Solid State Materials for Hydrogen Storage

SAND2019-3176PE

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

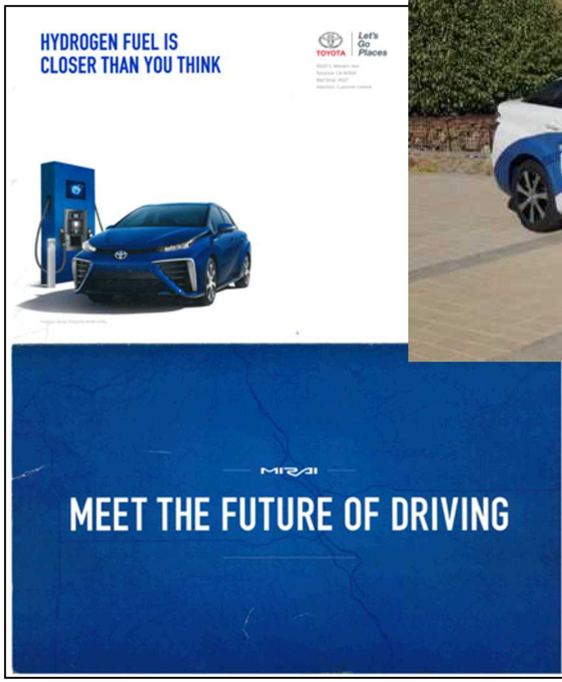




This presentation does not contain any proprietary, confidential, or otherwise restricted information

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.

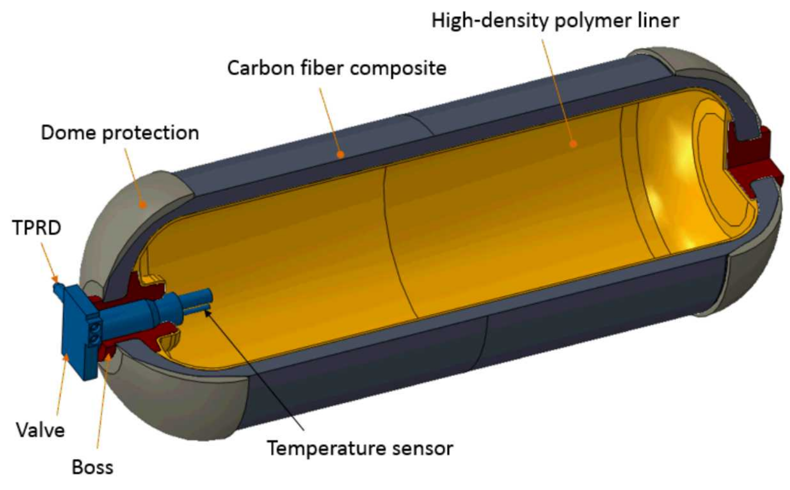
Hydrogen-powered cars are now commercially available



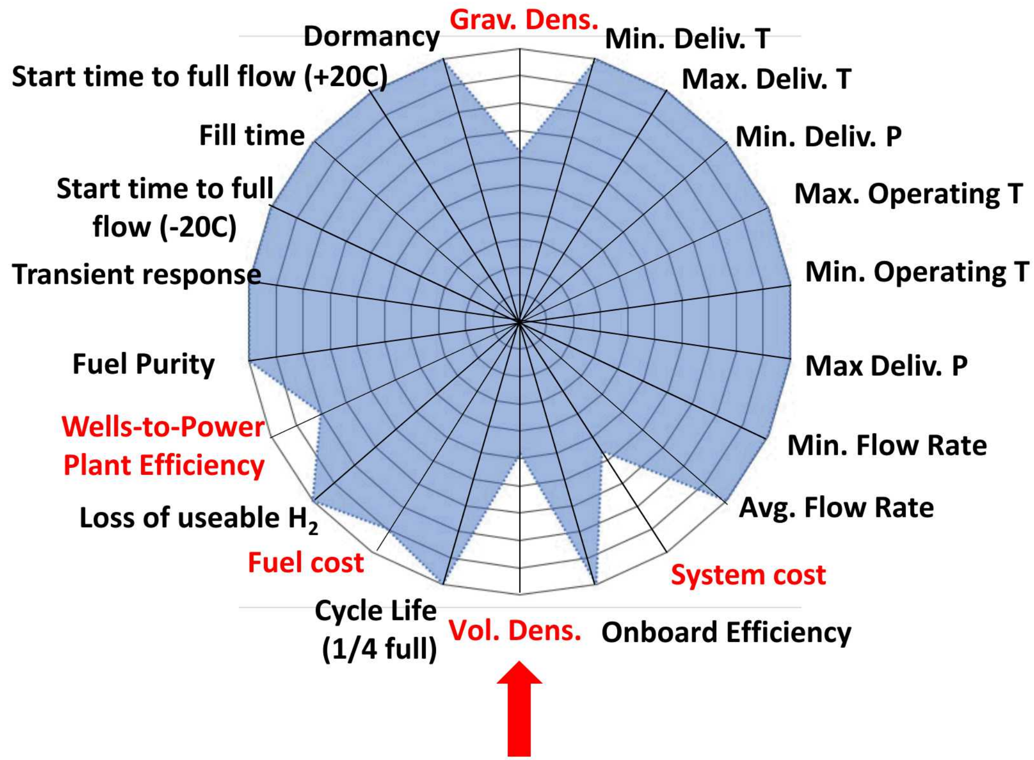
- **700 bar pressurized tanks**
- **265 – 312 mile range**
- **Refueling stations being installed in some areas**

