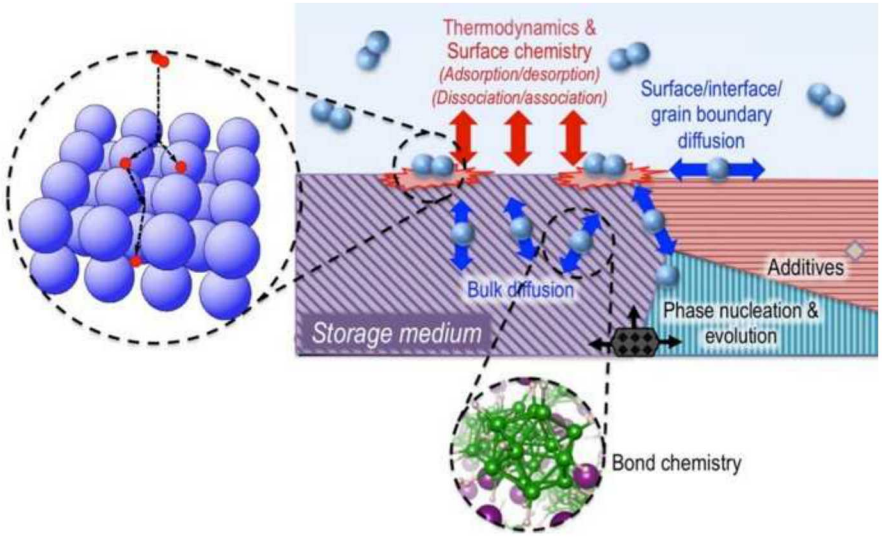


Hydrogen storage represents a thermodynamic "Goldilocks Challenge"

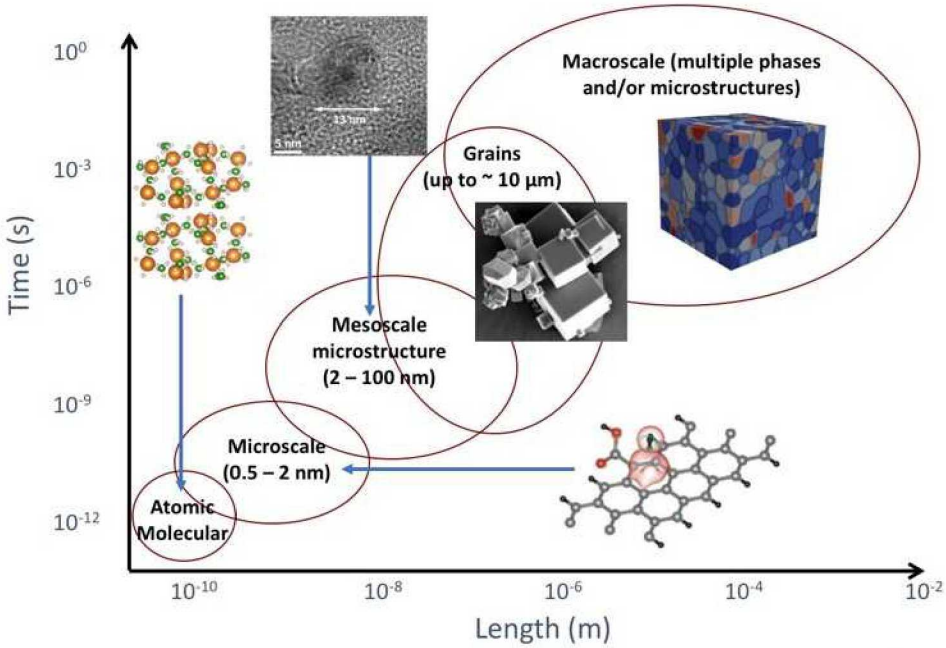
Thermodynamic properties are not the only Goldilocks Challenge

Poorly understood phenomena at length scales from < 1 nm to μm govern storage material behavior

Distinct chemical/physical processes affect the bulk properties of storage materials



Multiple length scales must be taken into account



"Design rules" are needed to guide materials discovery

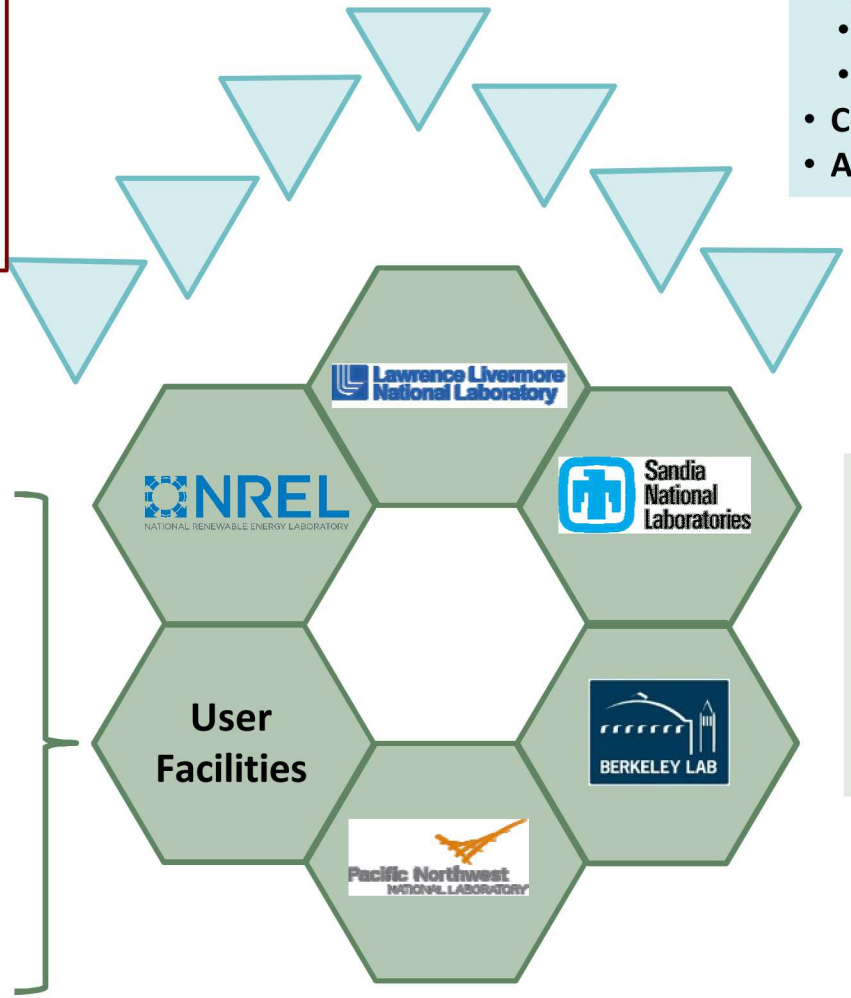
Hydrogen Materials Advanced Research Consortium (HyMARC): highly coordinated capabilities to accelerate materials discovery

HyMARC Phase 1:
- FY16 – FY 18
- 3 DOE Labs
- Budget $3M/yr

HyMARC Phase 2:
- FY19 – FY22
- 5 DOE Labs
- Budget $6 M/yr

HyMARC
Hydrogen Materials Advanced Research Consortium

Seedling Projects
- Applied material development
  - Novel material concepts
  - High-risk, high-reward
- Concept feasibility demonstration
- Advanced development of viable concepts



NIST Center for Neutron Research

ALS ADVANCED LIGHT SOURCE

MOLECULAR FOUNDRY

SLAC NATIONAL ACCELERATOR LABORATORY

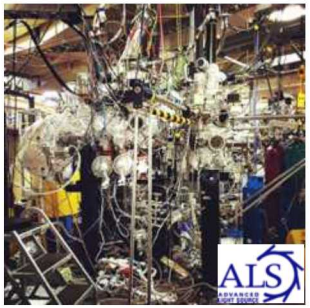
- Foundational R&D
- Computational models
- Synthetic protocols
- Advanced characterization tools
- Validation of material performance
- Guidance to FOA projects
- Database development

https://www.hymarc.org/

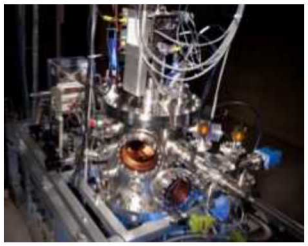
HyMARC

HyMARC employs a comprehensive suite of characterization tools to probe all relevant length scales

