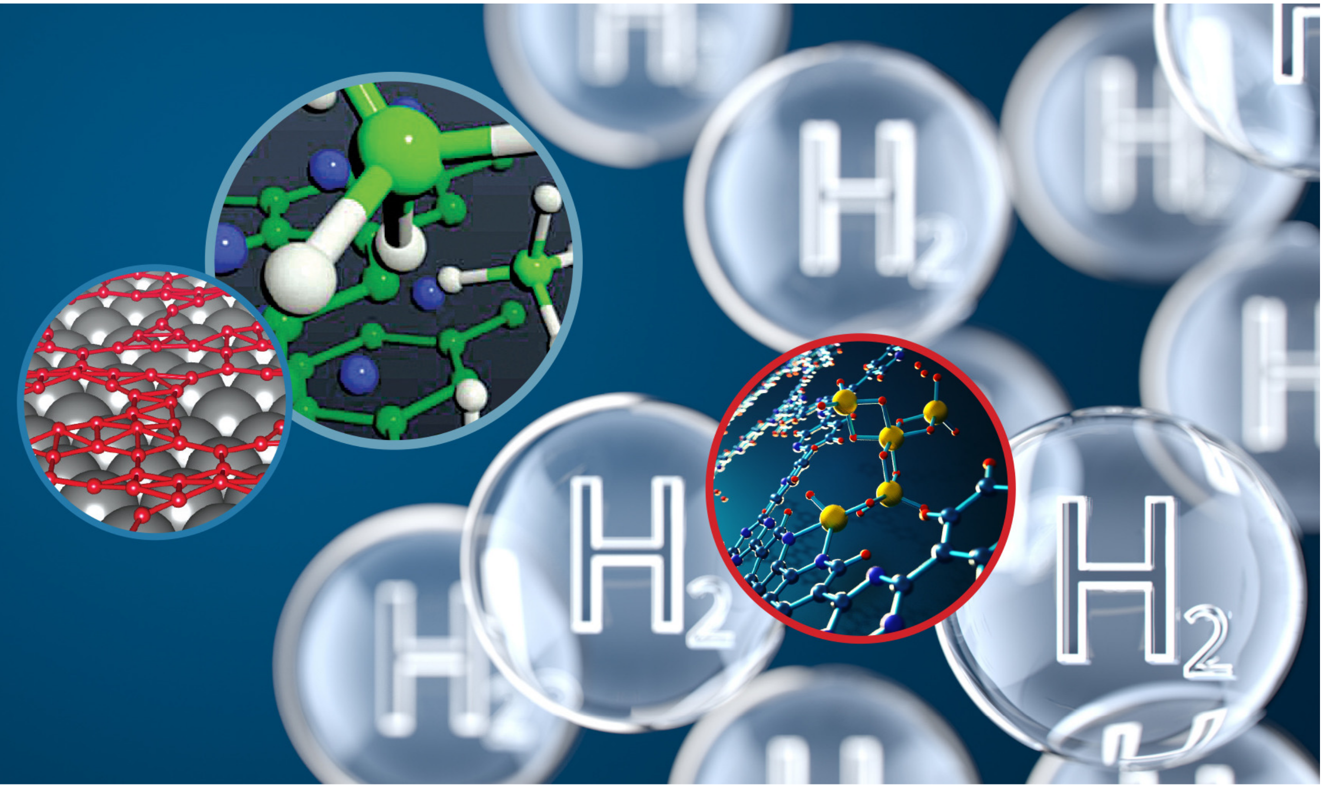
HyMARC Overview

Mark Allendorf

Senior Scientist

Sandia National Laboratories

Livermore, CA



Sandia National Laboratories

Lawrence Livermore National Laboratory

BERKELEY LAB

HyMARC
Hydrogen Materials Advanced Research Consortium

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

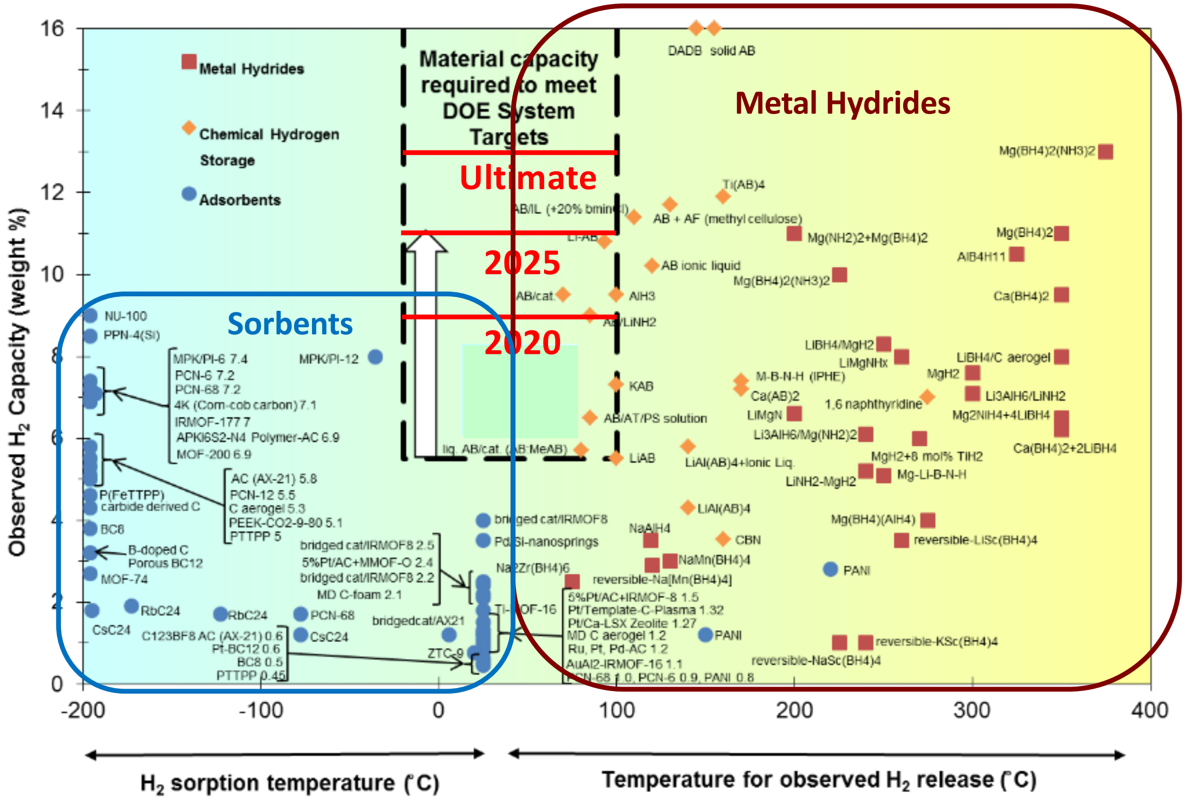
Pacific Northwest
NATIONAL LABORATORY

SAND2023-09832C

Hydrogen storage represents a thermodynamic “Goldilocks Challenge”