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

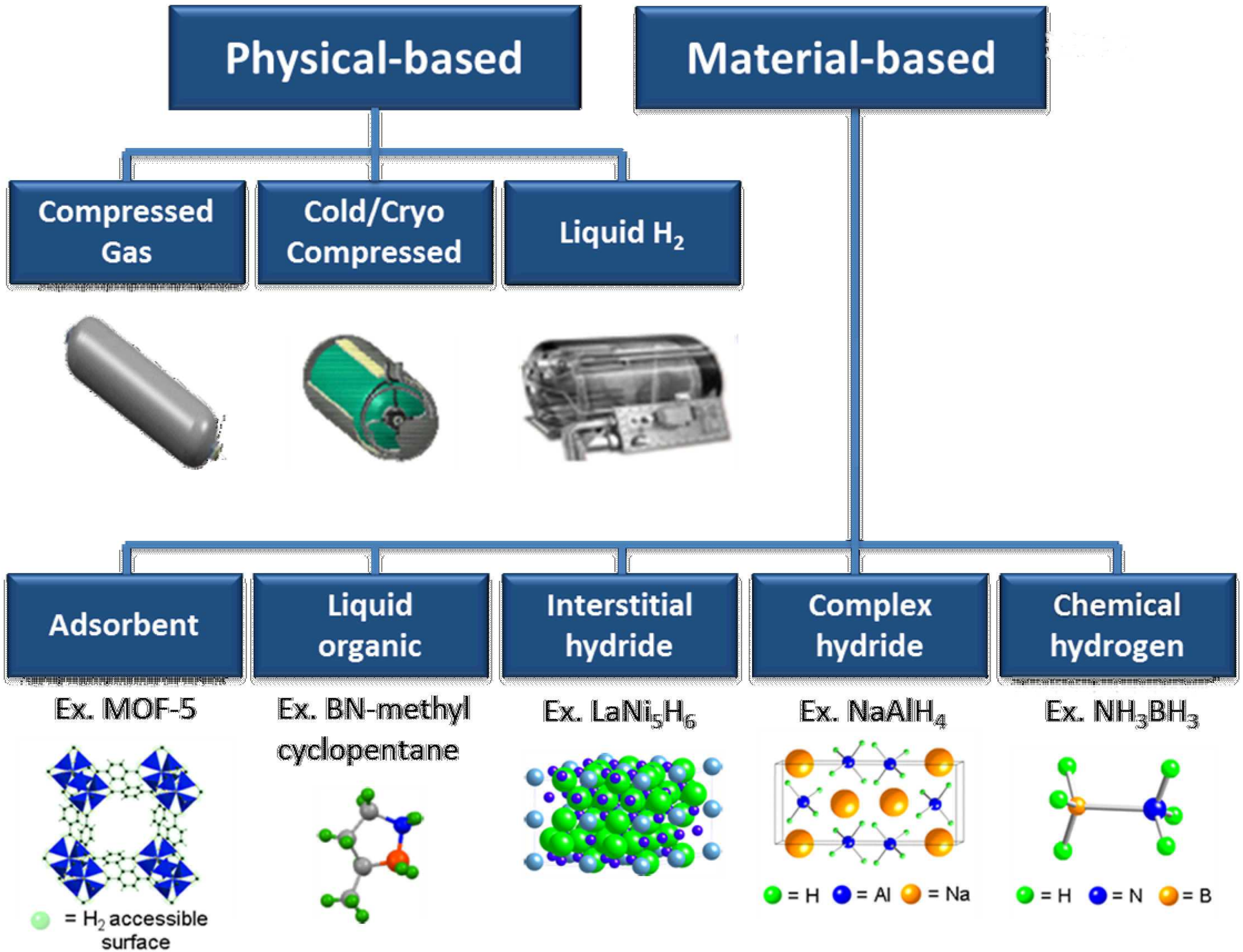


TPRD = Thermally Activated Pressure Relief Device
Credit: Process Modeling Group, Nuclear Engineering Division. Argonne National Laboratory (ANL)