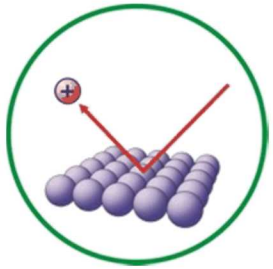
Atomic/molecular (0 – 1 nm)



AP-XPS
ALS/BL 11.0.2



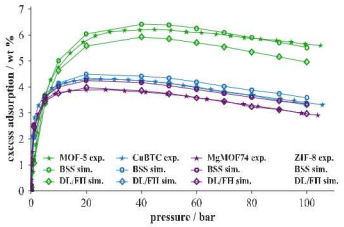
Lab-based AP-XPS

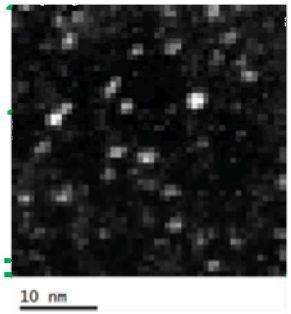


Low Energy Ion Scattering

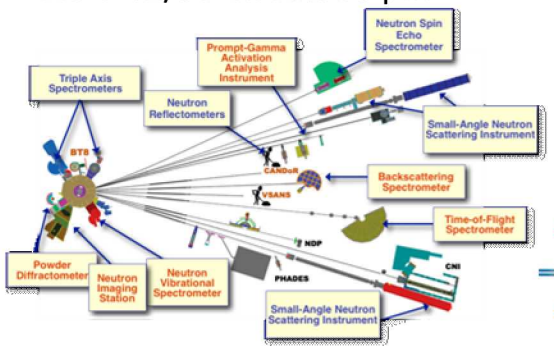
Molecular/micro (0.5 – 2 nm)

Microporosimetry/BET

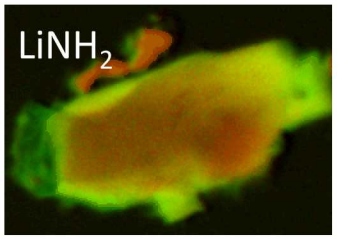


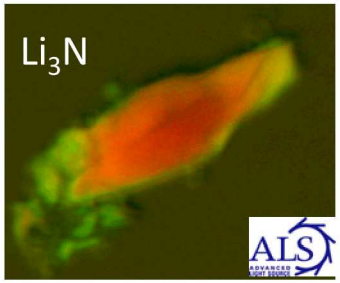


AC-TEM/STEM res. 63 pm



Mesoscale (2 - 100 nm)





STXM (30 nm res.)

Neutrons:

- Spectroscopy
- Scattering
- Diffraction

NIST Center for Neutron Research

Grains (≤ 10 µm)

Macroscale/Bulk

Ultrahigh Pressure Reactor (1000 bar)

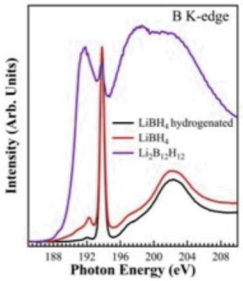
H-D exchange

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

Length (m)

Simulations span multiple scales

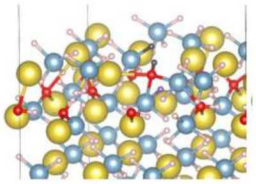
Atomic/molecular
(0 – 1 nm)

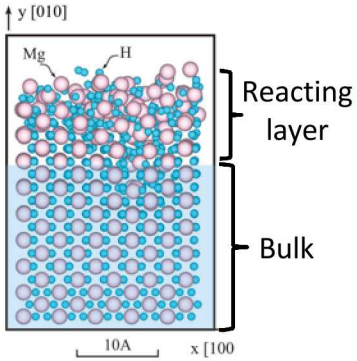


Computational Spectroscopy

Hydrogen chemisorption & physisorption

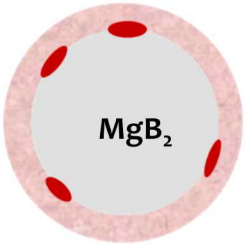
Molecular/micro
(0.5 – 2 nm)

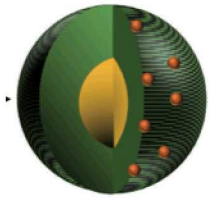




Surface/interface chemistry

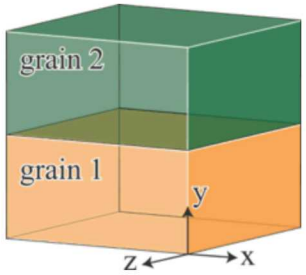
Mesoscale
(2 - 100 nm)





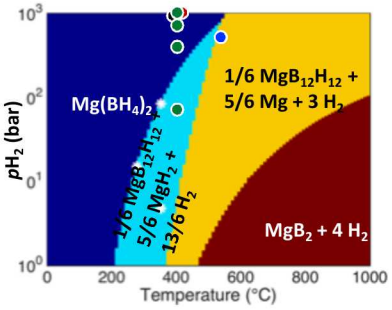
Nucleation kinetics
Phase microstructures

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*

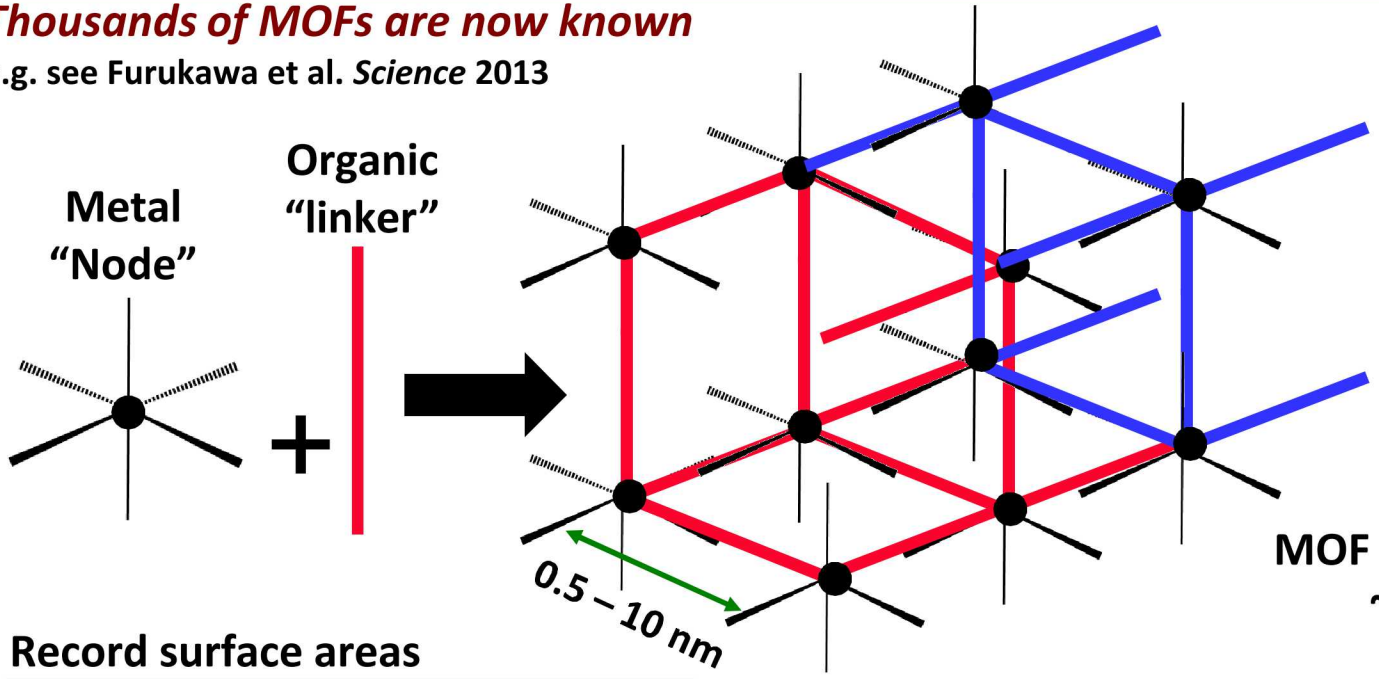
10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