Design of hydrogen storage materials faces numerous tradeoffs

- **Thermodynamics vs. useable capacity**
- **Thermodynamics vs. kinetics**
- **Physical properties (e.g. melting point or viscosity) vs. capacity**



The application space for hydrogen energy carriers has expanded dramatically

nature chemistry

Perspective

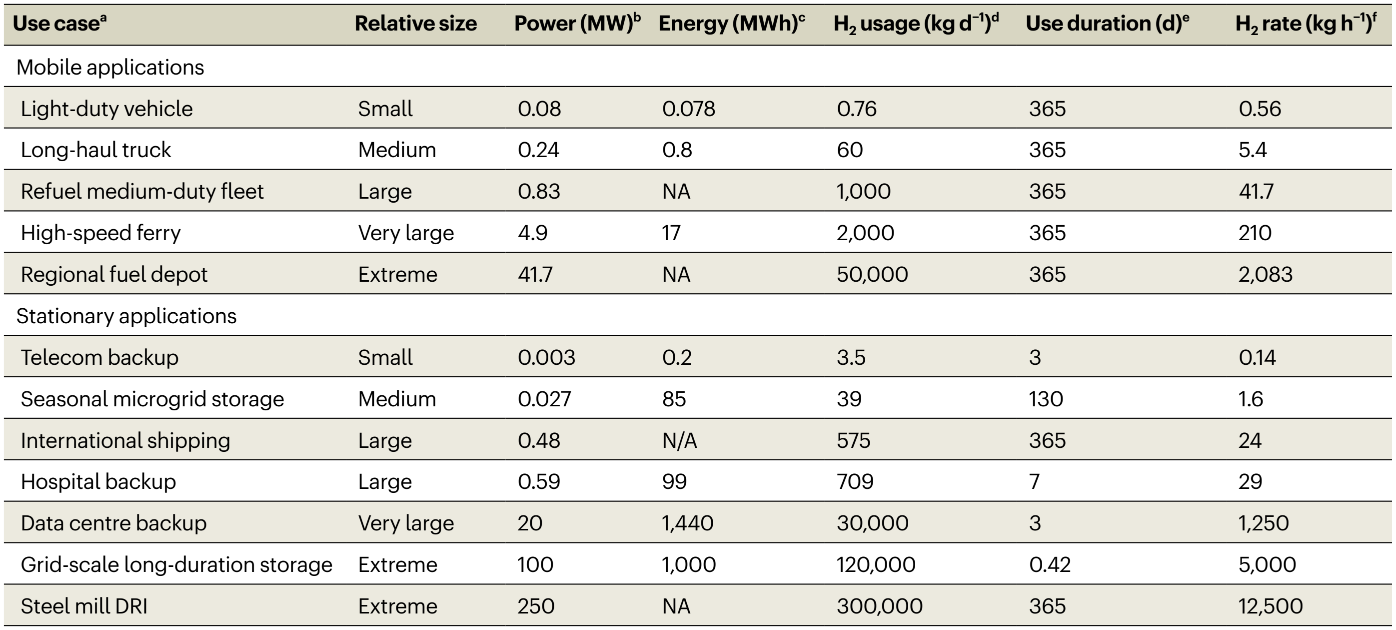
https://doi.org/10.1038/s41557-022-01056-2

Challenges to developing materials for the transport and storage of hydrogen

Received: 14 October 2020
Accepted: 2 September 2022

Mark D. Allendorf [1], Vitalie Stavila [1], Jonathan L. Snider[1], Matthew Witman [1], Mark E. Bowden [2], Kriston Brooks[2], Ba L. Tran[2] and Tom Autrey [2]

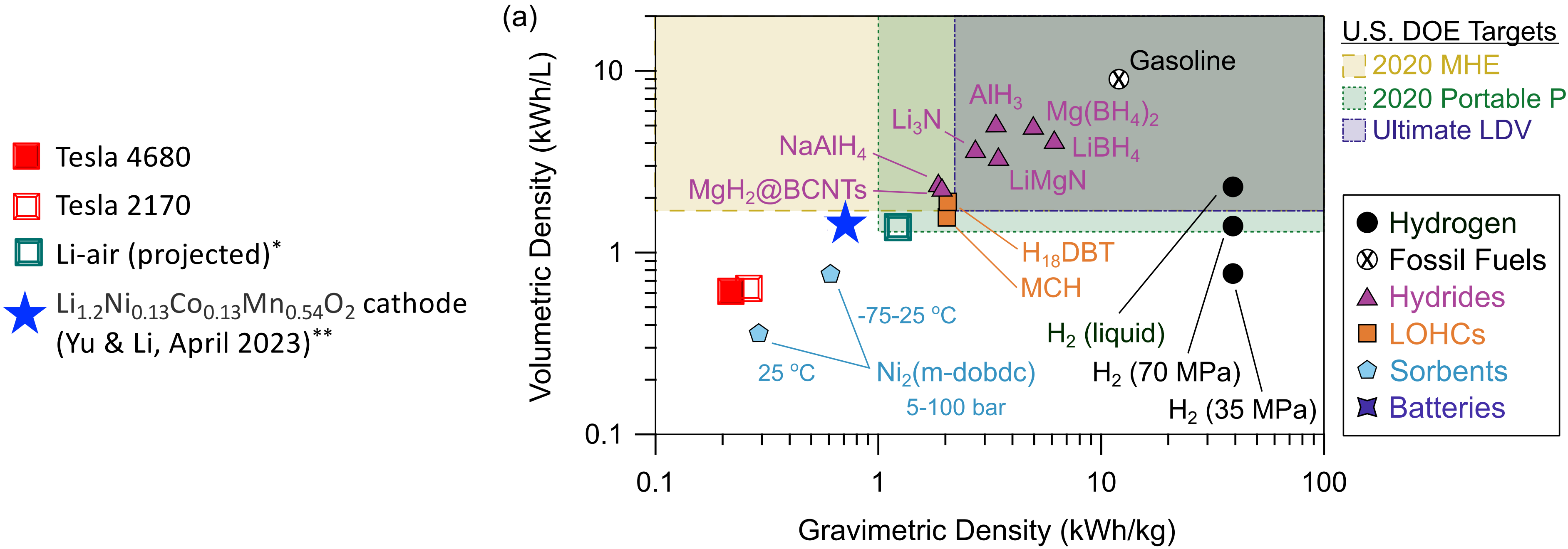
Examples of use cases for hydrogen carriers, illustrating a range of power, energy, hydrogen usage and storage requirements



Use case[a]	Relative size	Power (MW)[b]	Energy (MWh)[c]	H_2 usage (kg d^{-1})[d]	Use duration (d)[e]	H_2 rate (kg h^{-1})[f]
Mobile applications						
Light-duty vehicle	Small	0.08	0.078	0.76	365	0.56
Long-haul truck	Medium	0.24	0.8	60	365	5.4
Refuel medium-duty fleet	Large	0.83	NA	1,000	365	41.7
High-speed ferry	Very large	4.9	17	2,000	365	210
Regional fuel depot	Extreme	41.7	NA	50,000	365	2,083
Stationary applications						
Telecom backup	Small	0.003	0.2	3.5	3	0.14
Seasonal microgrid storage	Medium	0.027	85	39	130	1.6
International shipping	Large	0.48	N/A	575	365	24
Hospital backup	Large	0.59	99	709	7	29
Data centre backup	Very large	20	1,440	30,000	3	1,250
Grid-scale long-duration storage	Extreme	100	1,000	120,000	0.42	5,000
Steel mill DRI	Extreme	250	NA	300,000	365	12,500

Allendorf, Stavila, et al.
***Nature Chemistry* 2022**
DOI 10.1038/s41557-022-01056-2

How do the energy densities of SOTA battery technology compare with metal hydrides?