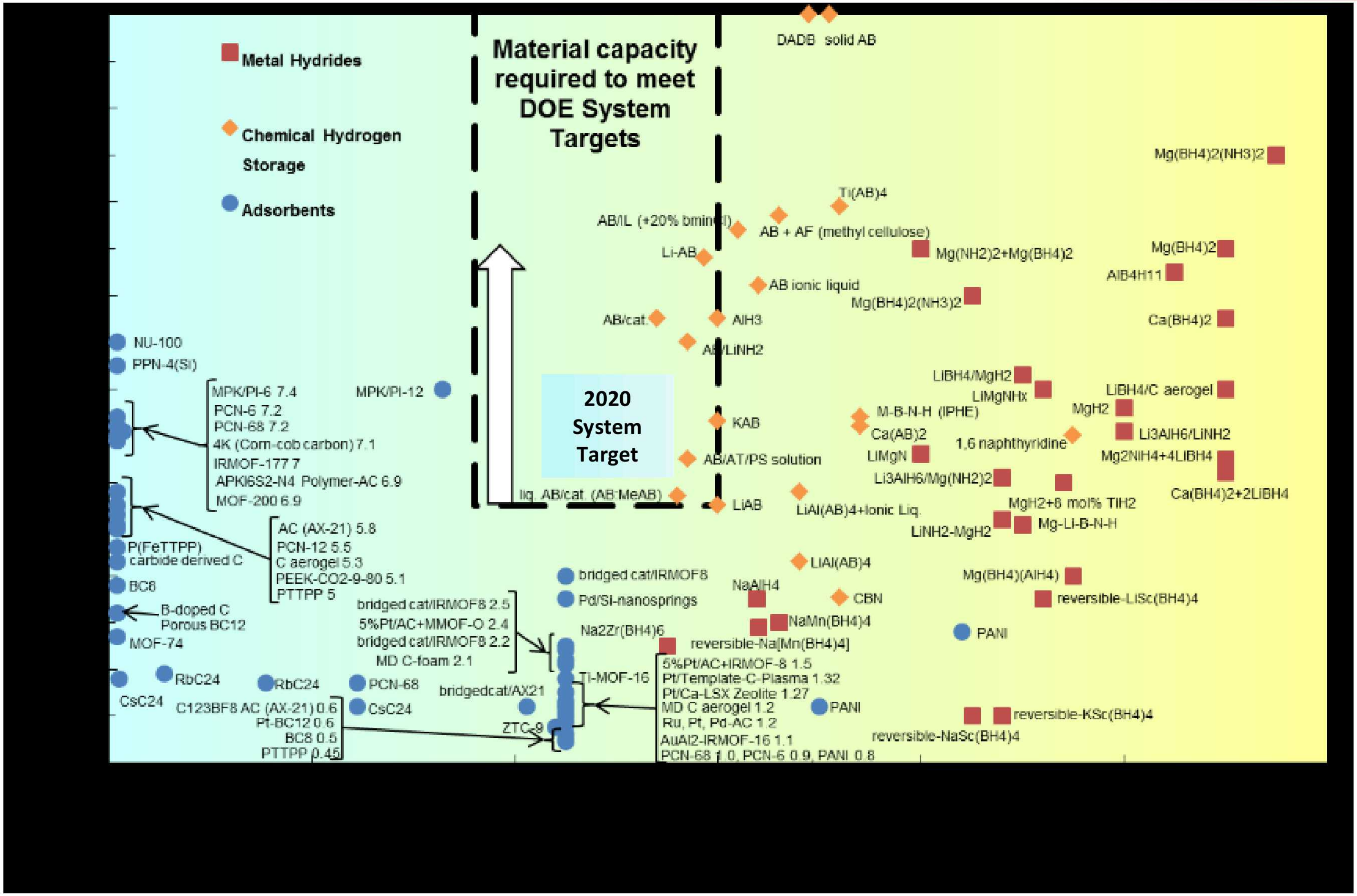


Unachievable using 700 bar

How is hydrogen stored?

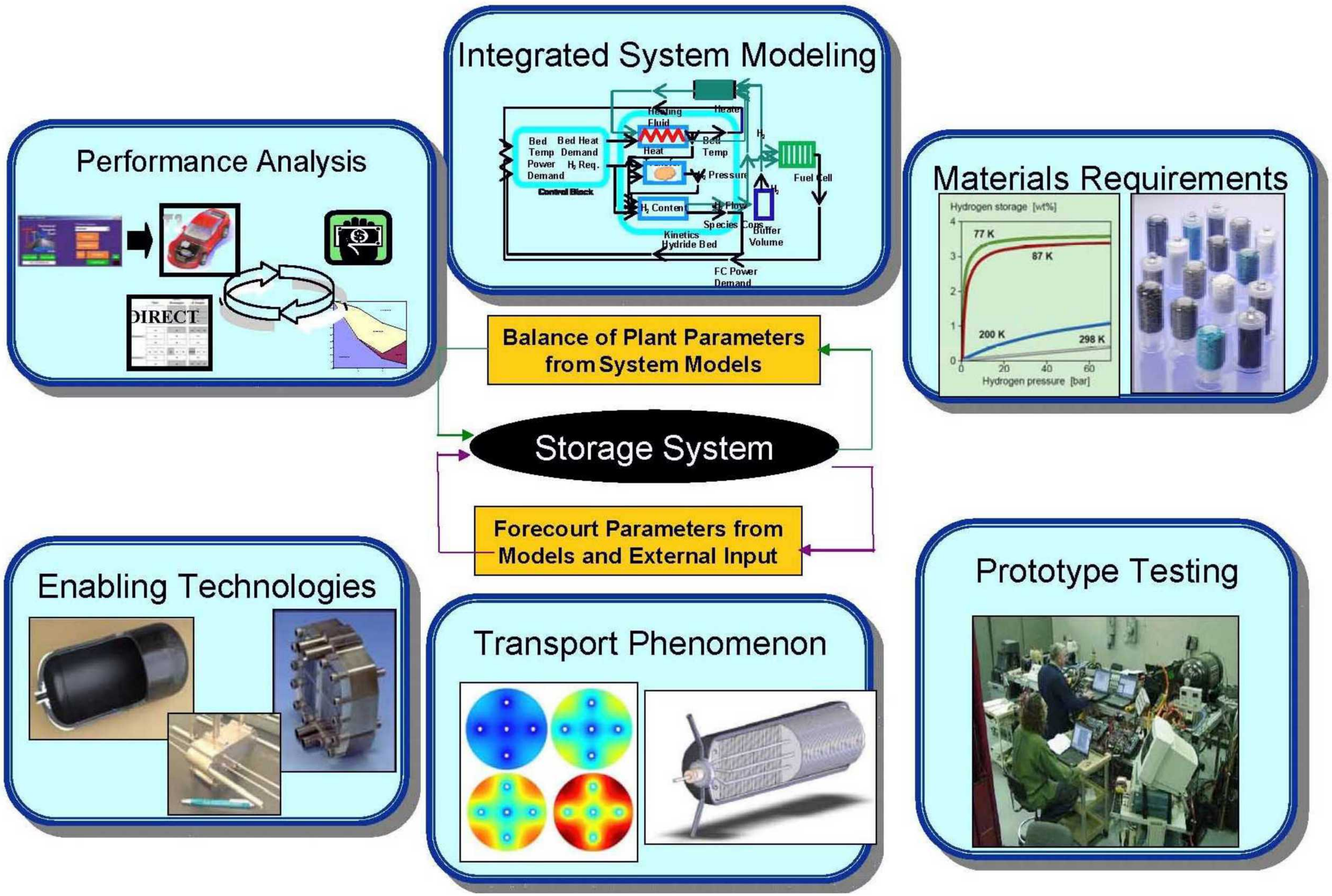


2005-2013: 3 DOE/EERE-funded Centers of Excellence focused on materials development



Although many materials were investigated, none were identified that met all DOE technical targets

2009-2015 Hydrogen Storage Engineering Center of Excellence



HSECoE formed to address lack of knowledge concerning system and engineering aspects of complete materials-based hydrogen storage systems