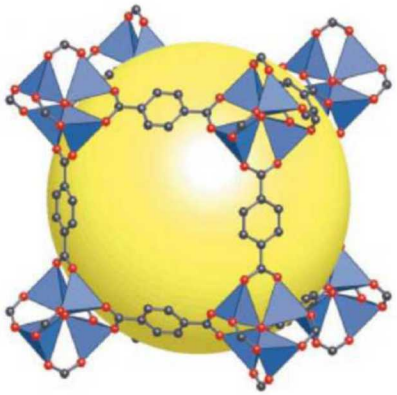
Metal-Organic Frameworks (MOFs) are among the most promising hydrogen sorbents

Thousands of MOFs are now known

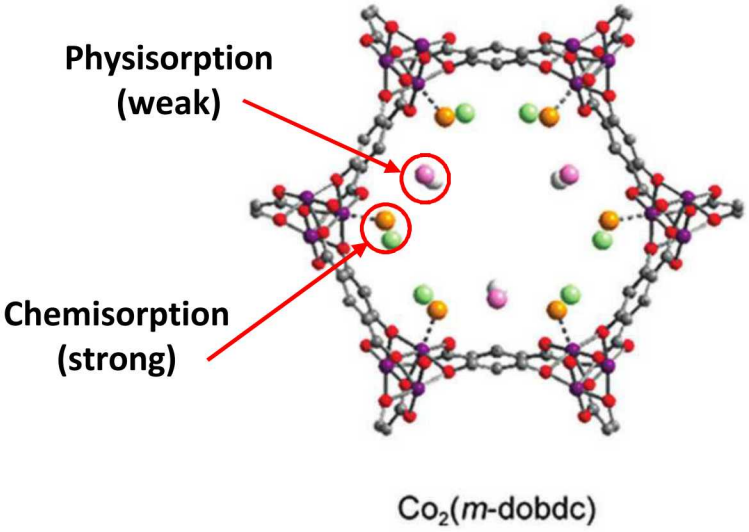
e.g. see Furukawa et al. *Science* 2013



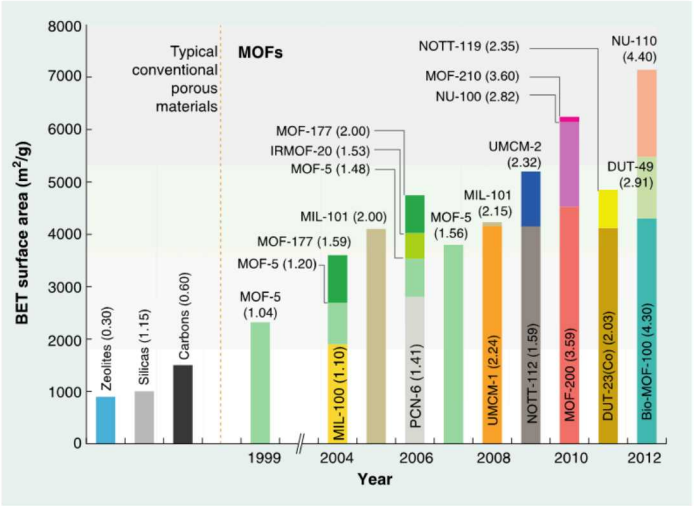
MOF-5



MOF H_2 binding energies
~ 2 – 33 kJ/mol



Record surface areas



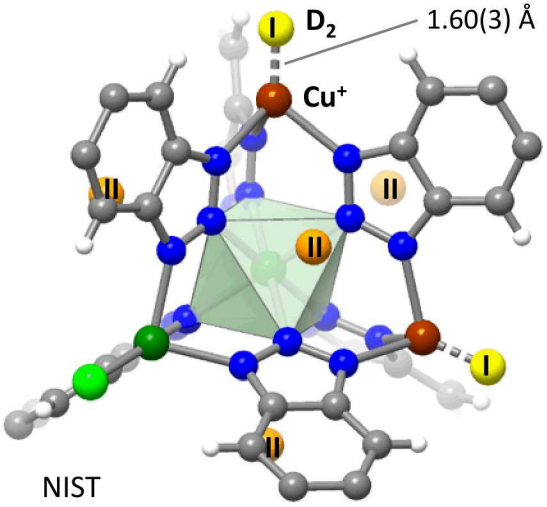
O.M. Yaghi et al. *Science* **341** (2013), 974

Allendorf, M. D. Hulvey, Z., T. Gennett et al.
Energy & Environ. Sci. **11** (2018), 2784. DOI: 10.1039/C8EE01(

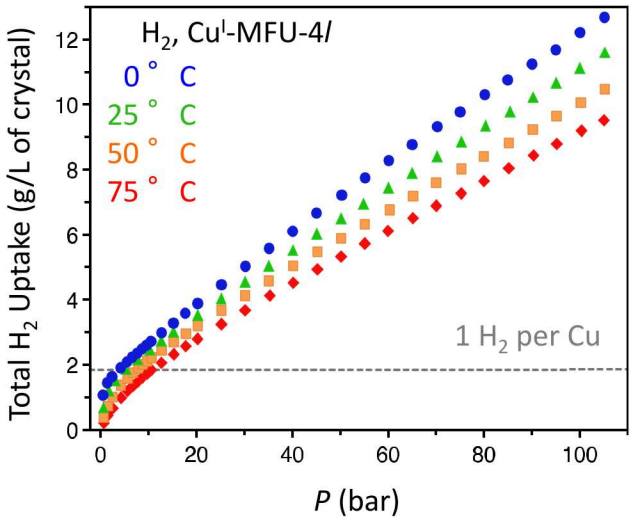
Recent HyMARC research indicates H_2 binding energies can be increased in MOFs

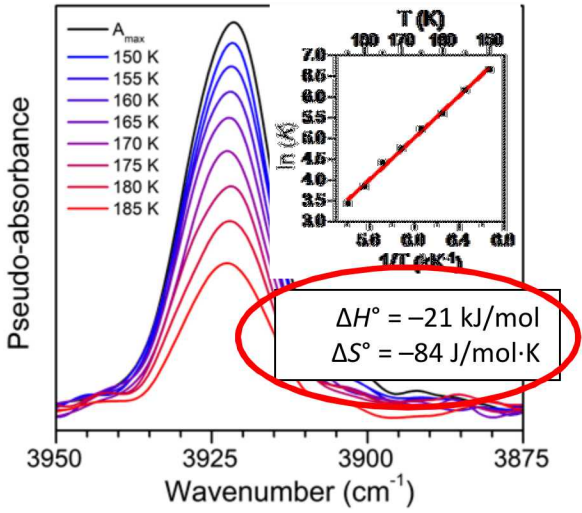
Copper and Vanadium MOFs have heats of adsorption 21 – 33 kJ mol^{-1}

Research of J. R. Long and coworkers



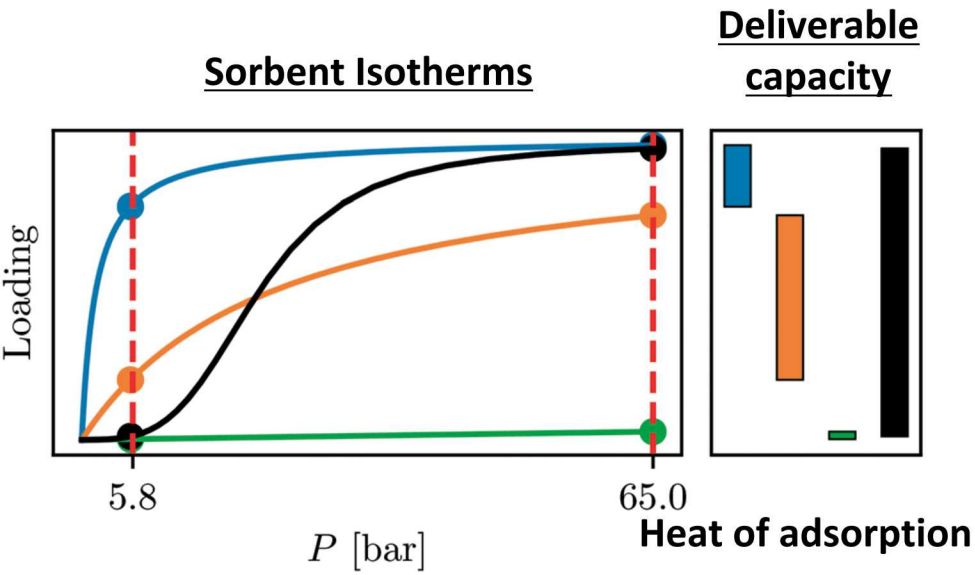
NIST





- ***In situ* powder neutron diffraction:** Extremely short Cu–D_2 distance observed in Cu^{I}-MFU-4*l* by neutron powder diffraction. Corroborates strong binding enthalpy and large red-shift of u(H–H) observed from DRIFTS.
- **High-P adsorption:** Open Cu^+ sites saturate at relatively low pressures. Volumetric usable capacity for Cu^{I}-MFU-4*l* surpasses Ni_2(*m*-dobdc) at 75 ° C.
- **DRIFTS in $V_2Cl_{2.8}$(btdd):** VTIR confirms high enthalpy of adsorption. Enthalpy–entropy relation distinct from M_2(dobdc) family.