Allendorf, Stavila et al. *Nature Chemistry,* DOI 10.1038/s41557-022-01056-2

Targets of the battery community are 1 kWh/L and 1 kWh/kg, which are lower than many main-group metal hydrides

---

* *J. Phys. Chem. Lett.* 2010, 1, 14, 2193–2203 https://pubs.acs.org/doi/10.1021/jz1005384

** https://physicsworld.com/a/lithium-ion-batteries-break-energy-density-record/

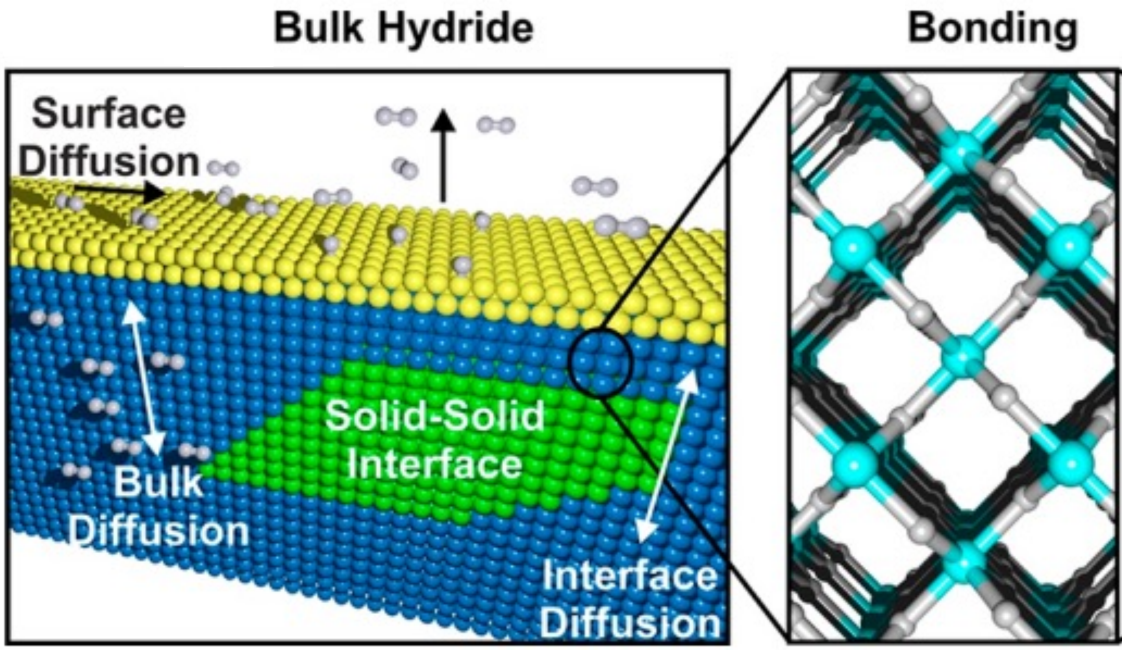
The hydrogen economy: it’s not just production. Transport and storage are critical

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**
- **Composite tanks: 550 kg of hydrogen at 250 bar**
- **Typical gas station stores 75,000 – 230,000 L (20,000 – 60,000 gallons)**

Processes accompanying hydrogen storage reactions in metal hydrides

$$\Delta H_{\text{effective}} = \underbrace{\Delta H_{\text{react}}}_{\text{Thermodynamics}} + \underbrace{E_{\text{activation}}}_{\text{Kinetics}}$$

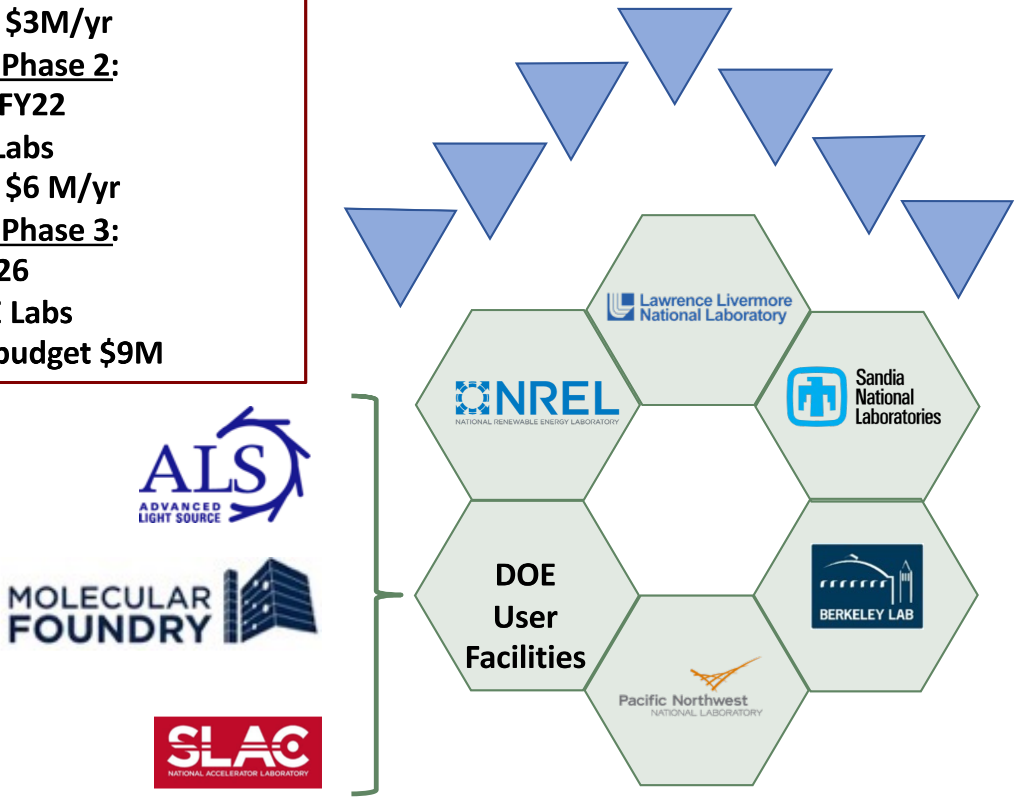


Hydrogen Materials Advanced Research Consortium (HyMARC): accelerating materials discovery → scaleup → demonstration of materials-based storage