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 $8 M/yr***

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

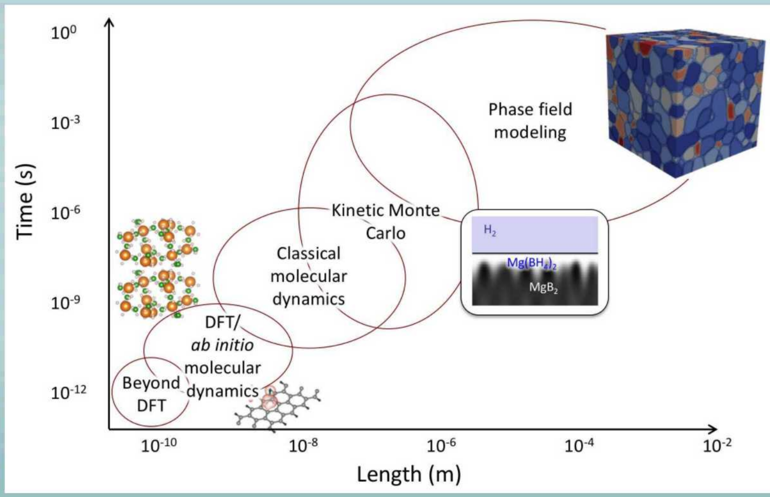
- **Foundational R&D**
- **Computational models**
- **Synthetic protocols**
- **Advanced characterization tools**
- **Validation of material performance**
- **Guidance to FOA projects**
- **Database development**

HyMARC objective: accelerate discovery of breakthrough storage materials by providing capabilities and foundational understanding

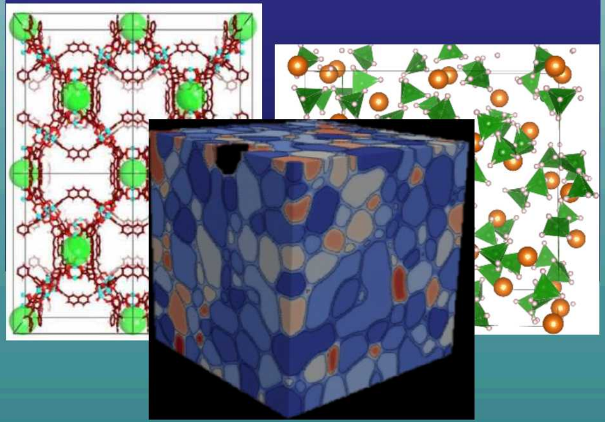
Foundational understanding of phenomena governing thermodynamics and kinetics limiting the development of solid-state hydrogen storage materials

HyMARC will deliver **community tools and capabilities:**

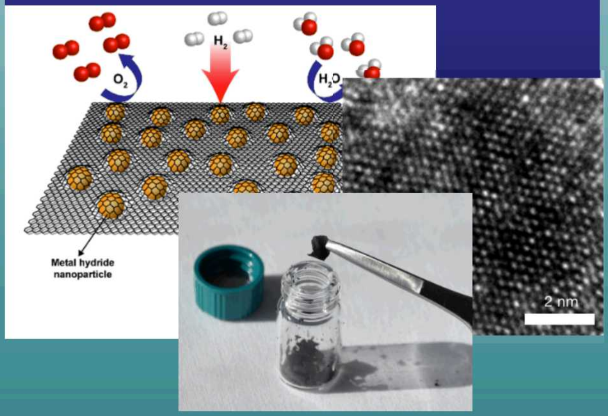
- **Computational models and databases** for high-throughput materials screening
- **New characterization tools and methods** (surface, bulk, soft X-ray, synchrotron)
- **Tailorable synthetic platforms** for probing nanoscale phenomena