Ultimate gas deliverable capacity material? Nonporous-to-porous deformations without volume change



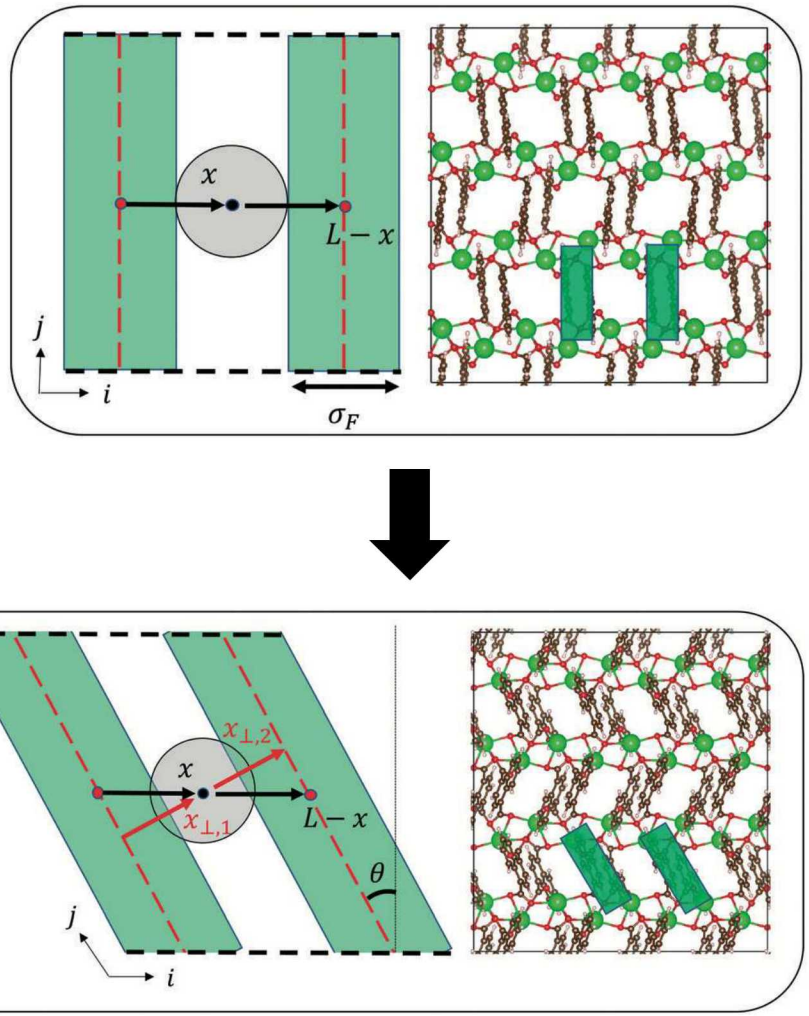
Heat of adsorption

Too strong

Optimized

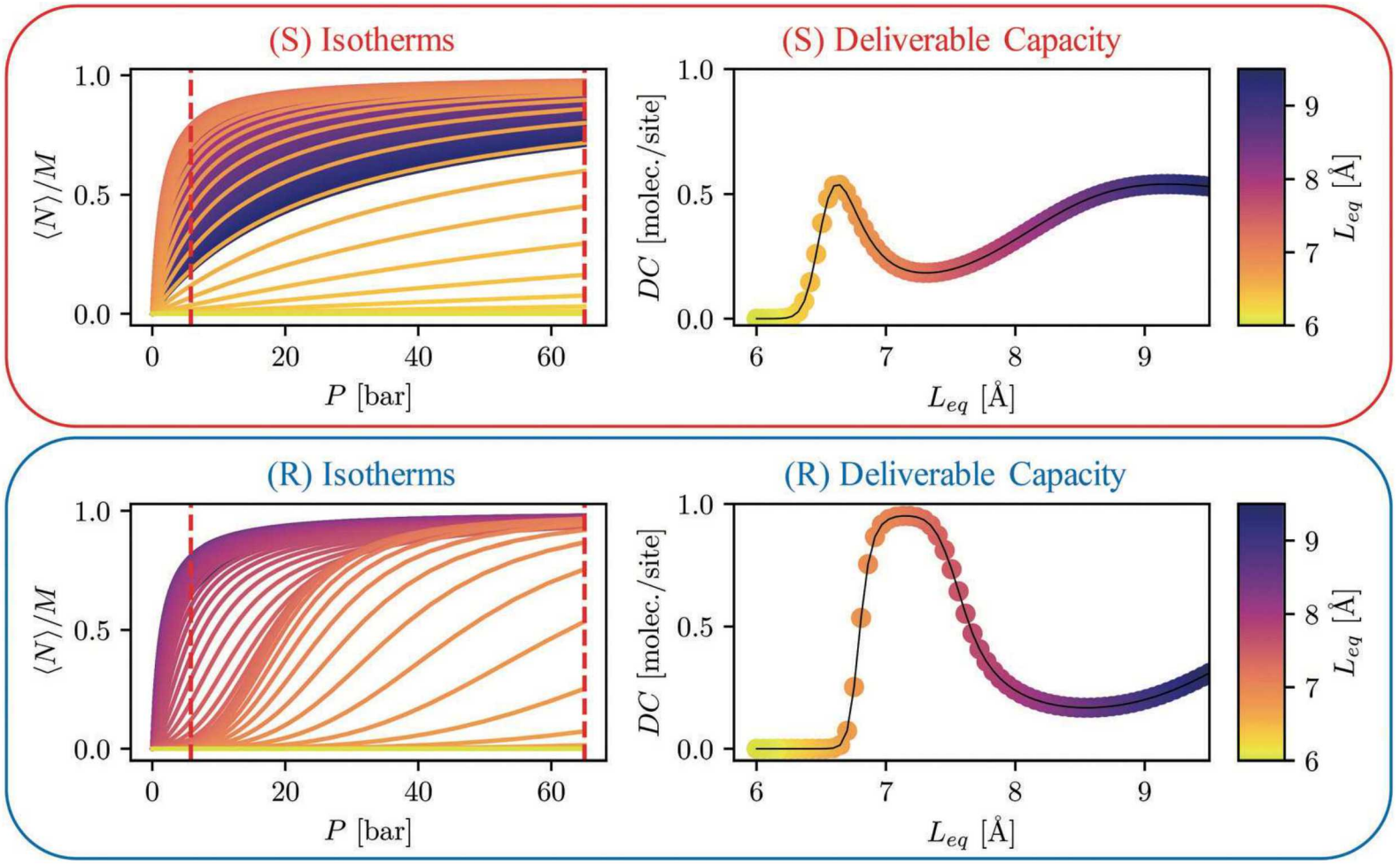
Too weak

Flexible



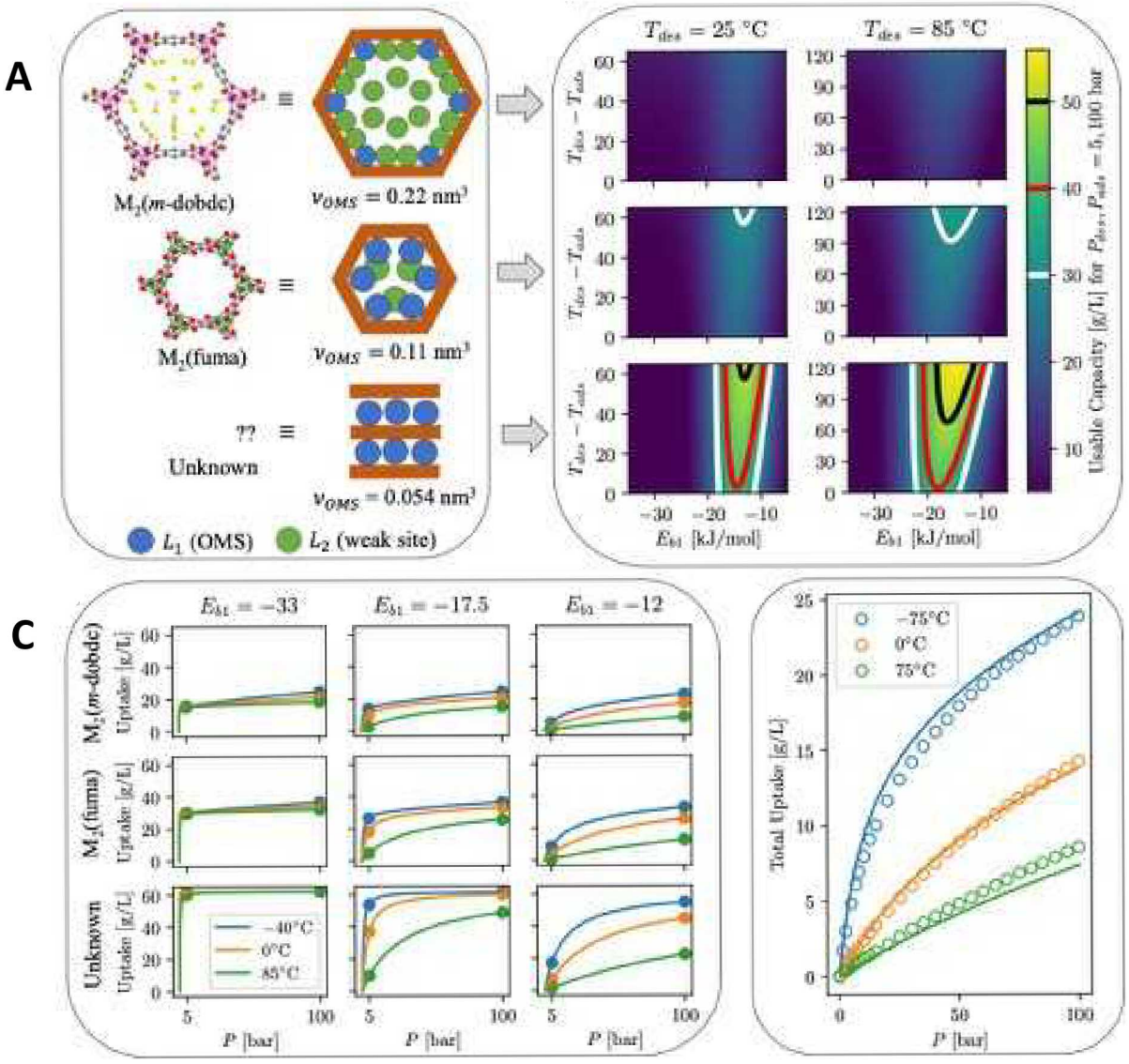
M. Witman et al. *Molec. Systems Design Eng.*
Accepted for publication Oct. 2020

Methane isotherms and deliverable capacity plotted as a function of L_{eq}



M. Witman et al. *Molec. Systems Design Eng.*
Accepted for publication Oct. 2020

The strong physisorption conundrum and the role of flexible sorbents

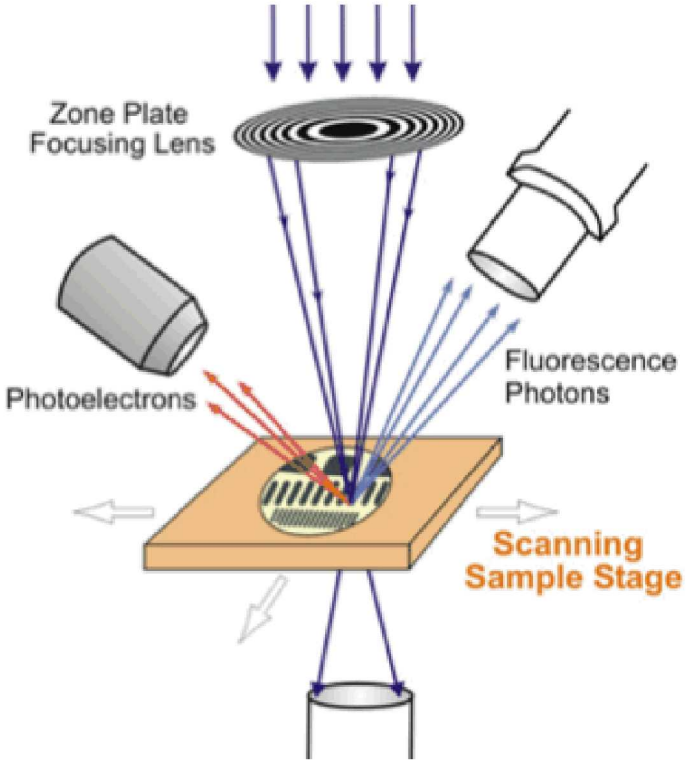


Can we image phase evolution in hydride storage materials?