HyMARC Phase 1:
- **FY16 – FY18**
- **3 DOE Labs**
- **Budget $3M/yr**

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

HyMARC Phase 3:
- **FY23-26**
- **5 DOE Labs**
- **FY23 budget $9M**



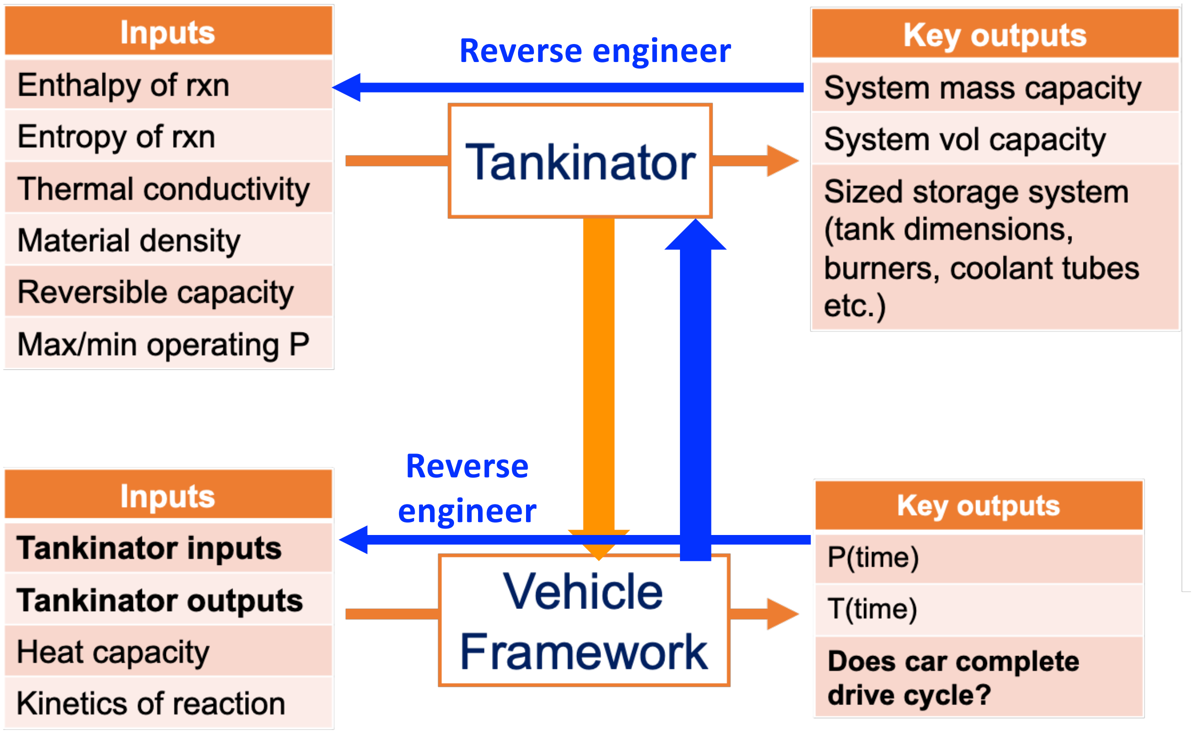
Seedling Projects
- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**

HyMARC responsibilities
- **Comprehensive: metal hydrides, sorbents, hydrogen carriers (e.g. LOHCs, NH_3)**
- **Materials discovery & optimization**
- **Multiscale modeling**
- **Systems modeling**
- **Advanced characterization tools**
- **Validation of material performance**
- **Database development**
- **Guidance to FOA projects**

https://www.hymarc.org/

Systems analysis + material synthesis & characterization = “Co-Design”

Storage system modeling tool workflow



Inputs
Enthalpy of rxn
Entropy of rxn
Thermal conductivity
Material density
Reversible capacity
Max/min operating P

Reverse engineer

Tankinator

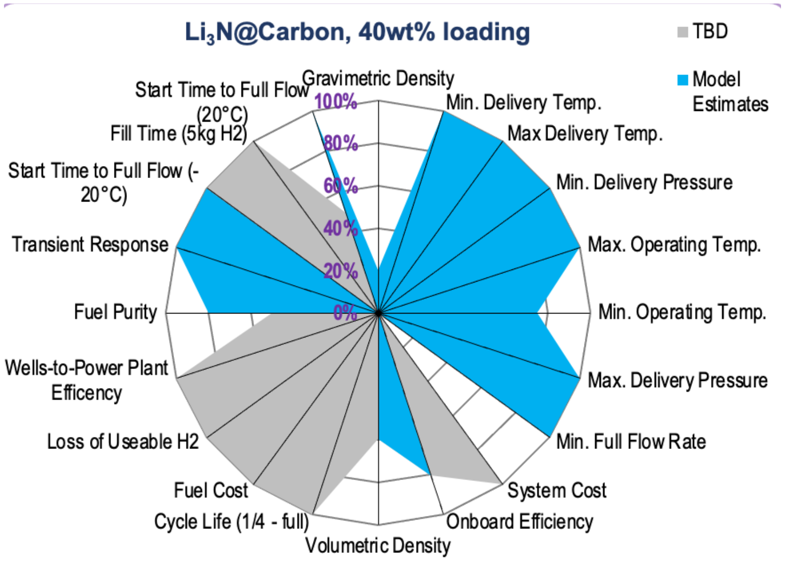
Key outputs
System mass capacity
System vol capacity
Sized storage system (tank dimensions, burners, coolant tubes etc.)

Inputs
Tankinator inputs
Tankinator outputs
Heat capacity
Kinetics of reaction

Reverse engineer

Vehicle Framework

Key outputs
P(time)
T(time)
Does car complete drive cycle?



<u>Example</u>: what’s needed to make a nanoscale metal hydride practical?

Reduce the temperature for H_2 desorption to ≤250 ℃

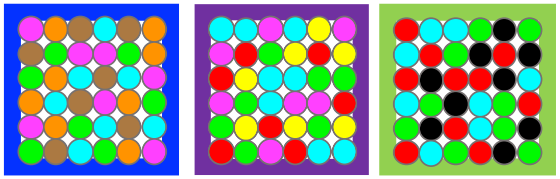
→ Enables aluminum fuel tank instead of stainless steel

→ Reduces number of cooling tubes and H_2 consumption by burner

HyMARC is dramatically accelerating material discovery and optimization using data science and machine learning methods

HyMARC Hydrogen Materials Advanced Research Consortium

(1) HEA overview:



- ≥ 4 elements, ~ equimolar
- Defined lattice type
- Solid solution character necessitates a compositional ML model

(2) Enumerating refractory HEA space

E = {Al, Ti, V, Cr, Zr, Nb, Mo, Pd, Hf, Ta}

$$\binom{E}{4}+\binom{E}{5}+\binom{E}{6} \rightarrow \text{672 compositions}$$

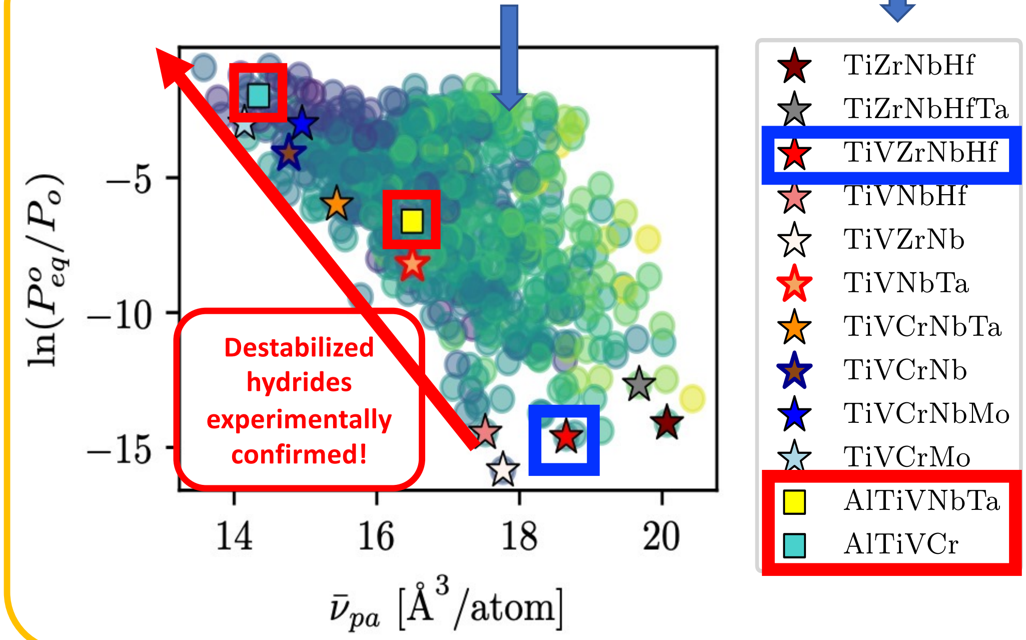
Far too many for experiments…

(2) Fit model parameters using known training data, then assess accuracy based on the known test set

(3) Screening refractory HEA space

Predicted by ML model

Experimental values



Destabilized hydrides experimentally confirmed!

Witman, Ek, Ling, Chames, Agarwal, Wong, Allendorf, Sahlberg, Stavila. *Chem. Mater.* 30 (11), **2021**

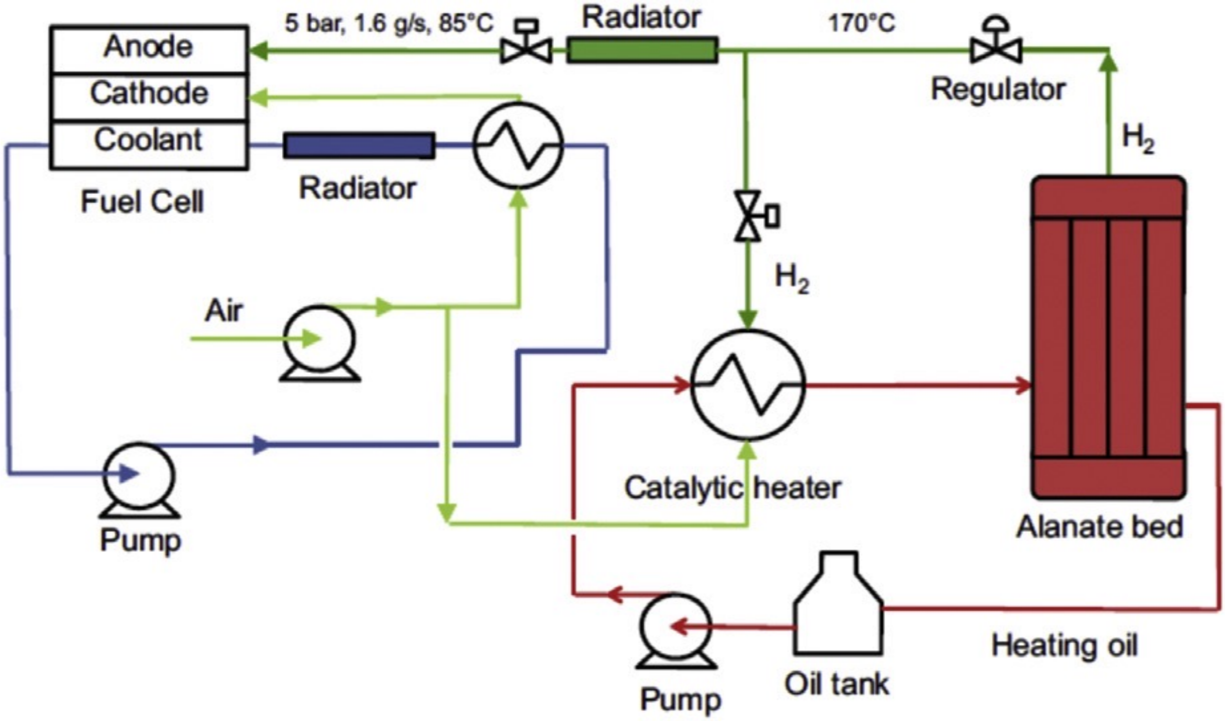
Translating laboratory discoveries to higher TRL: High-pressure hydride scale-up reactor

Objective: bring on-line the GM Hydride Station, a multi-bed hydride PCT reactor designed and fabricated for the GM hydride tank project, to enable measurements and testing to increase the TRL of HyMARC-developed storage materials.

Capabilities:

- 2 separate hydride beds
- H_2 source volumes up to 8 L at 2500 psi (167 bar)
- Pressures up to 230 bar feasible with compressor
- 1000 W heating units
- Calibrated desorption volumes up to 40 L

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



K. P. Brooks et al. *Int. J. Hydrogen Ener.* **45** (2020) 24917-24927

Required model inputs:

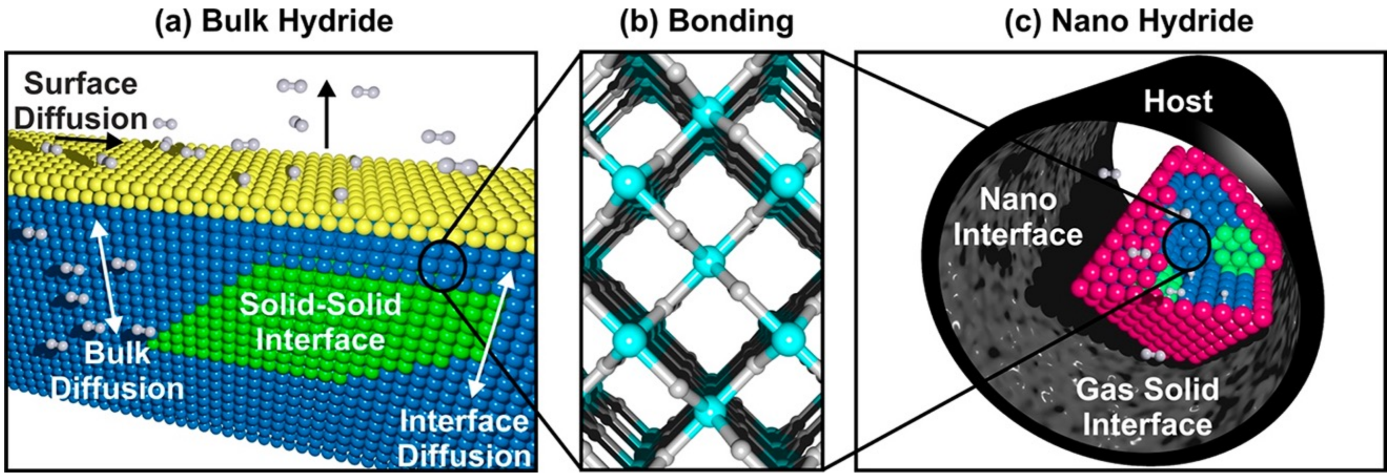
Intrinsic material properties:

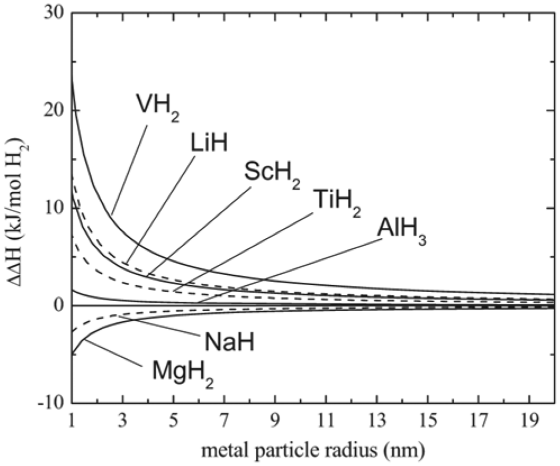
- **Composition (hydride loading)**
- **Reaction thermodynamics**
- **H_2 desorption kinetics**
- **Thermal conductivity**

System design parameters:

- **Tank material**
- **Bed density (hydride packing density)**
- **Max. operating T, P**

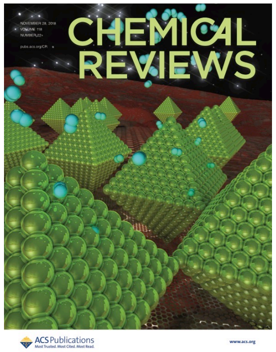
Moving beyond bulk: Nanoscale Hydrides





Kim, K. C. *Nanotech.* 2009, 20, 204001

- **Improved thermodynamics and accelerated kinetics**
    - Increased surface energy → greater thermodynamic driving force
    - Reduced diffusion lengths → decreased/eliminated mass transport limitations
    - Host-guest charge transfer → weakened M-H bonds
- **Stabilizes hydride nanoclusters against agglomeration**
- **Pathway for heat management**



A. Schneeman et al. *Chem. Rev.* **2018**, *118*, 10775−10839

Temperature-programmed H_2 desorption of nano-$NaAlH_4$ in a MOF host

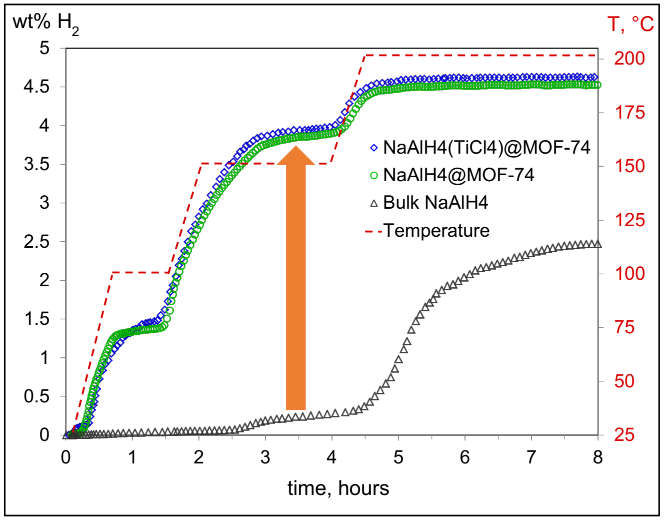
- **Highly improved kinetics vs bulk**
  - T_{onset} = ~30 °C
- **Capacity almost 2X bulk at 200 °C**
- **Ti does not affect H_2 desorption kinetics**

→ Difference almost entirely due to nanoscale and template effects

→ This is very different from bulk $NaAlH_4$

- **Initial desorption = 4.5 wt%**

→ Suggests nearly complete dissociation to NaH + Al + H_2



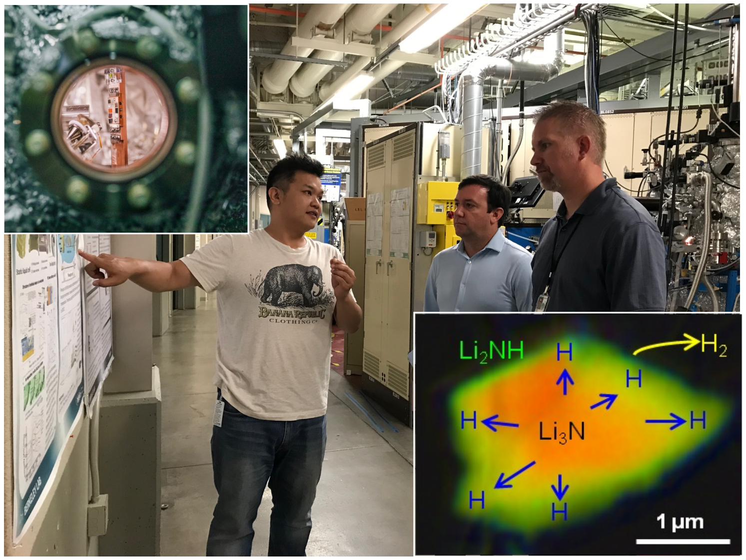
Ti (mol %)	H_2 capacity (% M/M)	$E_a(d)$ (kJ mol^{-1})	ref
0 (bulk)	5.12	118.1	26
2% (bulk)	4.25	79.5	26
0 (10 nm pores)		58	3
0 (4 nm)		46	4
0 (1 nm)		53.3	7
3 (≤1.2 nm)	4.2	57.4	this work

V. Stavila et al. *ACS Nano* 2012, **6**, 9807

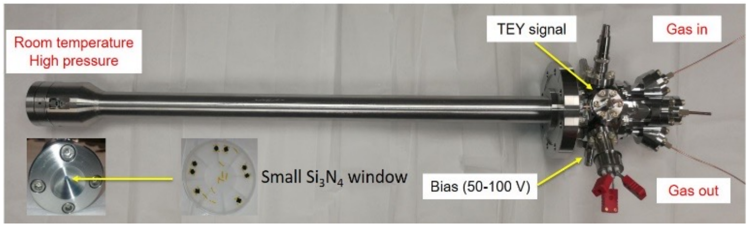
HyMARC partnerships with DOE/Office of Science user facilities link foundational science with application- driven materials discovery

Example: Advanced Light Source at LBNL

- **Dedicated time on 3 beamlines (XAS and STXM); HyMARC is the only EERE-funded project to be granted this status**
- **22 publications in high-impact journals, including *JACS*, *Nat. Mater.*, *Adv. Mater.*, *Nat. Commun.***
- **Installed new high-pressure/high-temperature cell for *operando* observation of storage material chemistry**
- **ALS measurements generated new structure-property relationships:**
  - Discovery of reversible metastable metal hydrides
  - Inverse core-shell mechanism of H_2 release by the lithium amide storage system ($LiNH_2$+2LiH)
  - Single-site catalysts for reversible dihydrogenation of Liquid Organic Hydrogen Carriers
- **Renewal proposal extending AP for 3 years approved June 2023**



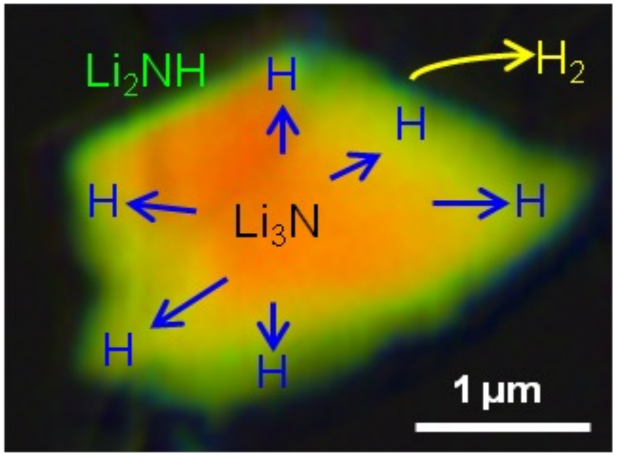
HyMARC-designed high-pressure gas flow cell for probing storage materials using X-ray absorption spectroscopy

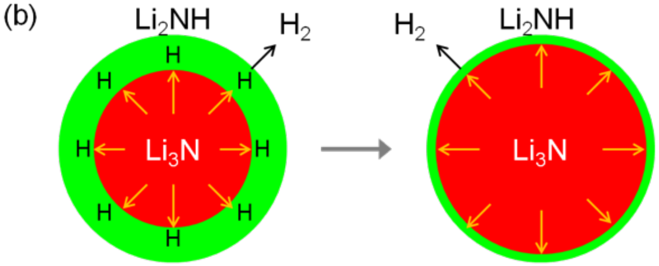


Paradigm shift: STXM composition maps show H_2 release from the surface is rate-limiting

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

Scanning Transmission X-ray Microscopy (STXM)
H_2 desorption at 450 °C (ALS BL5.3.2.2)





Absorption:

- **Proceeds as predicted previously**

Dehydrogenation:

- **Inverted core-shell → opposite microstructure from phase-field/Wulff prediction**

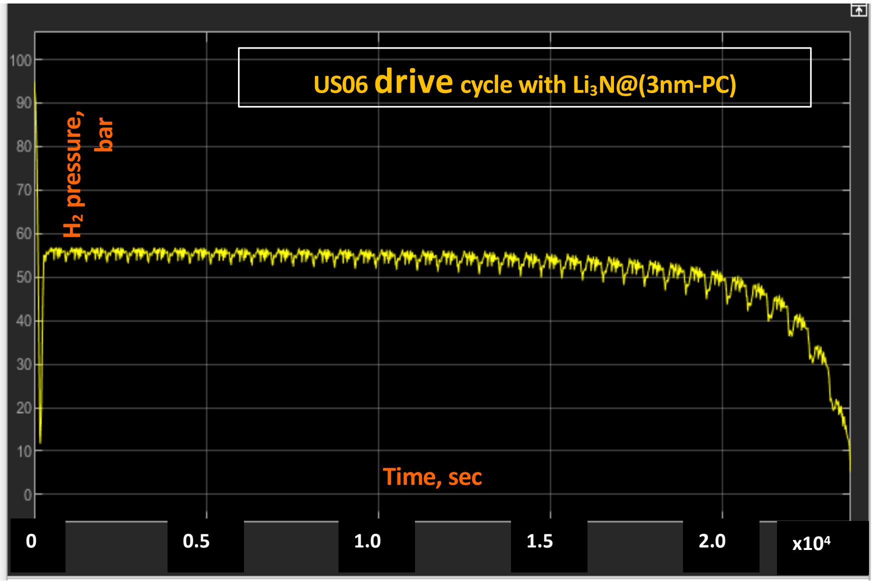
Possible explanations:

- **Surface energies alter thermo, favoring H-rich surfaces**
- **Surface dehydrogenation kinetics are slow**
- **Nucleation kinetics favor Li_3N in interior due to lower interface energies**

J. L White et al. *ACS Appl. Mater. Interfaces* **11**, 4930 (2019)

Nanoscale metal hydrides have faster H_2 uptake and release

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



Key results

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

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

→ Porous C host accelerates H_2 release throughout the tank due to faster heat transport

Design Parameters	Bulk-Li_3N	KH-6nm-Li_3N
Reversible cap. (theory) 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

Disruptive strategies are needed to overcome scientific and technical barriers to accelerated materials discovery: Metastable Metal Hydrides

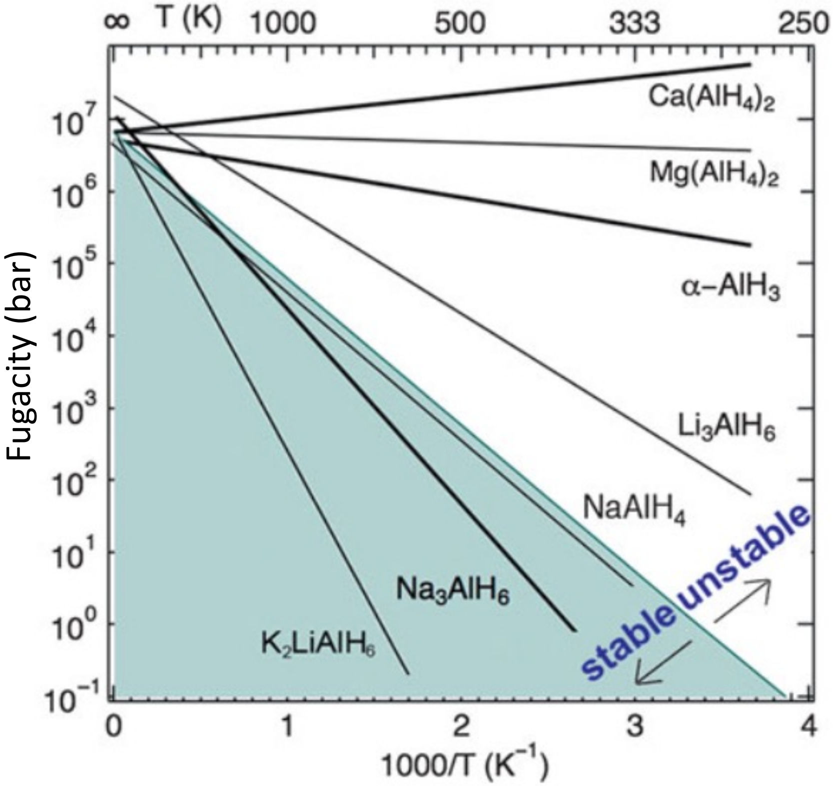
Bulk AlH_3 properties:

- Earth-abundant composition
- ~10.4 wt% grav. capacity
- Vol. capacity 2X L-H_2 (148 g H_2/L)
- Fast desorption
- Rehydrogenation thought to be thermodynamically impossible

AlH_3 chemistry:

- $AlH_3 \rightarrow Al(s) + 1.5H_2$
- $\Delta G = -48.5$ kJ/mol
- Experimental re-hydrogenation of aluminum:
  - 4.9 GPa (49000 bar), 330 C

Calculated van't Hoff plots for several stable and metastable hydrides

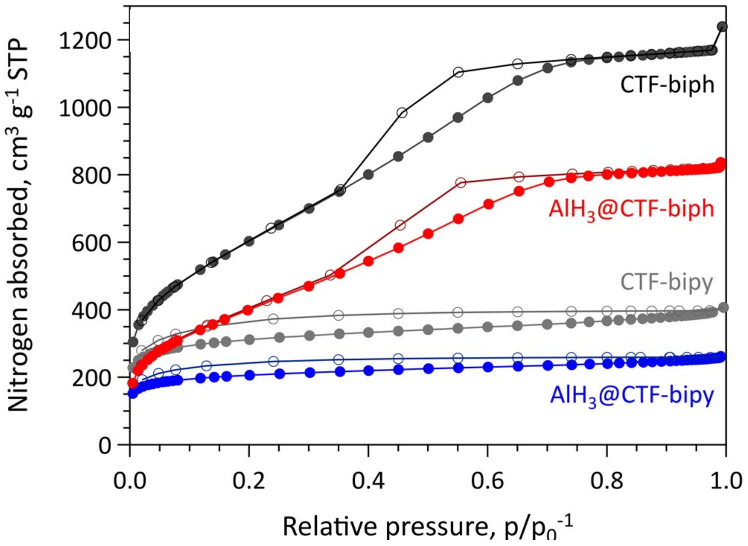


Graetz & Reilly
Scripta Mater. **56** (2007), 835

Nanoconfinement of alane (AlH_3) in Covalent Triazine Frameworks (CTF)

HyMARC Hydrogen Materials Advanced Research Consortium

N_2 adsorption isotherms (77 K)



Bulk rehydrogenation:

- **330 °C/49000 bar (4.9 GPa) (Saitoh et al. 2008)**
- **Ab initio: $\Delta G < 0$ above 7000 bar at 27 °C (Graetz et al. 2006)**

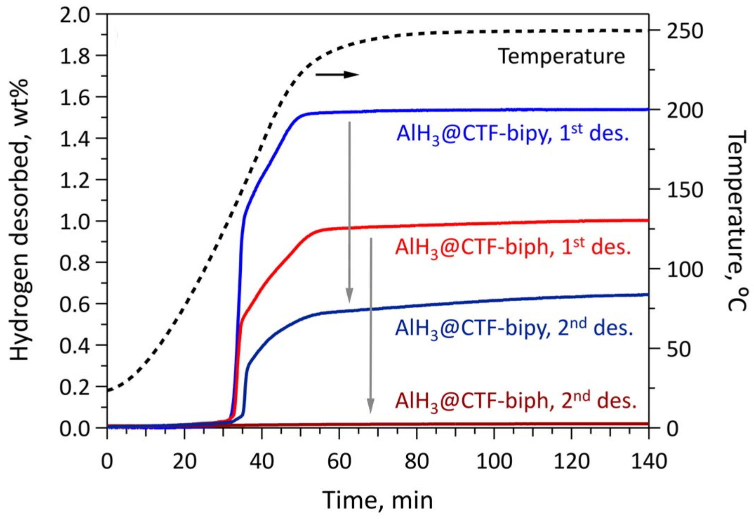
→ Nanoscaling reduces equilibrium rehydrogenation pressure by 10X – 70X

V. Stavila et al. *Angew. Chem. Int. Ed.* doi.org/10.1002/anie.202107507

Rehydrogenation at 60 °C, 700 bar H_2

Sieverts data for H_2 desorption

	AlH_3@CTF-bipy	AlH_3@CTF-biph
Cycle 1	1.52 wt%	1.00 wt%
Cycle 2	0.65 wt%	0 wt%
Cycle 3	0.58 wt%	--
Cycle 4	0.57 wt%	--



In conclusion…

- Hydrogen storage is an essential component of a renewable energy economy
- HyMARC is addressing the critical problems blocking the translation of materials discovery to pilot-scale deployment
- HyMARC is discovery science → system modeling → TEA → scale up
- Co-design of materials is critical to developing successful materials for complex, but highly constrained, applications

Acknowledgements

Sandia National Laboratories
- Dr. Vitalie Stavila
- Dr. Jon Snider
- Dr. Josh Sugar
- Dr. Lennie Klebanoff
- Dr. Farid El Gabaly

Pacific Northwest National Lab
- Dr. Andy Lipton
- Dr. Kriston Brooks
- Dr. Tom Autrey
- Dr. Mark Bowden

Technical University Dresden
- Dr. Andreas Schneemann

Lawrence Berkeley National Lab
- Dr. Chaochao Dun
- Dr. Jinghua Guo
- Dr. Yi-Sheng Liu
- Dr. David Prendergast
- Dr. Ji Su
- Dr. Jeff Urban

Lawrence Livermore National Lab
- Dr. Brandon Wood
- Dr. Maxwell Marple
- Dr. Shinyoung Kang
- Dr. Sichi Li
- Dr. Liwen Wan
- Dr. Tae-Wook Heo

National Renewable Energy Laboratory
- Dr. Tom Gennett

SLAC National Accelerator Laboratory
- Dr. Nicholas Strange

KAIST
- Prof. Eun Seon Cho
- YongJun Cho

Max-Planck-Institut Festkoerperforschung
- Prof. Bettina Lotsch
- Dr. Hendrik Schlomberg

Seoul National University
- Dr. Sungsu Kang
- Dr. Min-ho Kang
- Dr. Hayoung Park
- Dr. Jungwon Park

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

HyMARC
Hydrogen Materials Advanced Research Consortium

THANK YOU