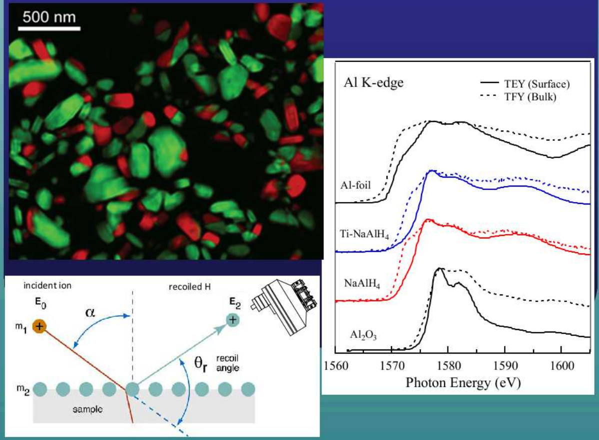
Theory, simulation, & data



Controlled synthesis

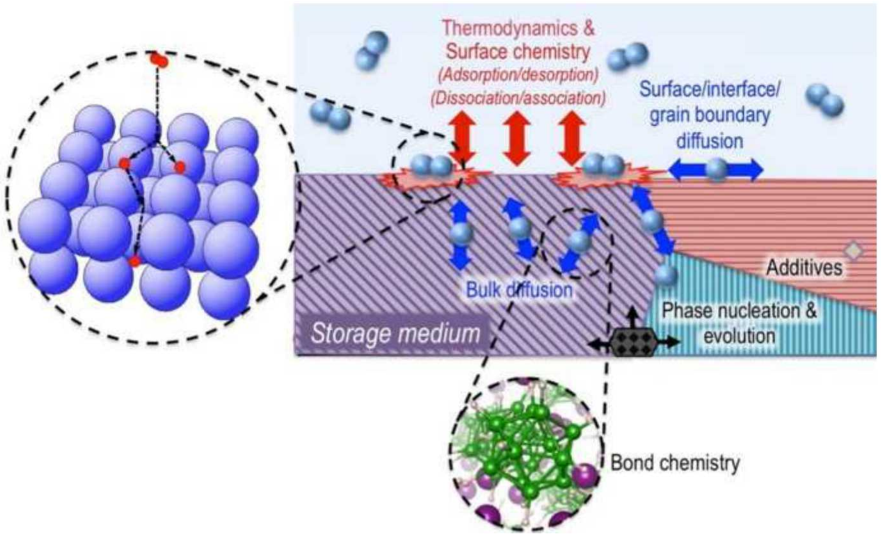


In situ characterization

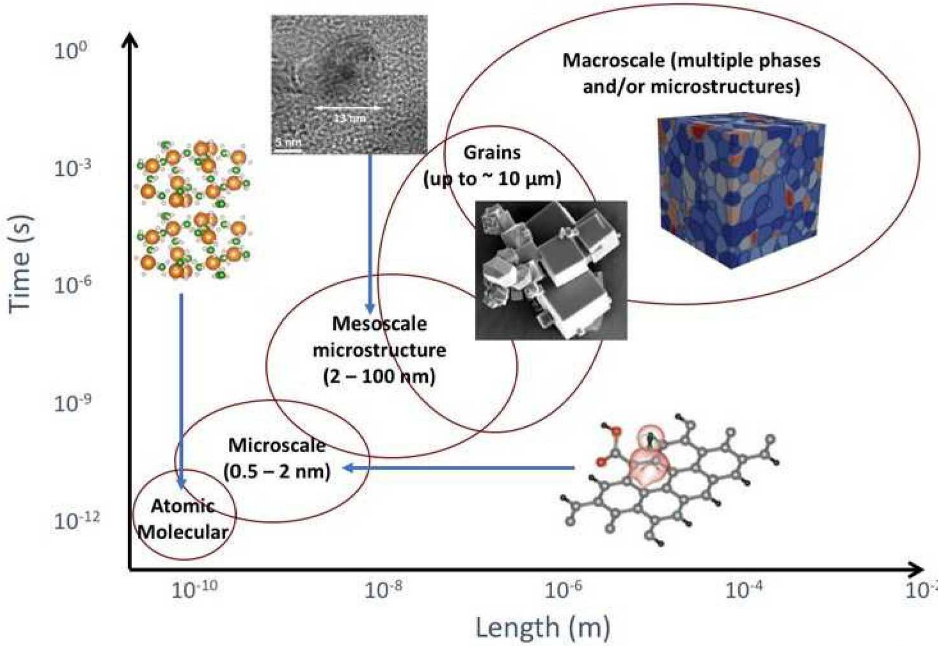


Relevance: poorly understood phenomena at length scales from < 1 nm to μm govern storage material behavior

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



Multiple length scales must be taken into account



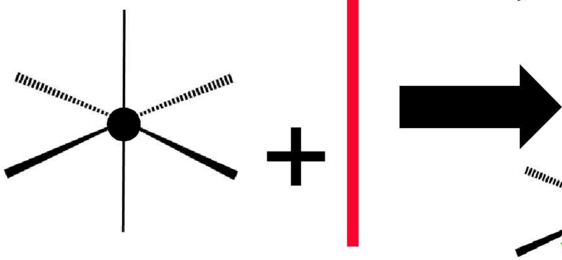
"Design rules" are needed to guide materials discovery

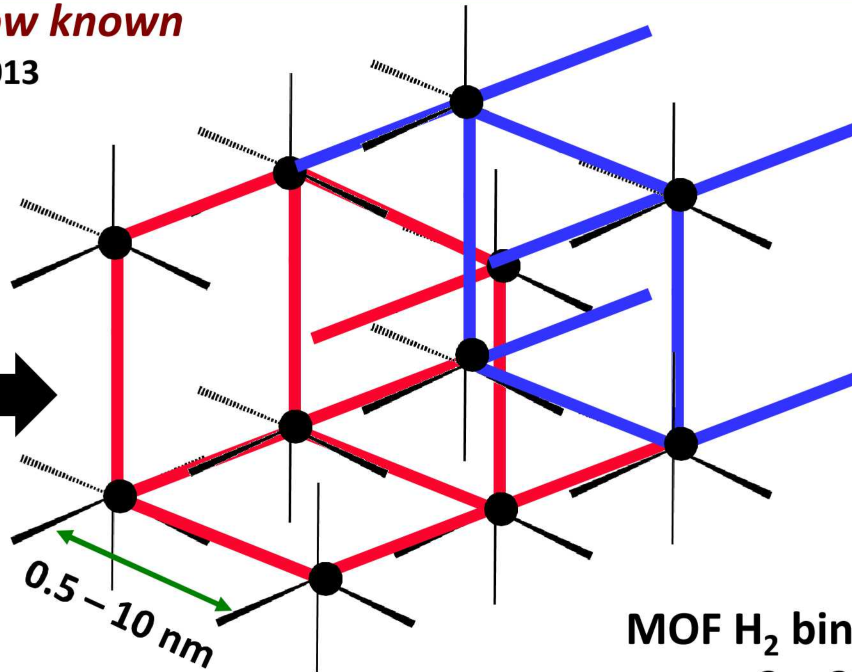
Metal-Organic Frameworks (MOFs) are among the most promising hydrogen sorbents