Uncovering the rate-limiting step in H_2 uptake/release help us design materials with kinetics that meet DOE targets for fill time

Mesoscale phase evolution (nm → μm) is commonly included in mechanisms of metal hydride chemistry, but experimental data needed for validation is lacking.

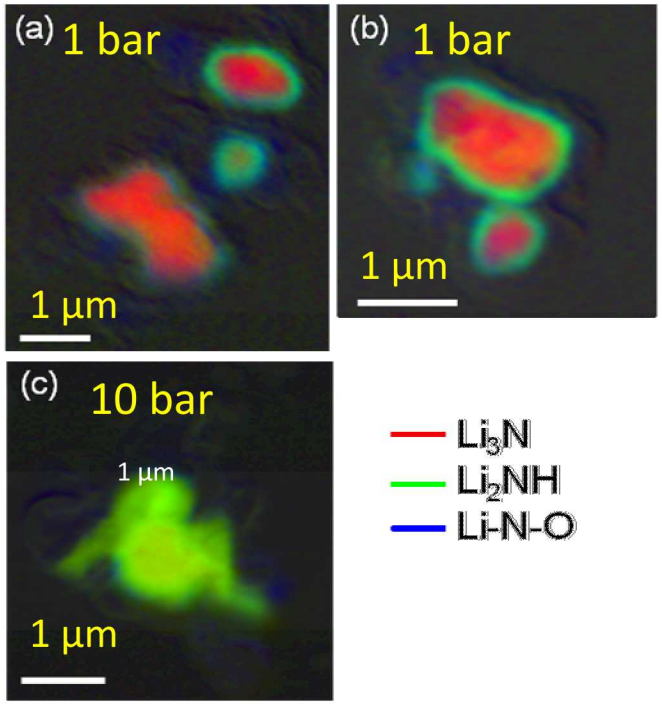
- **TEM: ineffective because hydrides decompose under electron beams**
- **Scanning transmission X-ray microscopy (STXM)**
  - Access through Approved Program at LBNL/Advanced Light Source
  - Generates **mesoscale chemical maps**
    - Beamline 5.3.2.2 allowed access only to N in this material
    - 30-nm resolution



STXM N K-edge maps of partially reacted $LiNH_2$+LiH and Li_3N

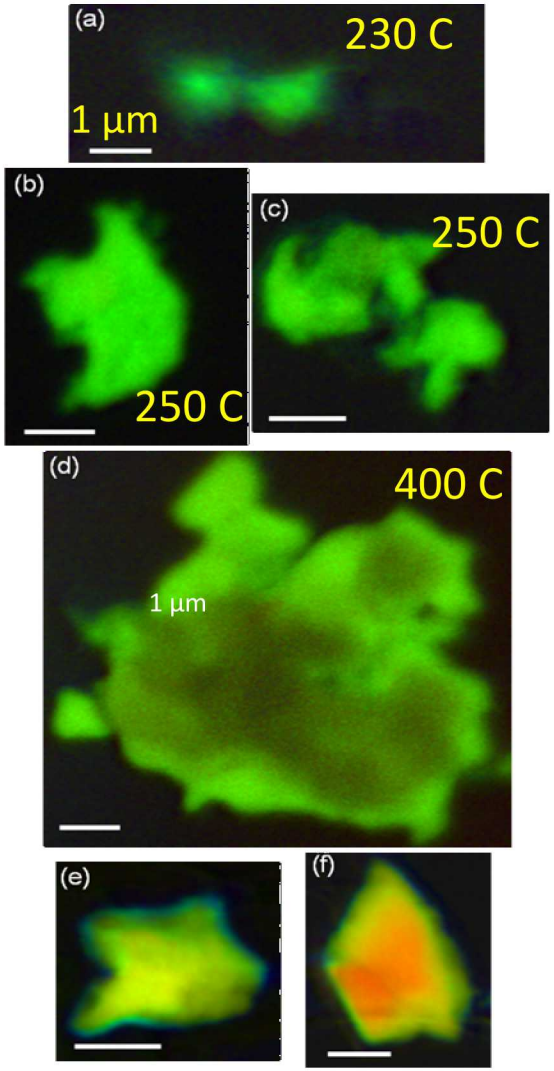
Hydrogenation

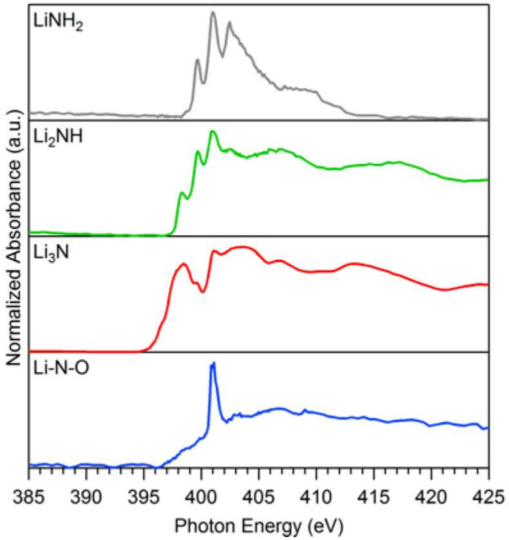
- Reaction at 200 C
- Very little $LiNH_2$ detected



Dehydrogenation:

- 400-450 C : Interior dehydrogenates first

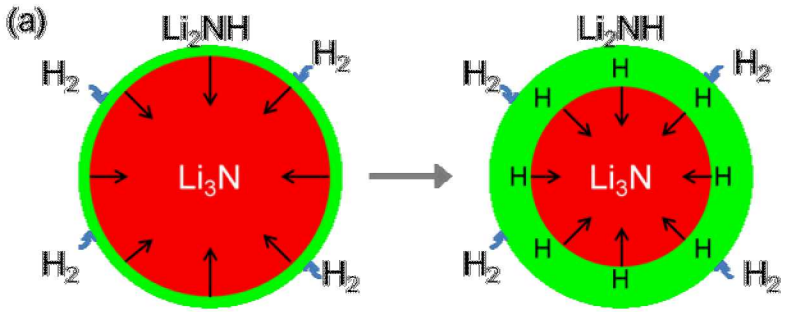


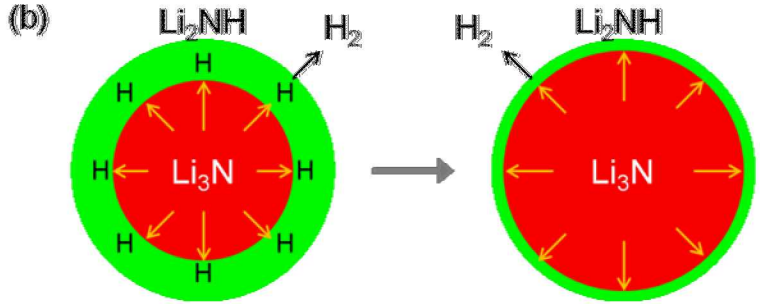


N K-edge X-ray absorption spectra, used as standards for mapping

STXM maps indicate reaction is limited by the rate of H_2 release from the surface

*Hydrogenation and dehydrogenation steps for complex metal hydrides are **conducted at different temperatures and pressures**, which can lead to different rate-limiting steps.*





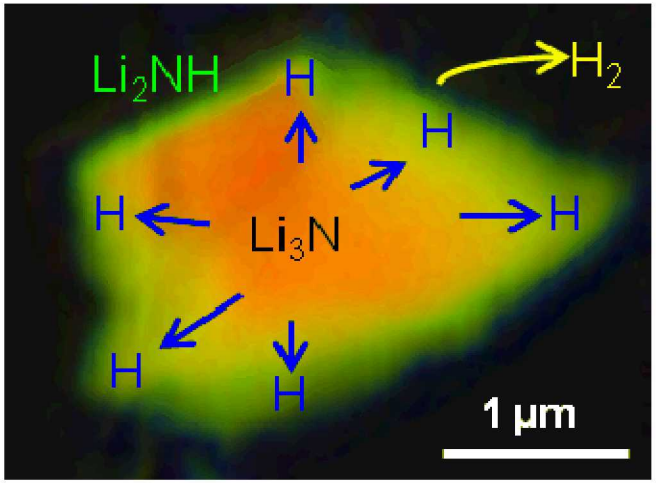
Inverted core-shell chemical map

<u>Hydrogenation</u>:

- **Proceeds as predicted by Wood et al.**

<u>Dehydrogenation</u>:

- **Slow surface kinetics lead to inverted core-shell → opposite microstructure from earlier prediction**



HyMARC more than doubled usable volumetric capacity of material-based storage over 2016 state of the art

Systems analysis identifies clear R&D pathway to beating both volumetric and gravimetric capacities of 700-bar compressed gas as well

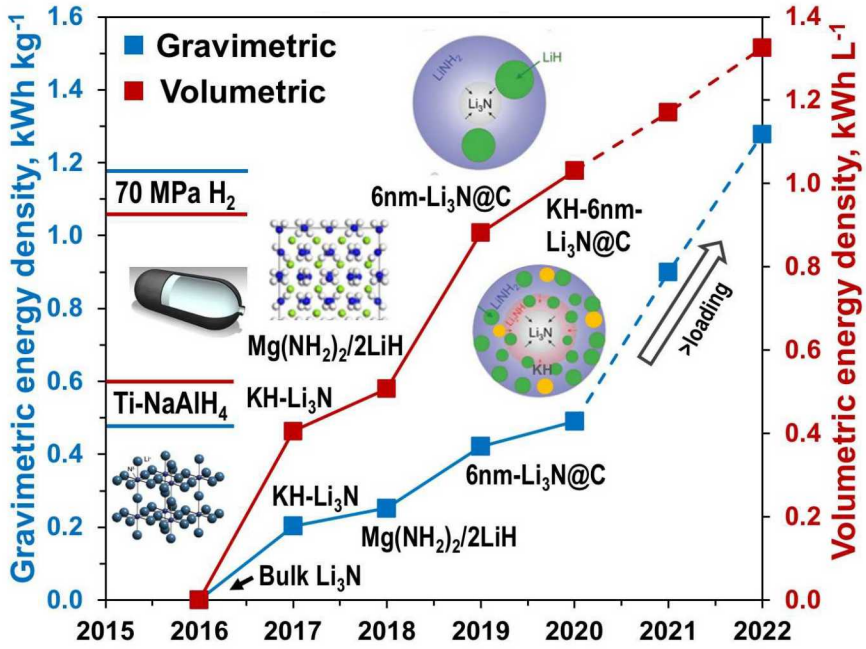
Key HyMARC discoveries

- H_2 release rate increased 2.8X by KH doping
- Patented synthesis method increases host loading, improves safety
- Full reversibility achieved by nanoscaling at 150 °C lower than bulk
- Porous C host accelerates H_2 release throughout the tank due to faster heat transport

Full systems analysis of hydride-composite storage materials enabled by HyMARC data:

- Hydride loading
- Thermodynamics of reaction
- H_2 desorption rate
- Thermal conductivity

Systems analysis for a realistic drive cycle using HyMARC data demonstrates the rapid increases achieved in energy density

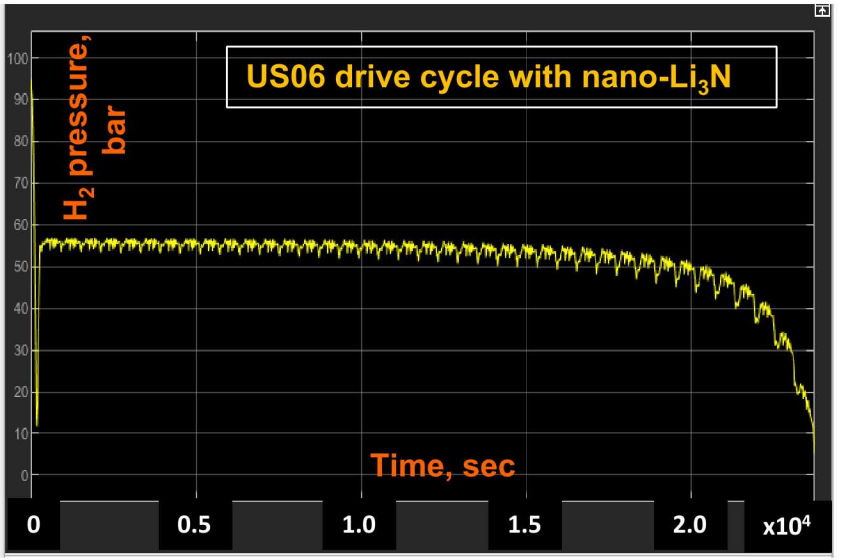


Systems analysis conducted in concert with material development defines pathway to successful materials

Systems analysis of hydride-composite storage materials enabled by HyMARC data:

- US06 drive cycle simulation
- KH-doped Li_3N@6-nm C composite
- Stainless steel tank
- HyMARC inputs:
  - Composition (hydride loading)
  - Packing density
  - H_2 desorption kinetics
  - Reaction thermodynamics
  - Thermal conductivity

Simulation of desorption over $2.5x10^4$ sec (~ 7 hours)



Key results

→ **Bulk material is unusable due to slow kinetics**

→ **Nanoscale material produces 55 bar H_2 at 250 °C**

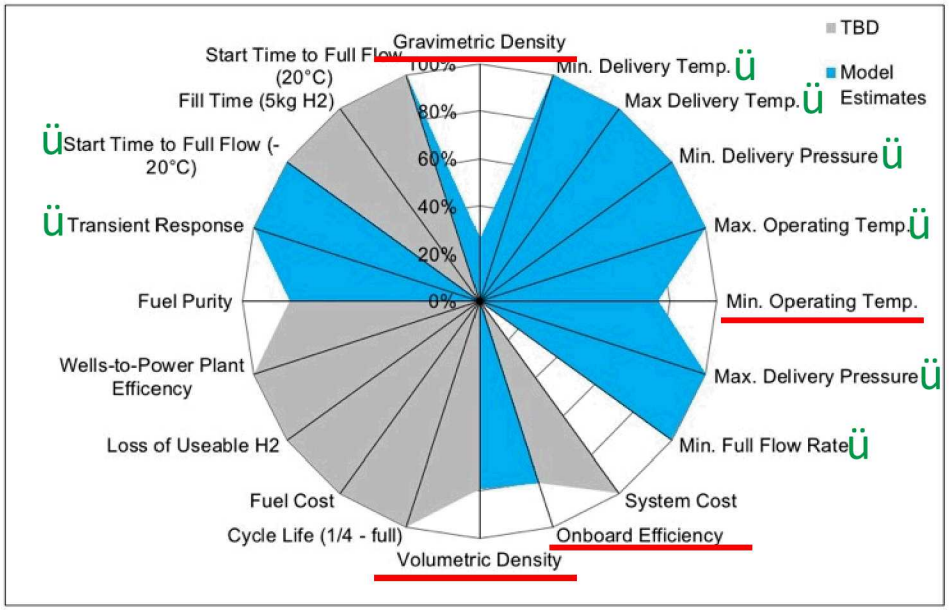
If we can reduce the tank operating temperature to 200 °C, we can:

→ Use aluminum fuel tank instead of stainless steel

→ Reduce number of cooling tubes and H_2 consumption by burner

Accomplishment: Comparison with DOE targets determined by systems model including kinetics using US06 drive cycle

- Of the 13 targets in the evaluation (shaded blue):
  - 9 are 100%
  - 3 are ≥ 75%
- Predicted $P(H_2)_{max}$ = 55 bar at 250 ˚C; DOE target = 12 bar
- Grav. Capacity is 30% of target
  - Due to burner weight of burner and cooling tubes



Take-home lessons:

- Assessing system performance based on one DOE target (e.g. bulk wt%) is overly simplistic
- Systems analysis and material design should be performed in parallel

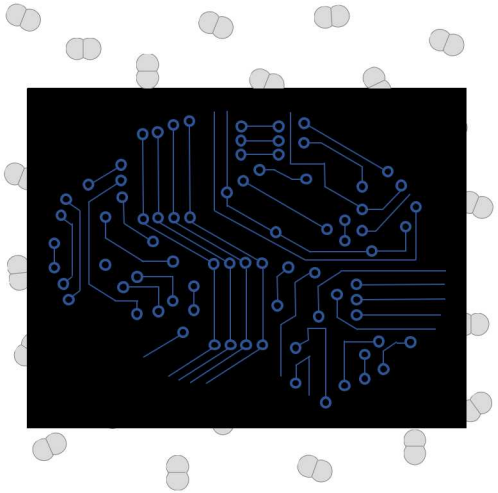
Development of machine-learning to discover new metal hydrides

Decades of research on metal hydrides has failed to identify any that meet all DOE targets. Are we missing something?

Research Question: Can machine learning (ML) yield physics-based insight to facilitate the design of novel metal hydrides exhibiting targeted thermodynamic properties ?

Approach:

1. Train an ML model to predict the equilibrium plateau pressure, P_{eq}, of a metal hydride
2. Utilize the ML model's *interpretability* to understand the underlying structure-property relationships from which P_{eq} can be predicted
3. Apply these structure-property relationships to *a priori* identify known intermetallic compositions with unknown hydrides *and* are predicted to exhibit a desired P_{eq}



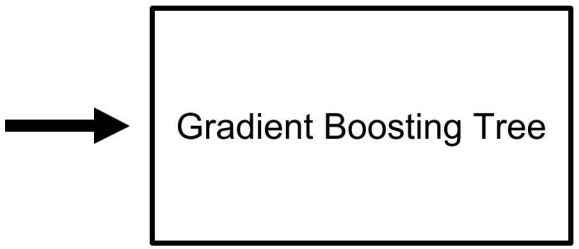
We created input features and chose an ML technique that promotes interpretability of the trained model to aid subsequent efforts in rational materials design

Features: each composition (a string) is mapped to a 145 dimensional vector computed from elemental properties using the Magpie code*

Model: Gradient Boosting Trees are interpretable, i.e. they rank how important each feature is to the property prediction

Prediction: $\ln P_{eq}^{o}$

	1	2	v_{pa}^{Magpie}	…145
LaNi5				
…				
Er6Fe23				



	$\ln P_{eq}^{o}$
LaNi5	
…	
Er6Fe23	

* Developed by Wolverton and coworkers

An example Magpie descriptor:

$$v_{pa}^{Magpie} = \sum_{i} x_i v_i$$

$x_i \equiv$ composition fraction of element i

$v_i \equiv$ ground state volume per atom of elemental solid *i*

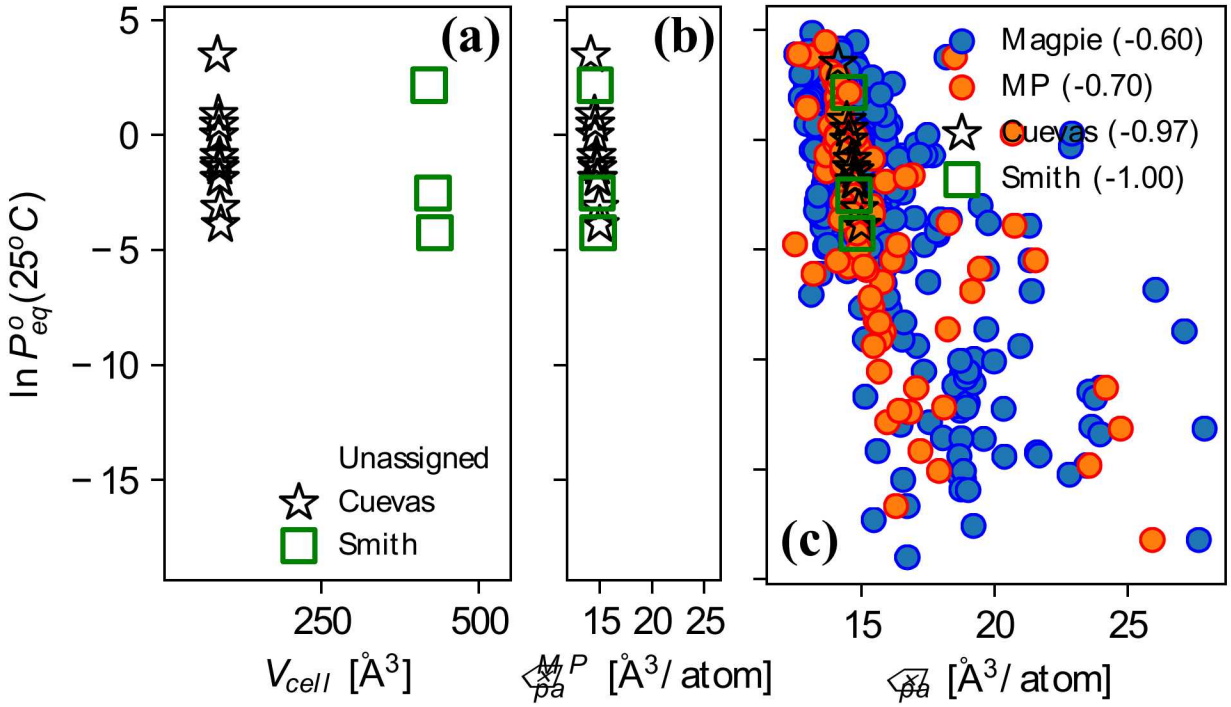
Our data-driven approach reveals that the v_{pa}: lnP^{o}_{eq} structure:property relationship is valid for a wide range of metal substitutions and intermetallic classes

1. Compute the structurally specific volume per atom for ~ 70 available structures in the Materials Project (MP) via:

$V_{cell} \equiv$ Volume of the intermetallic lattice computed in MP

$v_{pa}^{MP} = V_{cell}/n_{atoms}$

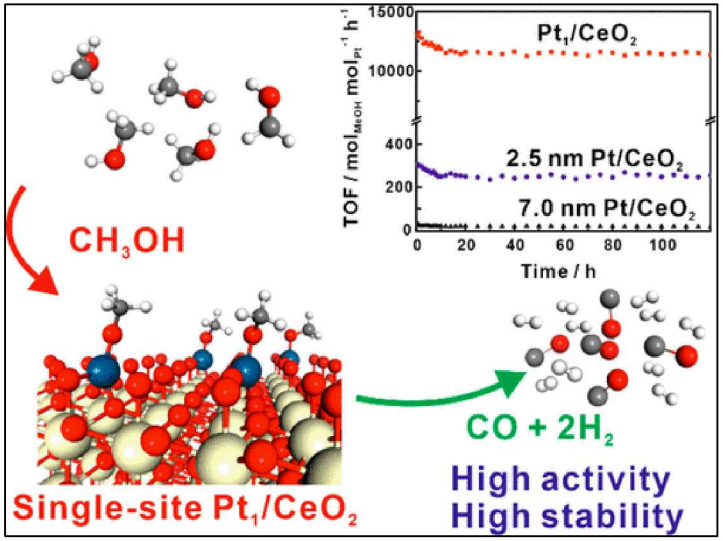
2. Investigate equilibrium pressure as a function of v_{pa}^{MP} and v_{pa}^{MP}:



Cuevas et al. noted the dependence of lnP^{o}_{eq} on V_{cell} in $LaNi_5$ substitutions

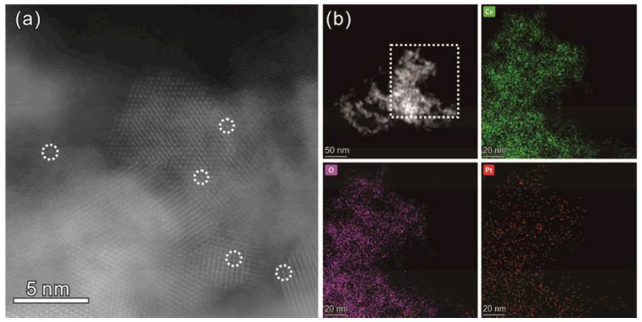
Smith et al. noted the same trend for R_6Fe_{23} [R=Ho,Er,Lu] substitutions

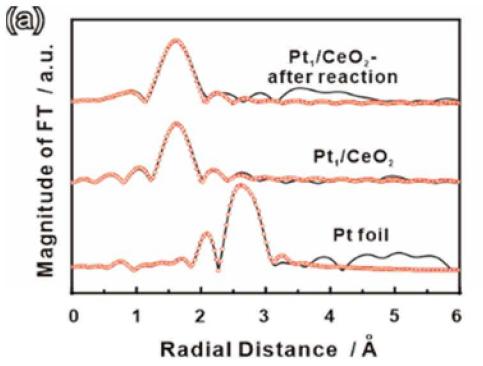
Single-Site Catalysts for Efficient Hydrogen Generation with Methanol

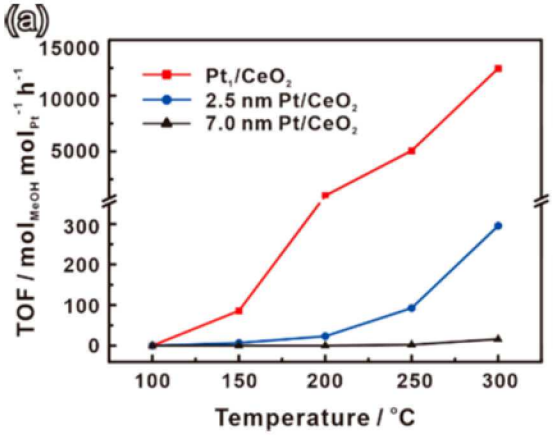


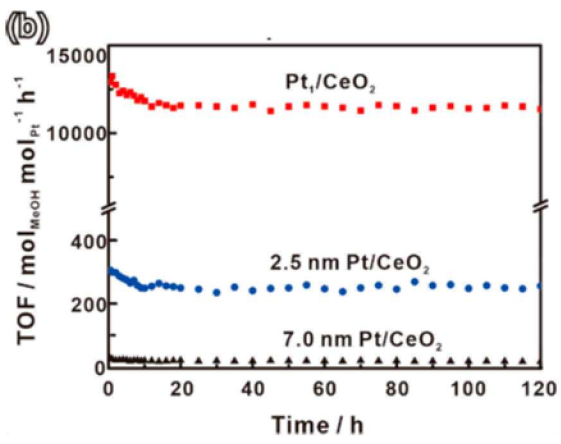
- Reaction rate of atomic Pt:
  - **12000-14000 $mol_{methanol}/mol_{pt}/hour$**
  - **40 times** that of Pt nanoparticles of 2.5 nm diameter
  - More than **800 times** that of 7nm Pt NPs.
- High reaction stability (**120 hours**).

Methanol Dehydrogenation









Ji Su, G. Somorjai. V. Stavila et al.
J. Am. Chem. Soc. 141 (45), 17995-17999

Take-home messages

- Compressed gas (700 bar): physically impossible to meet DOE volumetric target
- Solid-state materials have potential to meet DOE targets
- However, “Goldilocks Challenges” must be solved to enable materials-based storage systems to be practical
- HyMARC: a DOE National Laboratory team, is focused on accelerating materials discovery:
  - Foundational research
  - Development of advanced characterization tools
  - Computational modeling across all relevant length scales
  - Innovative materials synthesis and development
  - Collaboration and assistance to Seedling projects

Acknowledgements

Sandia National Labs

- Sapan Agarwal (machine learning)
- Farid El Gabaly (XPS)
- Andreas Schneeman (MOFs)
- Jon Snider
- Vitalie Stavila (catalysis)
- Josh Sugar (TEM)
- Jim White (XAS, STXM)
- Matt Witman (machine learning)

Lawrence Berkeley National Lab

- Ji Su (catalyst testing)
- Prof. Gabor Somorjai
- Jinghua Guo (ALS)
- Yi-Sheng Liu (ALS)

Lawrence Livermore National Lab

- Tae Wook Heo
- Brandon Wood
- Liwen Wan

Pacific Northwest National Lab

- Kriston Brooks (systems modeling)
- Tom Autrey
- Mark Bowden

Aarhus University

- Mathias Jørgensen (metal hydrides)

Nottingham University

- Prof. Sanliang Ling

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy?s National Nuclear Security Administration under contract DE-NA0003525.

We are grateful for the financial support of EERE/HFTO

Enabling twice the energy density for onboard H_2 storage