Thousands of MOFs are now known

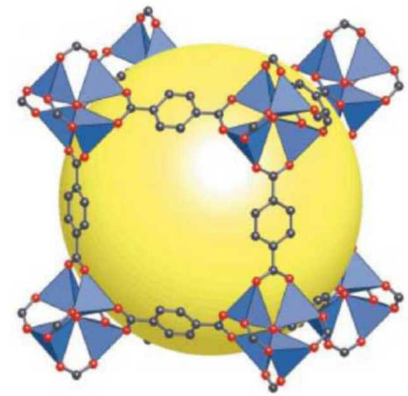
e.g. see Furukawa et al. *Science* 2013

Metal "Node" + **Organic "linker"**

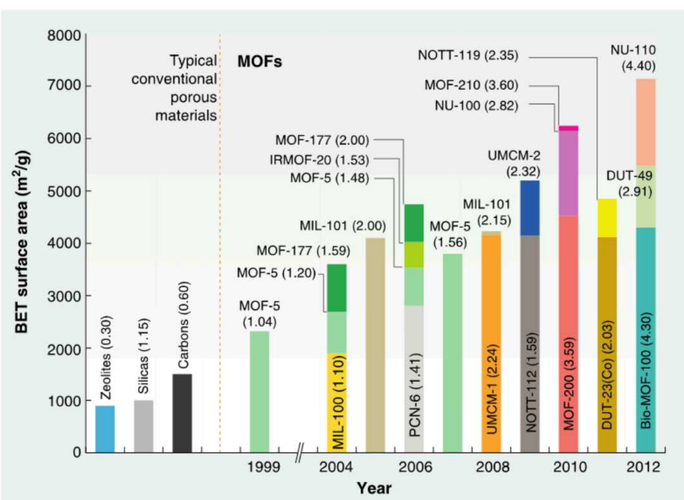




MOF-5

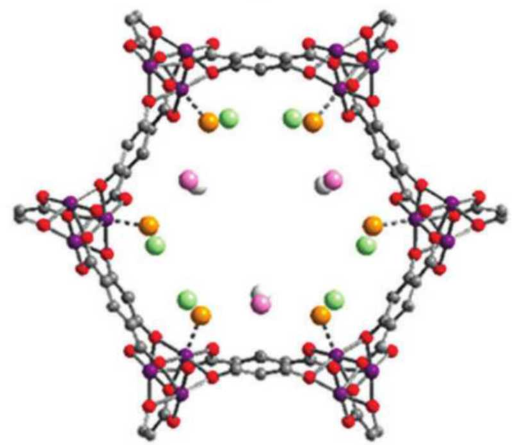


Record surface areas



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

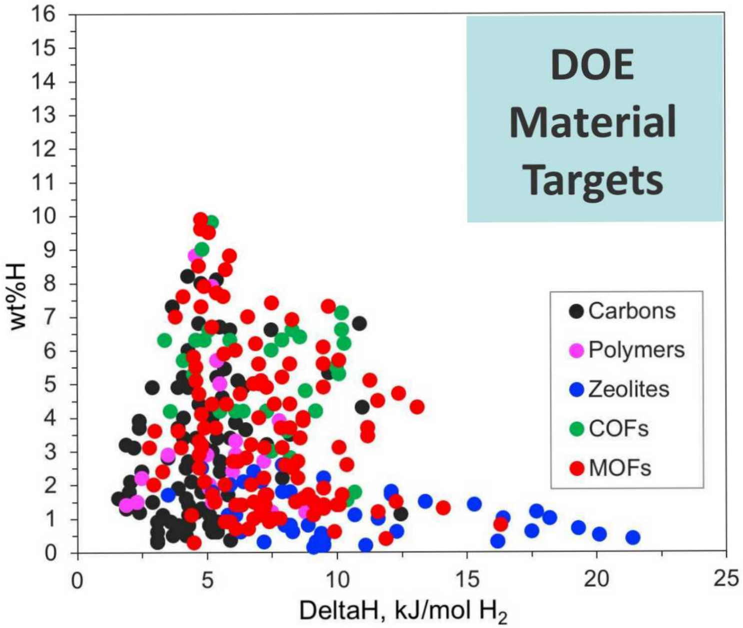
MOF H_2 binding energies
~ 2 – 33 kJ/mol



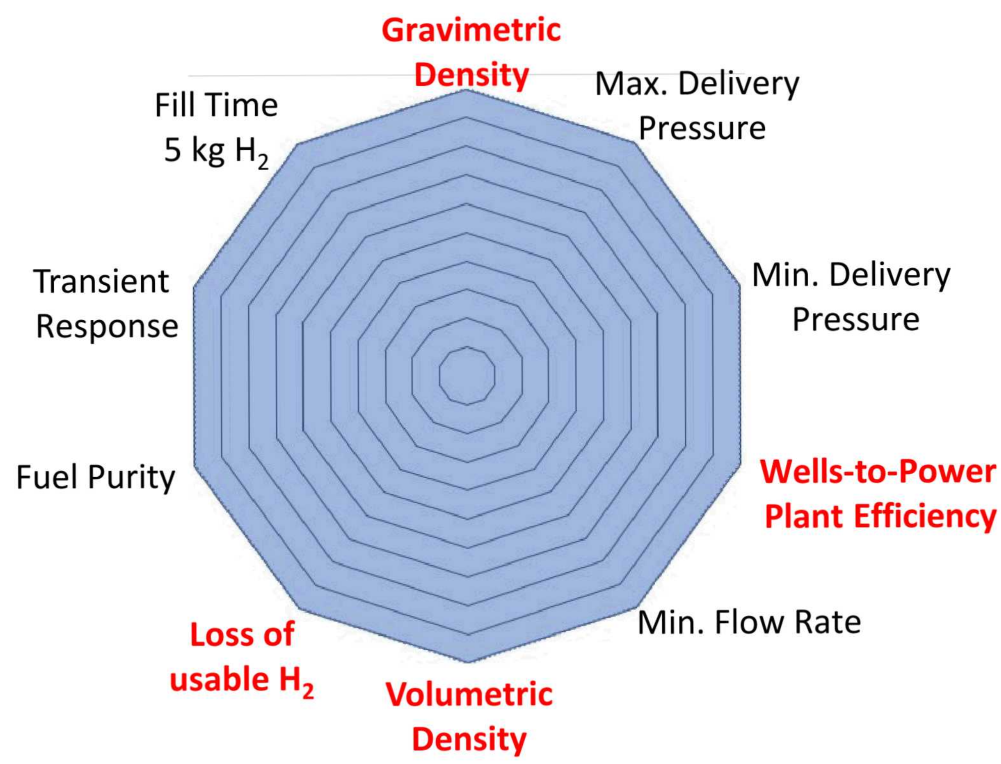
Co_2(*m*-dobdc)

No sorbent materials can meet all of the DOE targets

H_2 binds too weakly to provide sufficient capacity at ambient temperature

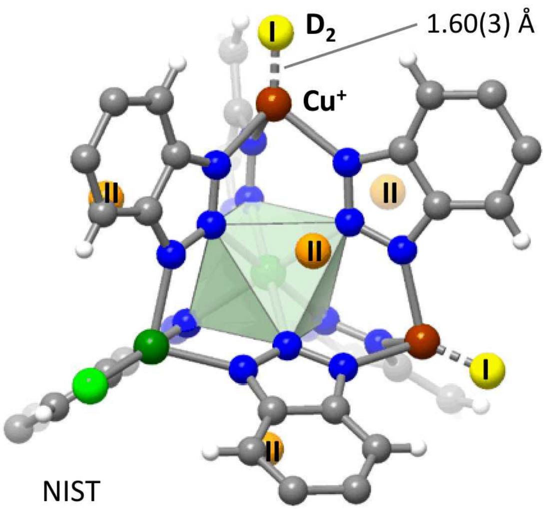


DOE Targets HyMARC is focusing on are in **red**

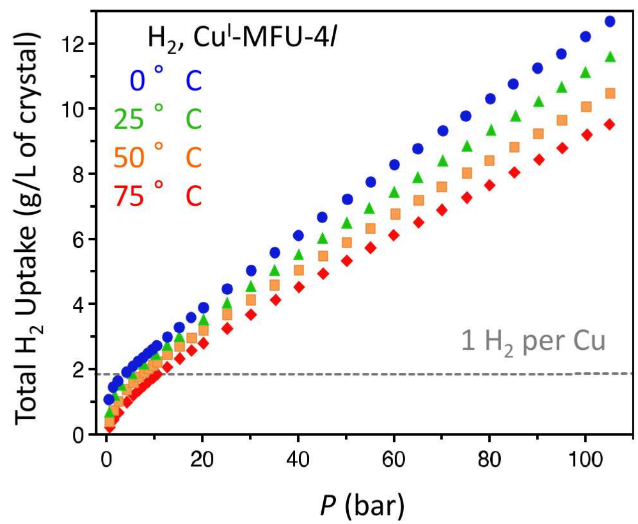


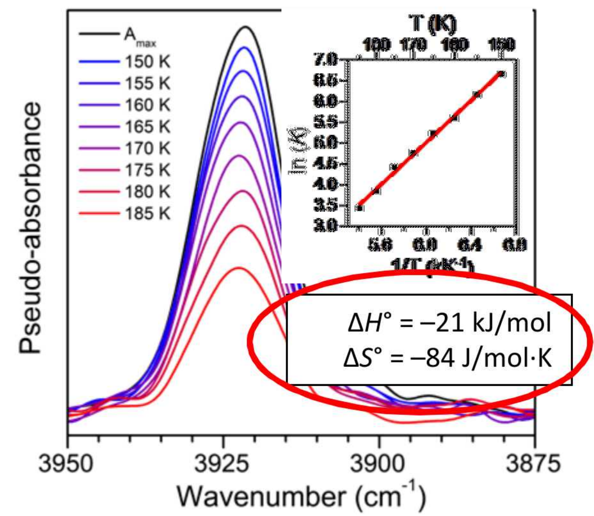
Recent HyMARC research indicates H_2 binding energies can be increased in MOFs

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.

High hydrogen capacity metal hydrides, but strong chemisorption and H_2 release/uptake are limiting

$$M(AH_x)_y \underset{\text{Abs.}}{\overset{\text{Des.}}{\rightleftharpoons}} MA_y + 1/2xyH_2$$

$$2NaAlH_4 \overset{TiCl_3}{\rightleftharpoons} 2NaH + 2Al + 3H_2$$

Bogdanovic *et al. J. Alloys Comp.* **1997**, *253-254*, 1
Bogdanovic, Schwickardi, *U.S. Patent* 6,106,801, **2000**

$$Mg(NH_2)_2 + 2LiH \rightleftharpoons Li_2Mg(NH)_2 + 2H_2$$

Cheng *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 5828
Luo *et al. J. Alloys Comp*. **2004**, *381*, 284

$$2LiBH_4 + MgH_2 \rightleftharpoons 2LiH + MgB_2 + 4H_2$$

Pinkerton *et al. J. Phys. Chem. C* **2007**, *111*, 12881
Vajo *et al. J. Phys. Chem*. C. **2005**, *109*, 3719

$$Mg(BH_4)_2 \rightleftharpoons MgB_2 + 4H_2$$

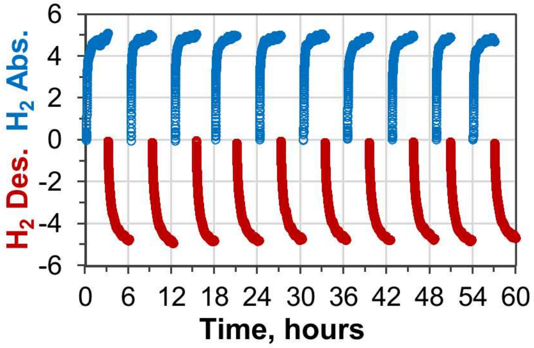
Soloveichik *et al. Int. J. Hydrogen Energy*, **2009**, *34*, 916
Severa *et al. Chem. Commun*. **2010**, *46*, 421

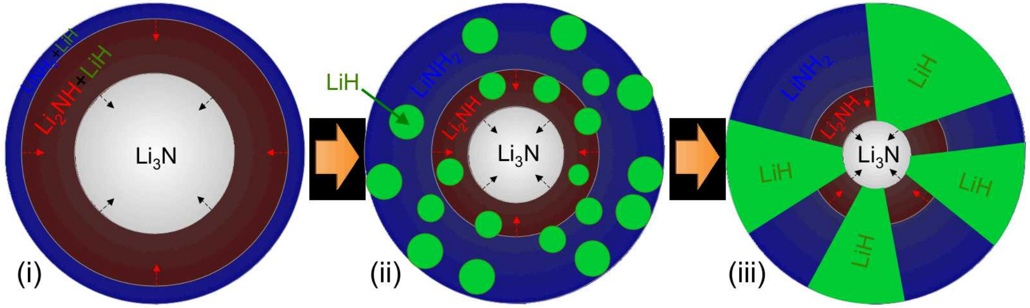
Problems & Challenges

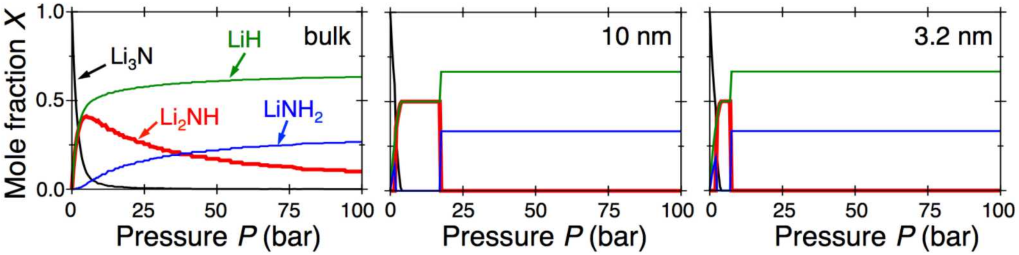
- *high dehydrogenation temperatures*
- *high pressure required for rehydrogenation*
- *stable intermediates ($[B_{12}H_{12}]^{2-}$, $[NH]^{2-}$, etc.*
- *contamination of H_2 gas with impurity gases*
- *loss of capacity upon cycling*

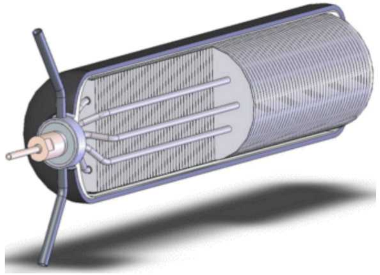
Nanoscale metal hydrides accelerates release kinetics

Design Parameters	bulk-Li_3N	KH-6nm-Li_3N
Reversible capacity. wt%	8.2	**5.4**
Thermal cond., W m^{-1} K^{-1}	1.0	**9.6**
Density of hydride bed, kg m^{-3}	710	**760**
Total system mass, kg	312	**252**
Total hydride mass, kg	112	**116**
Tank outer diameter, m	0.46	**0.45**
Tank length, m	2.21	**2.19**
System volume, m^3	0.256	**0.227**
% 2025 Gravimetric Target	33	**40**
% 2025 Volumetric Target	55	**62**







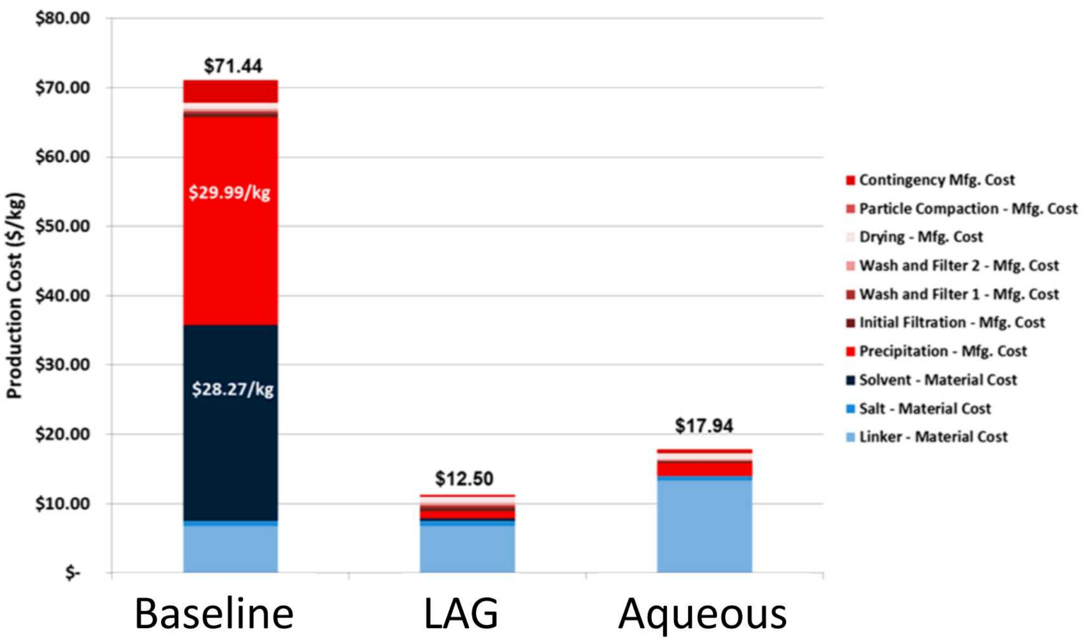


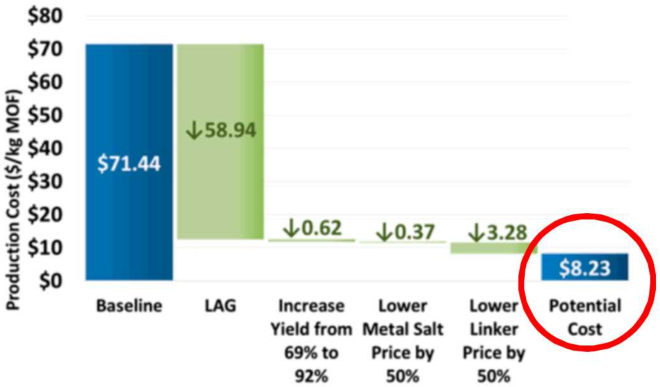
MHFE-SAH tank design

⇒ Used HSCOE Metal Hydride Finite Element model to reveal non-intuitive tradeoffs and benefits of using nanoscale metal hydrides in an operational H_2 storage tank

Techno-economic analysis suggests large-scale production of MOF sorbents is economically feasible

Production of 2.5 Mkg/year of Mg_2(dobdc)
(dobdc4– = 2,5-dioxido-1,4- benzenedicarboxylate; Mg-MOF-74)





Baseline: solvothermal process
LAG: Liquid-Assisted Grinding
Aqueous: replace organic solvents with water

See D. DeSantis et al. *Energy & Fuels*, DOI: 10.1021/acs.energyfuels.6b02510

Take-home messages

Compressed gas (700 bar): physically impossible to meet DOE volumetric target

Solid-state materials have potential to meet DOE targets

HyMARC: a National Laboratory team 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**

In FY19, Research to develop *Hydrogen Carriers* was initiated (Tom Autrey, PNNL, lead)

We are grateful for the financial support of EERE/FCTO and for technical and programmatic guidance from Dr. Ned Stetson, Jesse Adams, and Zeric Hulvey

HyMARC

Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage