HyMARC Overview

Co-Directors:

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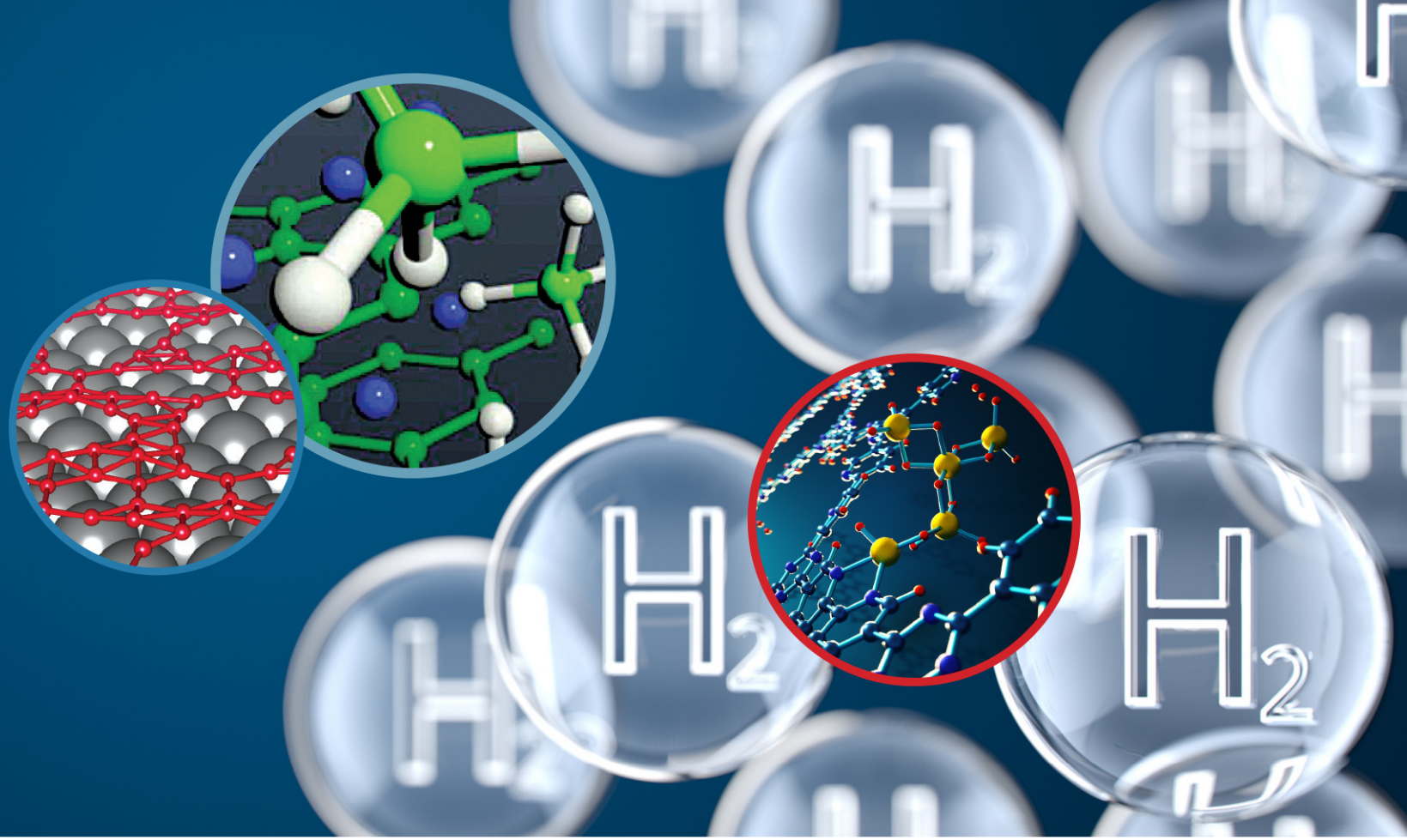
May 8, 2024



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DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID # ST127

Project Goal: develop and optimize materials for specific use cases, with levelized cost of storage less than physical storage, improved safety, and properties that meet DOE targets

- **Exploit the modeling, systems analysis, and material discovery/optimization capabilities developed by HyMARC-1 and HyMARC-2 to enable synergistic (storage system ↔ material) development**
  - Consider Liquid Organic Hydrogen Carriers (LOHCs), sorbents, and metal hydrides
  - Stationary and transportation use cases, esp. long- and short-term energy storage
  - Life cycle and safety analysis
  - Perform modeling across device scales, systems analysis, and TEA to determine where material-based storage solutions are advantageous compared with current technologies
- **Employ an effective co-design initiative (numerical modeling + system analyses + synthesis/characterization) to optimize materials for specific storage and transport applications**
  - E.g. systems analysis and modelling of the most promising materials advanced from HyMARC are being tested at both benchtop and kg-scale to assess their performance and provide engineering data for future demonstration activities.
  - Increase TRL of materials-based storage/carriers to allow opportunity for market penetration (from 3 to 6)
- **Develop a pilot STEM internship program with Minority-Serving Institutions**
  - Metro State University in Denver, CO, a historically Hispanic institution
- **Facilitate interactions with industry**
  - Establish an industrial advisory board

Overview

Timeline

Phase 1: 10/1/2015 to 9/30/2018
Phase 2: 10/1/2018 to 9/30/2022
Phase 3: 10/1/2022 to 9/30/2026
Project continuation determined annually by DOE.

Budget

Total FY23: $7,041,600
Total FY24: $5,500,000 (planned)

Barriers Addressed

General:
A. Cost, B. Weight and Volume, C. Efficiency,
E. Refueling Time

Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Partners/Collaborators

HyMARC – SNL, NREL, LLNL, LBNL, PNNL team members
NIST – Craig Brown; SLAC – Nicholas Strange

Immaterial inc	**AirBus**
GKN	**Microsoft**
SoCal	**Colorado School of Mines**
OCO Chem	**University of California, Berkeley**
Honeywell	**SyZyGy Plasmonics**
Stoke Space	**NuScale Power**

Relevance and Potential Impact

Project activity	Potential impact
System analysis/TEA	• Predict levelized cost of storage • Define technical targets for specific use cases
Material co-design, scale-up, and integration activities	Clean hydrogen deployment:[a] • Property data needed for system modeling • Understand material performance at realistic operating scales and conditions • Intermediate-scale storage systems to bridge lab-scale and demonstration • Advance material system TRL to 4 or 5
Development of storage materials comprised of earth-abundant elements	• Low-cost, safe hydrogen storage for high-impact uses of clean hydrogen such as backup power, stationary power, and heavy-duty vehicles[b]
Liquid organic hydrogen carriers for distribution and large-scale storage	• Increased capacity[b] • Faster charge/discharge rates[b] • Multi-cycle reversibility and increased round-trip efficiency[b]
Capability development	• Establish best practices • Validate novel materials developed by Seedling Projects

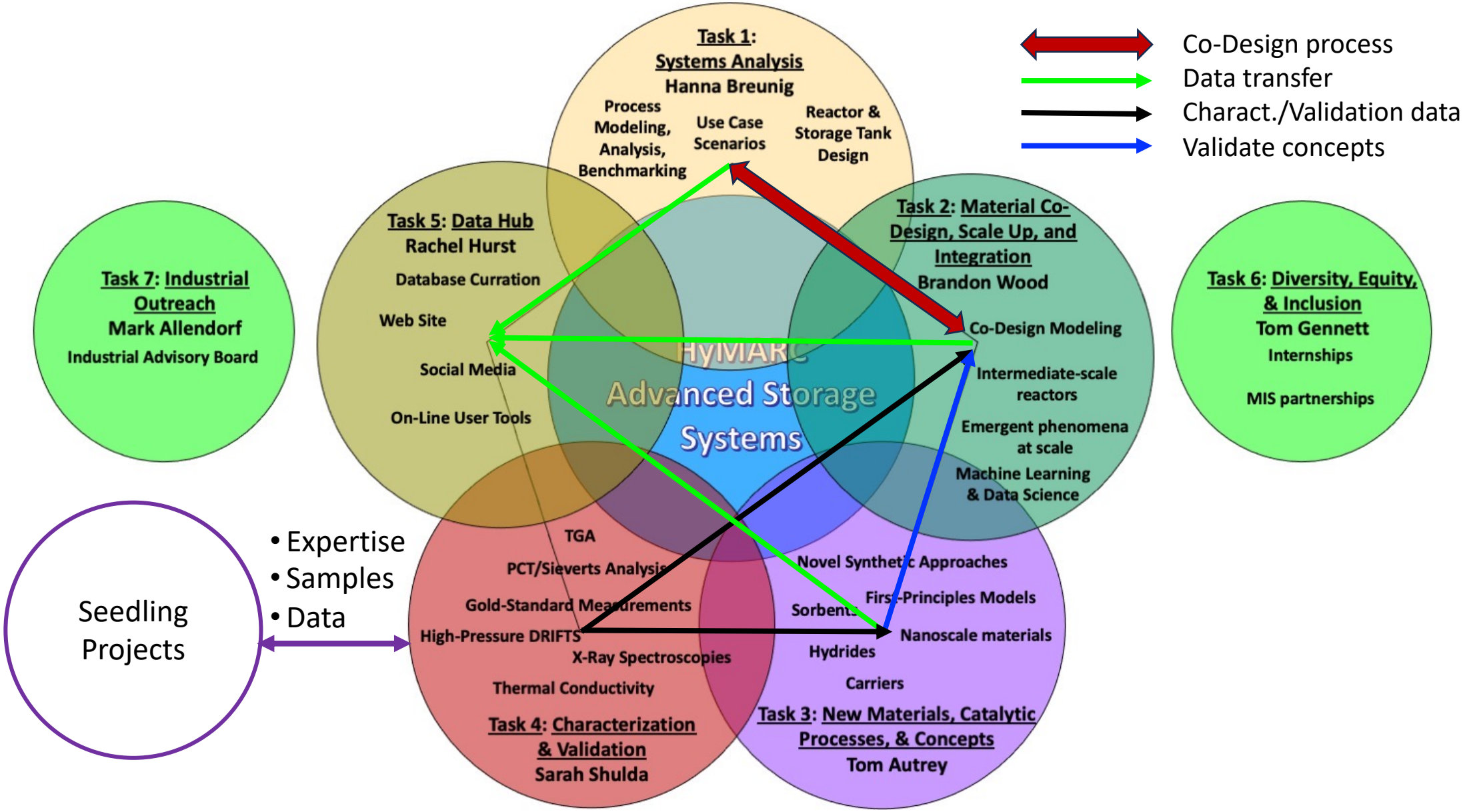
ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Hydrogen

U.S. National Clean Hydrogen Strategy and Roadmap

[a] Hydrogen Earthshot: https://www.energy.gov/eere/fuelcells/hydrogen-shot

[b] U.S. National Clean Hydrogen Strategy and Roadmap

Approach: seven tasks in HyMARC-3 are structured to transition materials discoveries to use cases with requirements determined by system modeling



Approach: Safety Planning and Culture

HyMARC was not required to submit a safety plan to the Hydrogen Safety Panel (HSP)

Safety is the priority within HyMARC

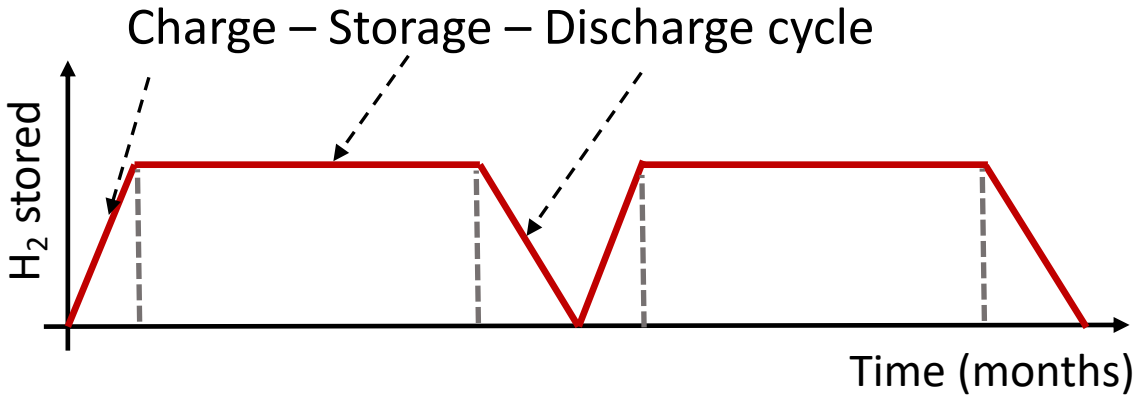
- **We follow all OSHA and DoE Hydrogen Safety Best Practices**
- **Publicly disburse any historic industry incidents and near misses with analyzed safety hazards**
- **Confirmed all electrical compliance and ready verification processes for new and built instrumentation, checked for bill of materials (Incorporated best practice)**

World-class expertise from Research Scientists, Engineers and Safety Personnel

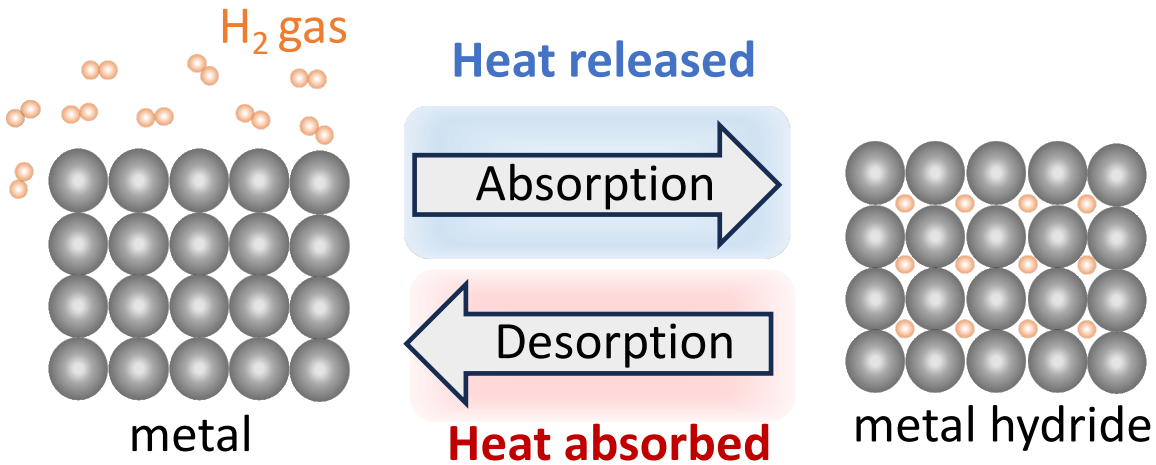
- **Personnel training - subject matter experts in hydrogen hazards, pressurized gas, electrical safety**
  - **All project team members attended 8-hour various training courses including those on: cryogenics, electrical, chemical waste, pressurized gas energetics, glovebox safety, etc.**
  - **Safety training and mentoring required of all visitors, interns, graduate students, postdocs etc.**
- **Systems are designed with safety prioritized and reviewed by safety engineers at the respective laboratories**
- **Detailed documentation of hazards, procedures, and maintenance are updated periodically**
- **Attention to personnel safety training and defined scope of work**
- **All safety protocols will be shared within the HyMARC DataHub**

Approach Task 1: focused evaluation of materials and end uses

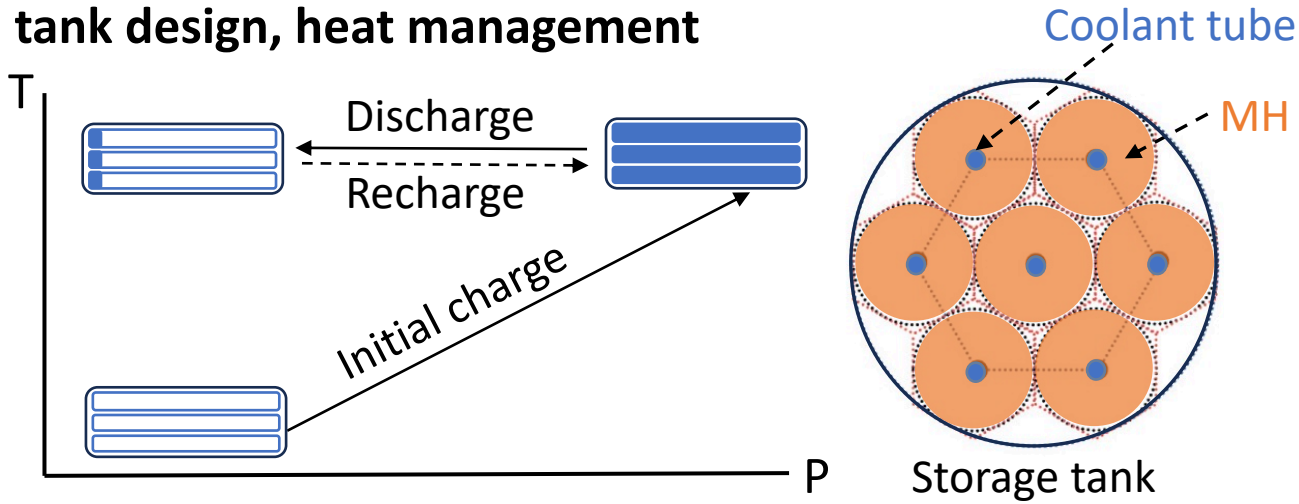
1. Define hydrogen storage application scenario & align with end users



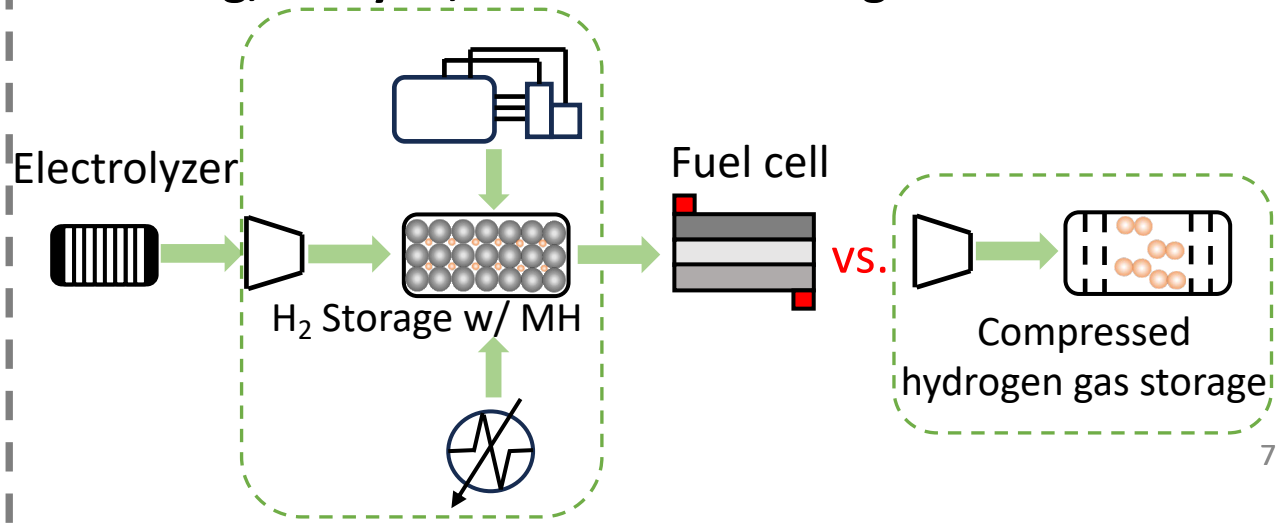
2. Select representative materials and obtain experimental data



3. Determine operational conditions, reactor & storage tank design, heat management



4. Apply standardized HyMARC process for process modeling, analysis, and benchmarking



Approach: HyMARC Levelized Cost of Storage used to reveal material strengths and weaknesses

$$LCOS = \left(\frac{1}{RTE} - 1\right) P_c + \frac{(C_P + C_E)}{M_{H_2}} \cdot \frac{(1 - T_x \cdot D_{pv})}{1 - T_x} \cdot \frac{r(1+r)^T}{(1+r)^T - 1} + \frac{O\&M\&L}{M_{H_2}}$$

- **Material analysis evaluation framework applied across HyMARC:**
  - Sorbents (AC, MOF, polymer encapsulated, ALF)
  - Metal hydrides (complex, interstitial)
  - Liquid organic hydrogen carriers: MCH/toluene, ethanol, methanol, formate
  - 170 bar, 350 bar, 700 bar
  - Cryogenic
  - Salt caverns
- **Application scenarios expanded to grid and industry:**
  - Bulk H2 Truck Transportation
  - Backup Power (1-24 cycles per year)
  - High-Cycled Power (24+ cycles per year)
  - Seasonal H2 Storage
  - Industry Scale Storage for Iron/Steel and Ammonia Plants

Reviewer request:
Cross-comparison with work by SA and ANL

Approach: Task 1 Major Milestones & Status

End Date	Type	Description	Progress	Criteria or Go/No-Go
Q1	LBNL: Q progress	Coated adsorbent analysis	**100%**	*Complete report on coated sorbents for stationary applications, and demonstrate coated sorbents achieve at least a 20% reduction in cost in a stationary application.
Q2	LBNL: Annual SMART	Material evaluation for hydride	**75%**	**Preliminary TEA and systems analysis of a metal hydride system model, identifying two quantitative metrics of importance, specific to stationary applications to outperform traditional liquid and compressed storage options.
Q3	LBNL: Q progress	MCH/toluene catalyst analysis	**25%**	***Modify TEA of MCH/toluene system in industrial applications and evaluate impact of at least two new catalyst concepts from seedlings and within HyMARC
Q4	LBNL: Q progress	Formate system analysis	**25%**	****Complete draft life cycle inventory for formate carrier system, aligning with PNNL and seedling data

*Reviewer comment to use LCOS to evaluate polymer coated frameworks
**Reviewer comment to expand LCOS across HyMARC and create “co-work”, not just collaborations. Moved from Q4 to Q2 due to rapid progress
***Reviewer comment to expand to end uses. Moved from Q2 to Q4.
****Reviewer comment to look for low carbon. We will be developing and integrating LCA this year. Moved from Q3 to Q4.

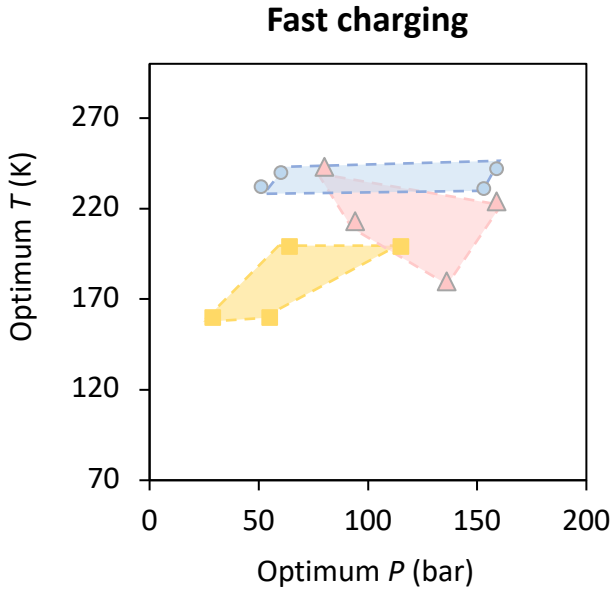
Accomplishments/Sorbents: automated pairing of materials with end uses

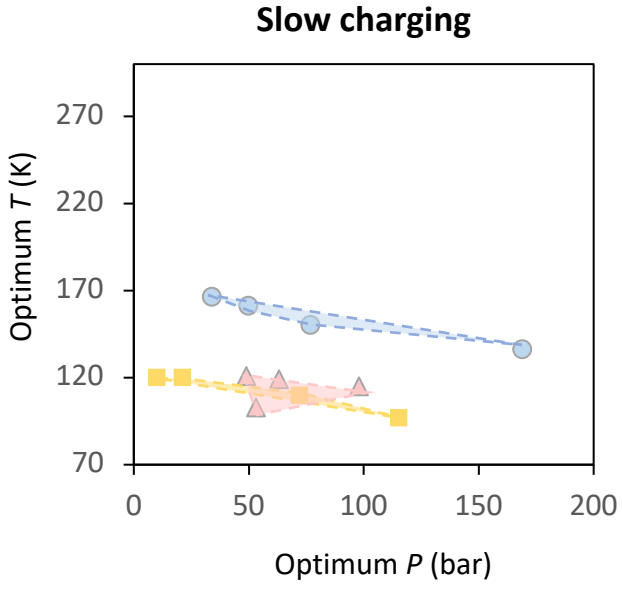
Major success: model in *Nature Energy, JACS*, and featured in *Science*

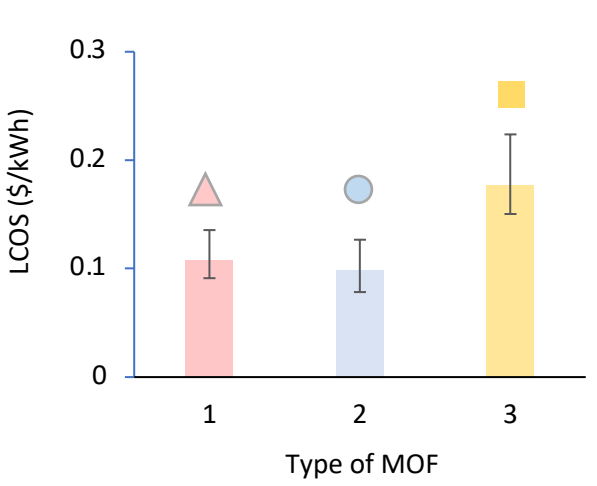
Peng et al. 2024, submitted

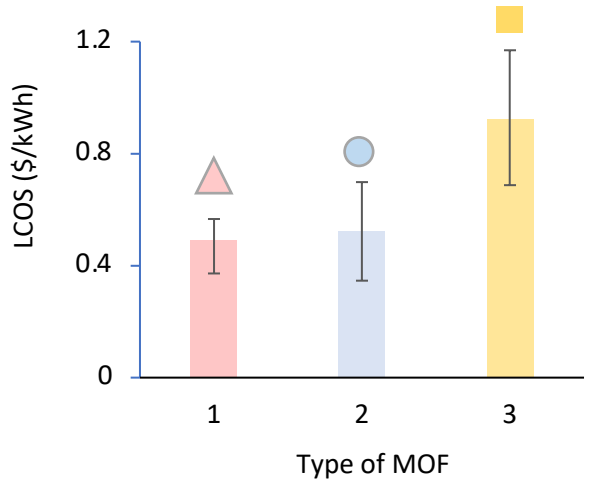
- Approach identifies:
  - Representative types of MOFs
  - Ranges of material uncertainties
  - Suitable application scenarios

MOF types	Type 1 △	Type 2 ○	Type 3 ■
Representative MOFs	MOF-5, SNU-70, IRMOF-20	Ni_2(m-dobdc), V-btdd	ALF
Target operation conditions	Generally higher uptake under cryogenic conditions	Relatively closer to ambient	Sub-ambient and low pressure
Desirable nature of MOFs	High surface area	Open metal sites	Small pores Use less exotic raw materials
Current status	Abundant experiments and models available (77 K, 5–200 bar)	Moderate experiments and models available	Limited experiments and models available





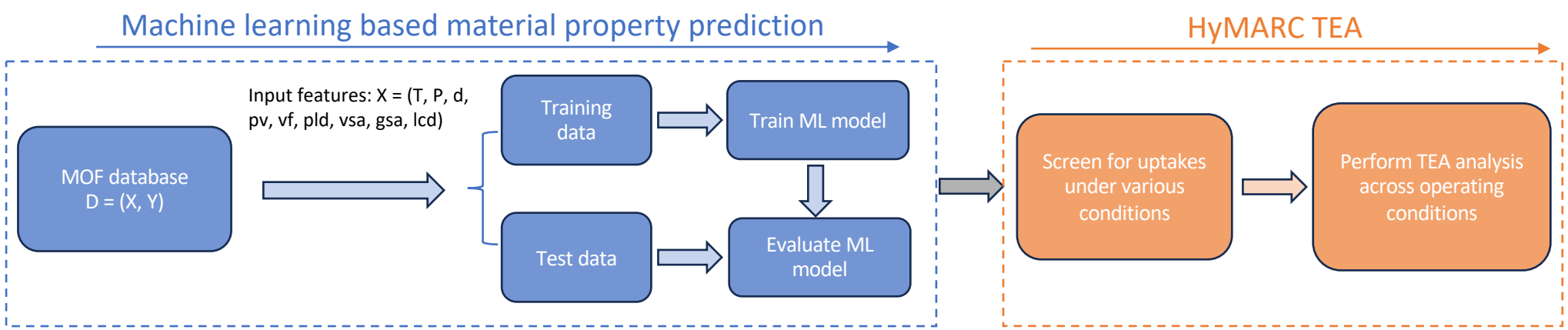




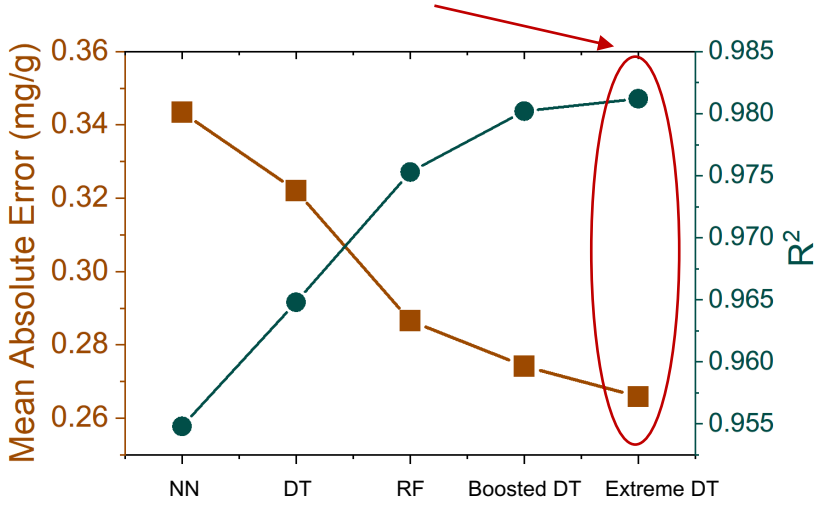
Peng, Breunig, & Long. LBNL

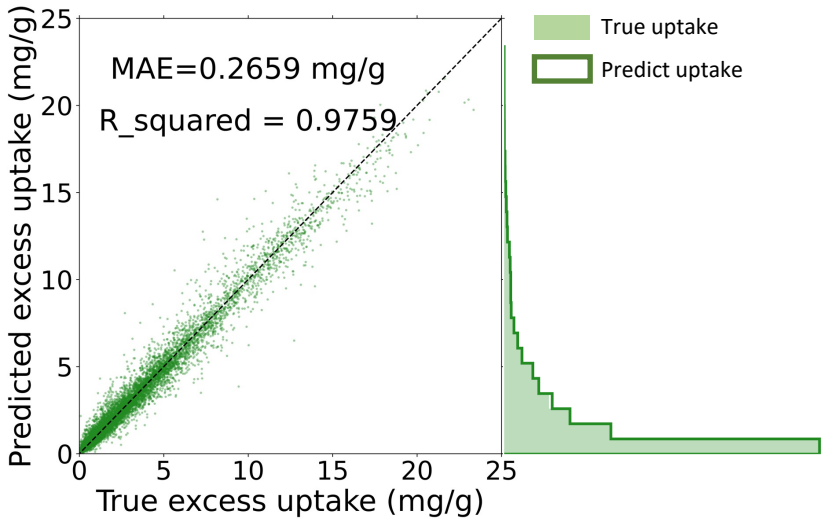
Progress/Sorbents: automation to unlock new insights

Combining machine learning with TEA to screen material databases and operation conditions



Best performing ML model





Align with critical materials initiatives

Peng & Wang. LBNL

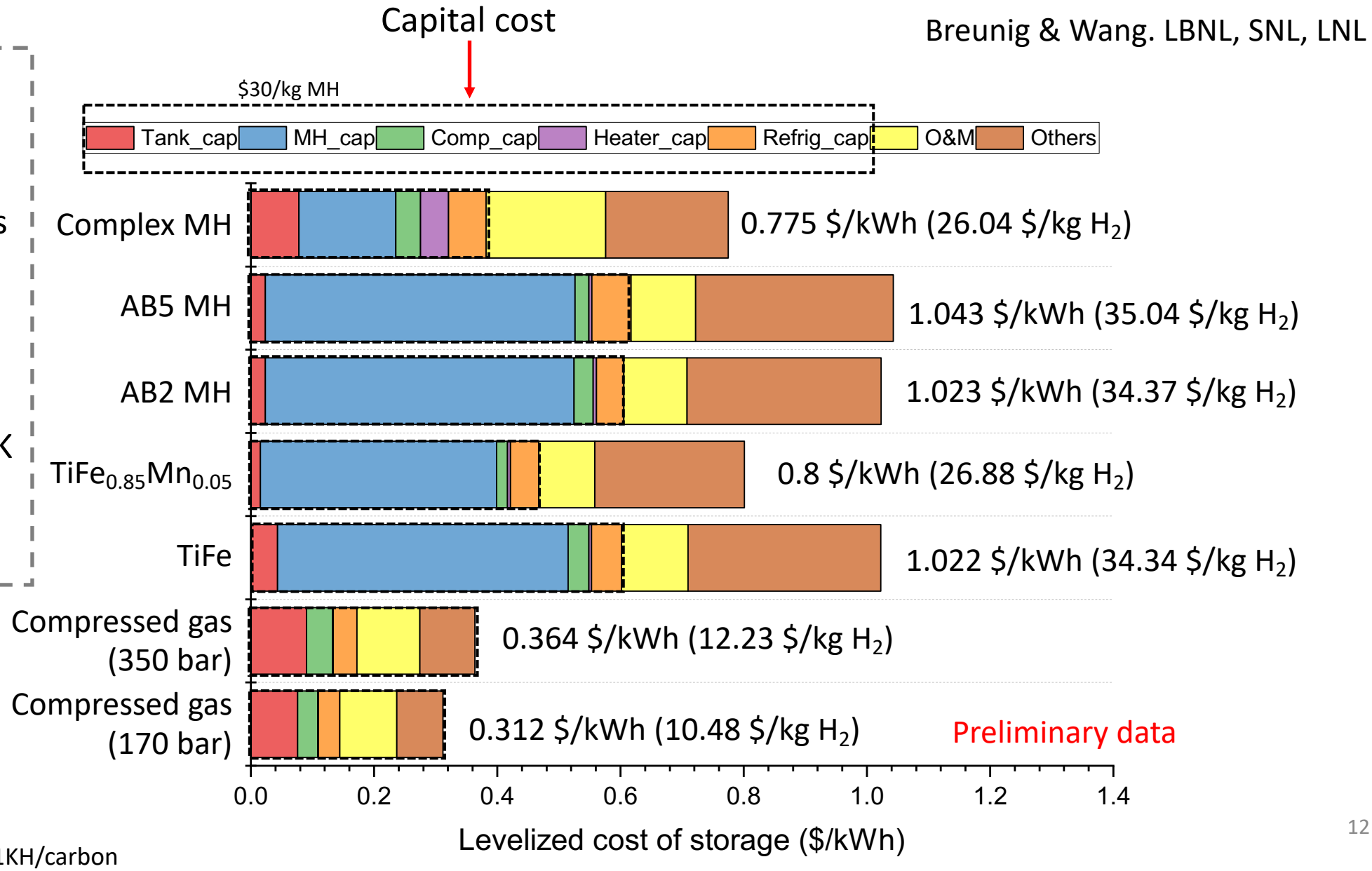
Accomplishments/Metal Hydrides: model for stationary power

Breunig & Wang. LBNL, SNL, LNL

System boundary:

Charge time: 12 hours
Discharge time: 96 hours
Cycles/yr: 12

H_2 temperature: 353 K
H_2 pressure: 2 bar



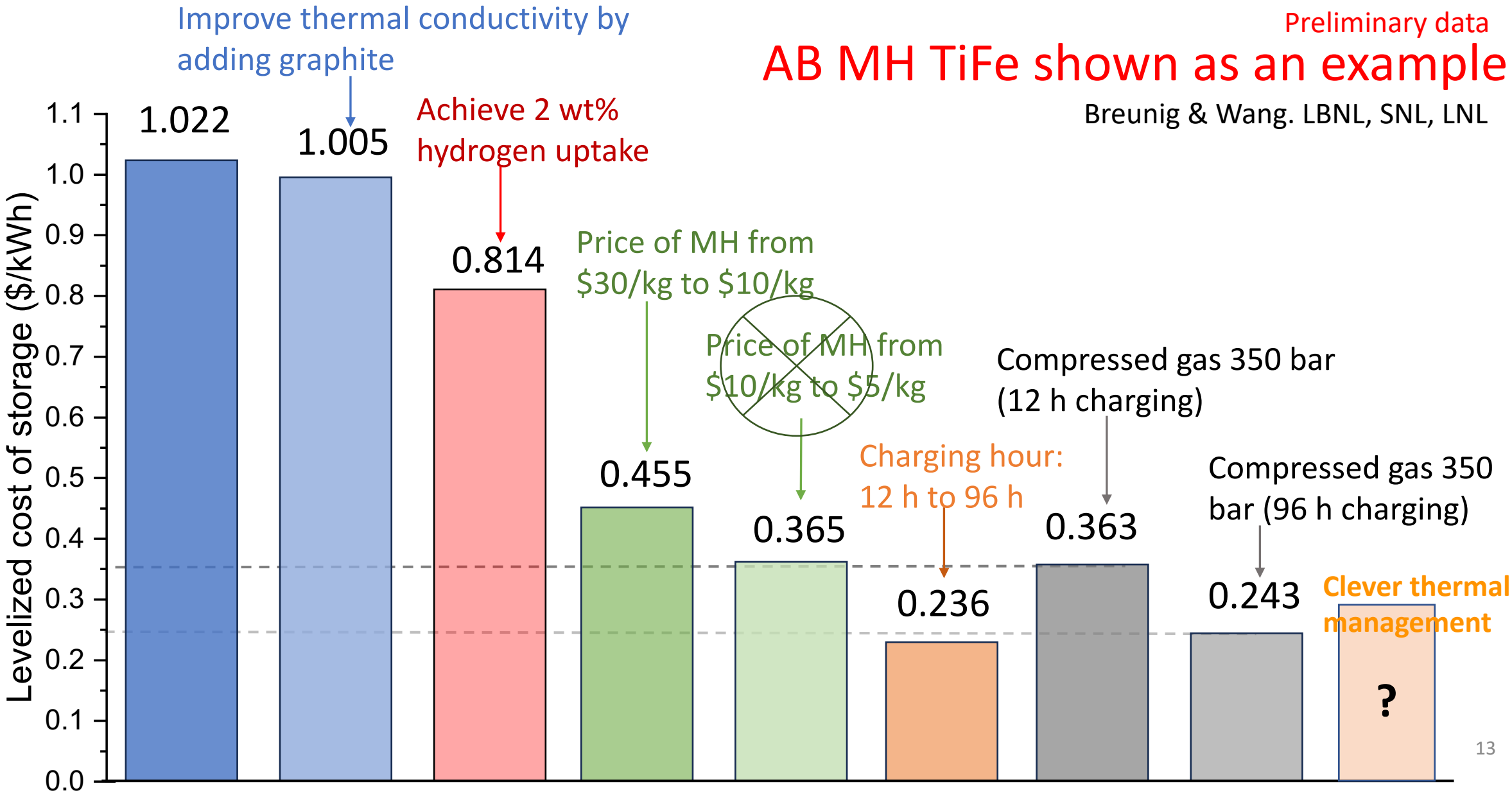
AB2 MH: $Ti_{0.95}Zr_{0.05}Mn_{1.55}V_{0.45}Fe_{0.09}$
AB5 MH: $MnNi_{4.6}Fe_{0.4}$
Complex MH: $1Mg(NH_2)_2$-2.1LiH-0.1KH/carbon

Progress/Metal Hydrides: research roadmap

Preliminary data

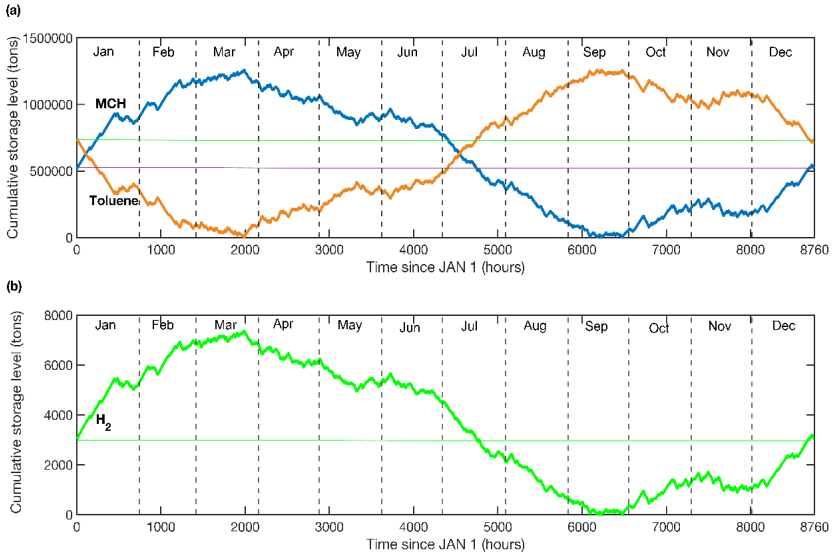
AB MH TiFe shown as an example

Breunig & Wang. LBNL, SNL, LNL

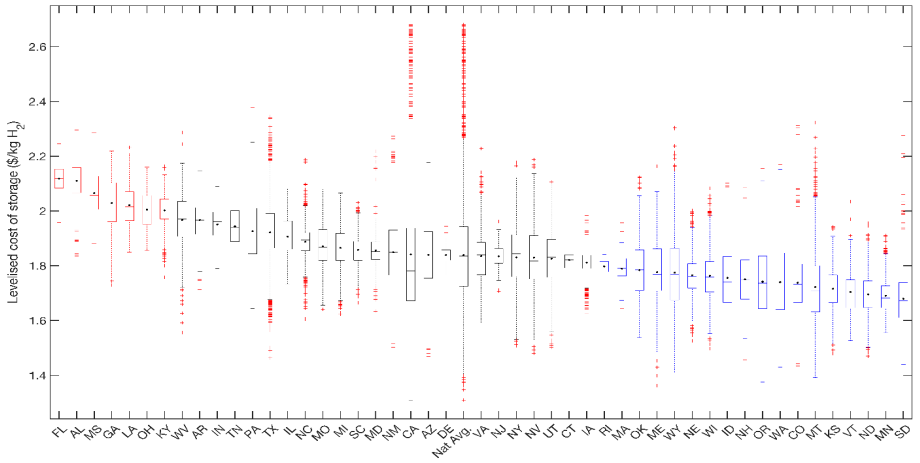


Associated projects: multi-lab collaboration to improve modelling of MCH/toluene for GW-scale electrolyzer applications

Liquid Organic Storage
Hydrogenation capacity
Dehydrogenation capacity
Annual H_2 storage
Maximum daily H_2 storage

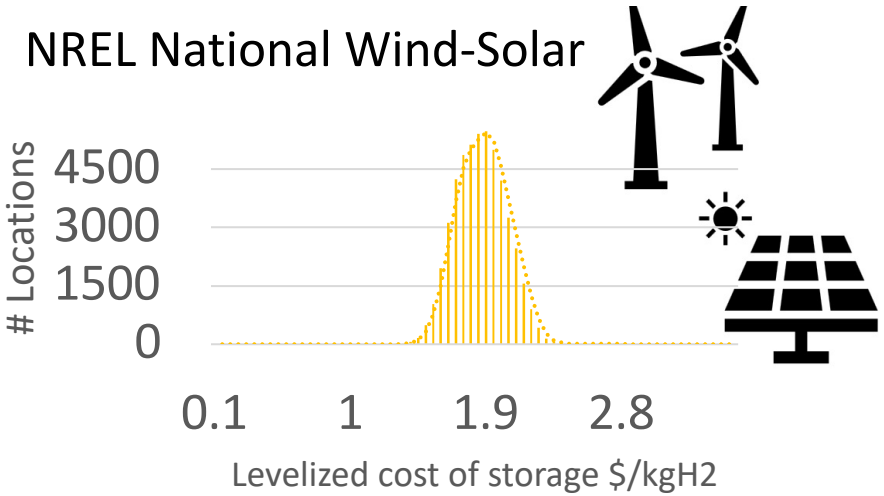


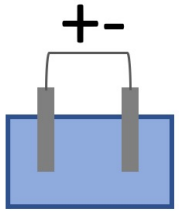
Breunig & Rosner et al 2024, submitted



MCH/toluene: $Y/kg-storage

NREL National Wind-Solar





e.g. $1/kg-produced

Storage system

H S D

Pipe to end user

e.g. $1 + X/kg-delivered

Approach Task 2: Materials Co-Design, Scale-up, and Integration

- This task represents the new HyMARC initiative involving the integration of previously developed materials, synthetic methods, multiscale models, and characterization tools to accelerate development and assess application-targeted deployment strategies.

- The most promising materials identified by the Task 1/Task 2 Co-Design process for specific use cases will be tested to assess their performance and provide engineering data for future demonstration activities.

- *We seek to increase the TRL of materials-based storage/carriers to create opportunities for demonstrations and market penetration*

Accomplishment Task 2: new high-pressure hydride scale-up reactor will translate laboratory discoveries to higher TRL

<u>Objective</u>: reactivate a multi-bed hydride PCT reactor, previously designed and fabricated for the GM hydride tank project (2012)*

- **Enable measurements and testing to increase material TRL**
- **Identify emergent phenomena at scale**

*T. A. Johnson, S. W. Jorgensen et al. *Int. J. Hydrogen En.* **37** (2012), 2835

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

Status:

- Individual components testing underway
- Computer and LabView software are operational
- Leak testing

Next steps:

- Shakedown tests with a conventional material (e.g. Hydralloy C5)

Targeting system to be fully operational by Sept. 30, 2024

Progress Task 2: test reactor to bridge gap to pilot demonstrations for liquid organic hydrogen carriers (LOHCs)

Scaling reactors up to 5 g H_2/h allows studies of LOHCs under realistic conditions in a continuous process

Flow reactor scale-up to provide:

- Continuous Process Monitoring
  - Feed Rates
  - Product Gas Flow
  - Product Gas Composition
  - Process Temperature
- Mass Balance Closure
- Catalyst lifetime studies

High pressure flow reactor capabilities:

- 400 °C and 150 bar
- 1 L H_2/min (5 g H_2/h)
- 50 mL liquid/min

Accomplishments Task 2/sorbents: H_2 Fuel Cell Demos with a MOF Tank

Fundamental questions to be addressed

- Is quality of H_2 stored in a MOF tank high enough to operate fuel cells?
- Is the amount of H_2 stored in a tank close to the expected amounts based on high-pressure isotherm data?
- Can a majority of stored H_2 be delivered to the FC stand?
- How much tank volume can be filled with adsorbents?

Progress towards demos

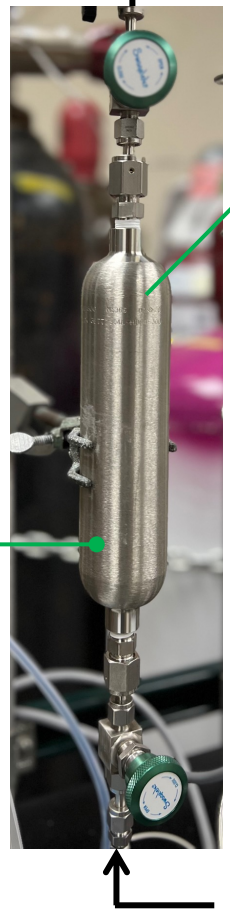
Achieved

- Designed the MOF tank system for H_2 fuel cell demos (FY24 Q3 milestone 75% complete)
- Assembled a Gen1 tank system with mass flow and pressure controllers
- Synthesized 100 g of Ni_2(*m*-dobdc) pellets

In progress

- Connecting controllers with a computer for automated data acquisition
- Initial charge-discharge testing using an empty tank
- Will begin fuel cell demos with Mukundan and Weber (LBNL)

Ni_2(*m*-dobdc) pellets



Planned specifications

- Charging time: 1-10 h
- Discharging (fuel cell operation) time: 1 h
- Max storage pressure: 170 bar
- Storage temperature: from RT to –50 °C

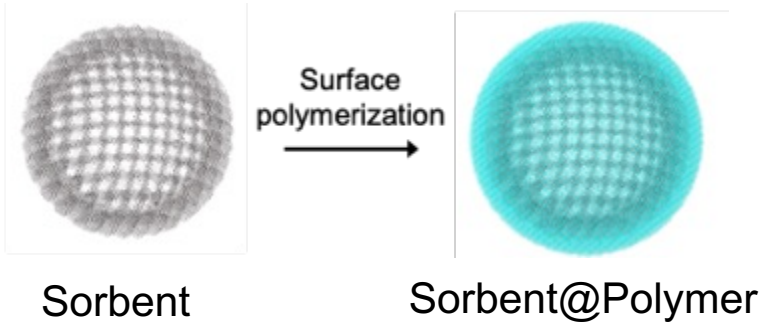
Pressure and/or flow rate controlled H_2 charging that is suitable for backup power supply applications

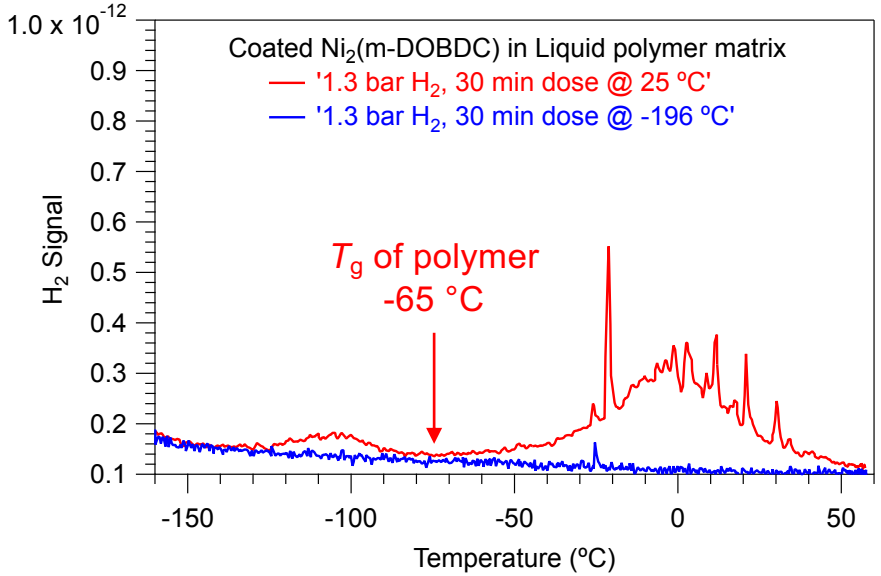
Accomplishment Task 2/sorbents: polymer-coated sorbents. Use cases identified; strategies for cost reduction developed

Relevant use cases: High-capacity H_2 carriers with minimal thermal management issues, short-term and/or stationary storage with rapid H_2 release (e.g., 100 bar and –50 to – 80 ºC)

- **Advantage: Polymer coatings can influence mass transport and enable storage in sorbents at refrigeration temps (see figure for proof-of-concept)**
- **TEA confirms sorbent price is key cost driver in H_2 storage: high surface area, low Q_{st} activated carbons obtained at scale for $1/kg**
- **Project now focusing on coatings to improve storage capacities in activated carbons and biochars at refrigeration temperatures**
- **Scalable coating techniques emphasized**

activated carbon sorbent
3500 m^2/g





Experimental approach

- Dose at low temp. (< T_g of polymer matrix)

→ H_2 is not adsorbed into coated sorbent (blue trace)

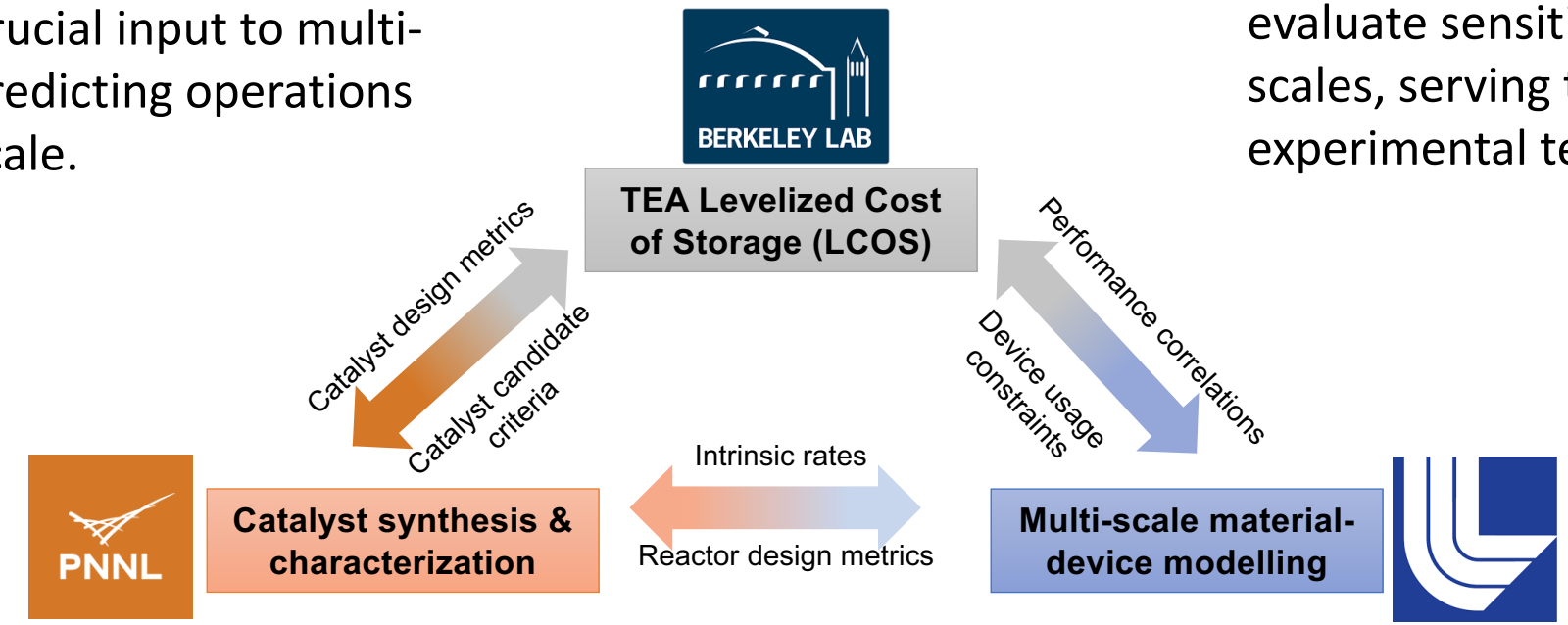
- Dose above T_g of polymer matrix

→ H_2 can be stored at refrigeration temp. (-80 °C) and released by warming above T_g (red trace)

Approach Task 2/LOHCs: intrinsic rates coupled to multi-scale modeling

- PNNL's capabilities to synthesize catalysts with controlled properties and measure intrinsic reaction rates provide crucial input to multi-scale models predicting operations at the device scale.

- LLNL Systems-to-Atoms (S2A) Toolkit can propagate co-design parameters and evaluate sensitivities through scales, serving to link experimental test data to TEA.

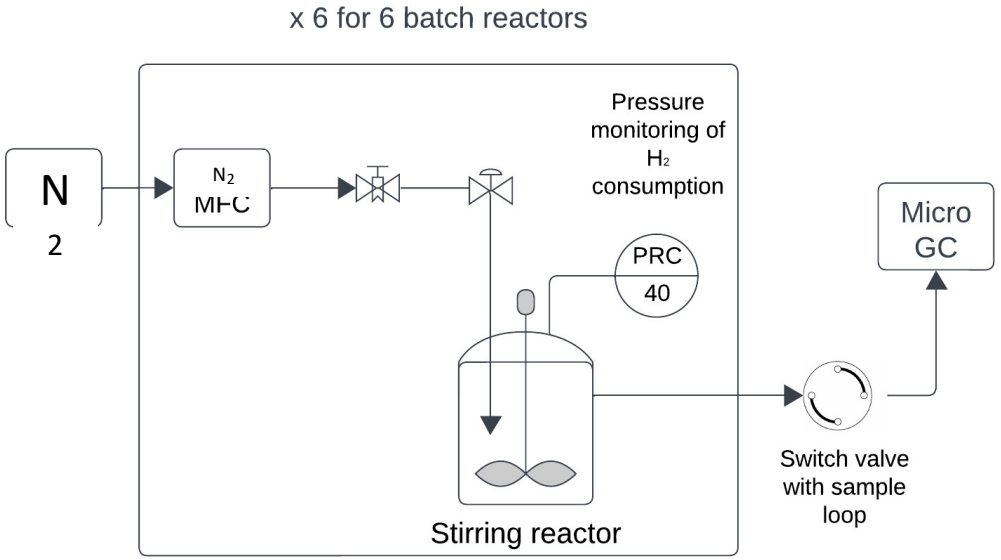


We use models that span hierarchical scales and incorporate kinetics independent of mass transport to predict engineering requirements for hydrogenation and dehydrogenation of LOHCs. This is essential for accurate prediction of the LCOS.

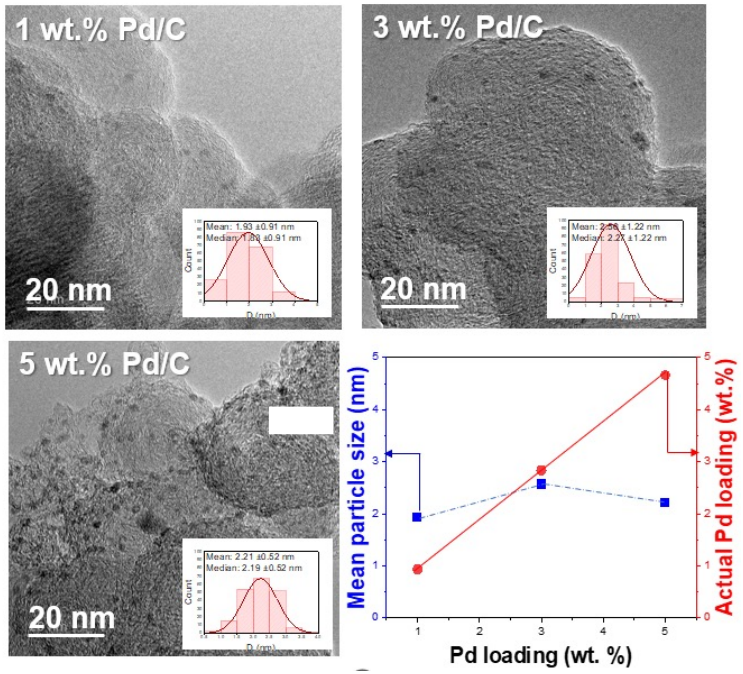
Progress Task 2/LOHCs: developed procedure to prepare uniform catalysts and tested apparatus for intrinsic rate studies

Milestone: Measurement of the intrinsic rates for hydrogen release from 4 M formate at 3 different stages of conversion and 3 temperatures with 3 different catalyst formulations, (i) 1 wt% Pd/C, (ii) 3wt% Pd/C (iii) 5wt% Pd/C

A system for measuring intrinsic rates using on-stream analysis has been designed and assembled



Pd/C catalysts prepared at 10 – 20 g scale with uniform particle size.



Milestone is 50% complete

- Processes to synthesis catalysts at variable loading with fixed particle size accomplished.
- Kinetic orders in catalyst and substrate determined.

The catalysts and reactor will be used to measure intrinsic dehydrogenation rates needed for systems modeling

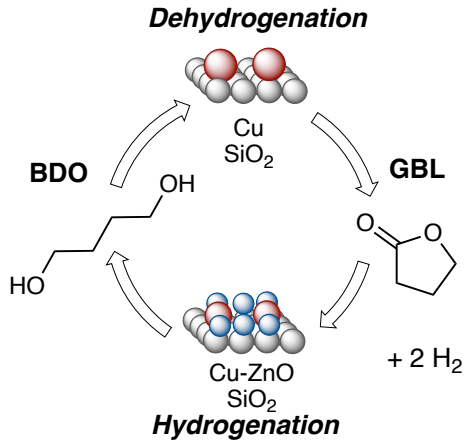
Accomplishment Task 2/LOHCs: Identified operations that dominate the levelized cost of storage (LCOS) for the BDO/GBL H_2 carrier system

We built a *kinetic process model* for butanediol (BDO) dehydrogenation and γ-butyrolactone (GBL) hydrogenation. This provides a framework for more detailed quantitative analysis of energy efficiency and costs (operating and capital) than our previous *equilibrium model*.

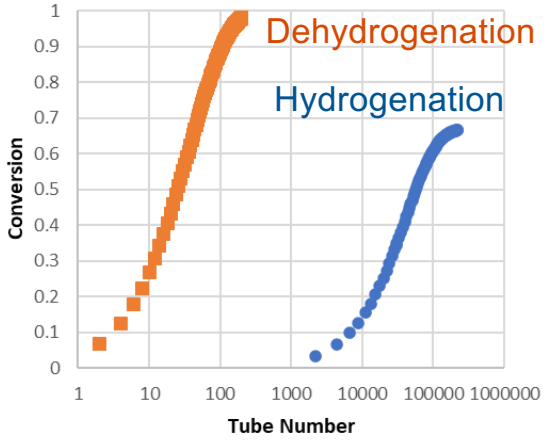
The kinetic model quantifies the costs of hydrogenation and dehydrogenation operations individually at higher resolution.

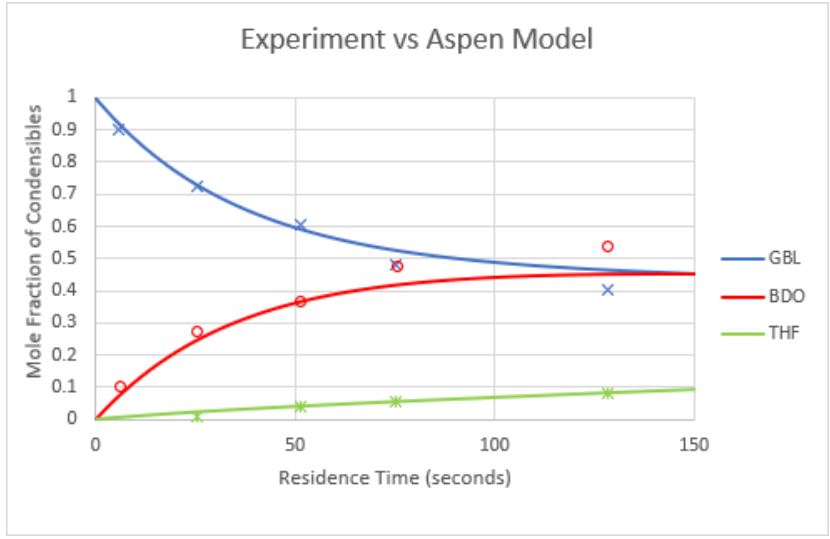
For hydrogenation and dehydrogenation rates to be equal:

- Hydrogenation is the dominant factor in the LCOS
- Irreversible side products increase LCOS substantially



Analyzed tube numbers for conversions of dehydrogenation, hydrogenation





Quantified LCOS as function of hydrogenation product selectivity

Product selectivity	Levelized cost $/kg H2
*100 %**	*3.4*
100%	6.2
95%	14.8
90%	23.4

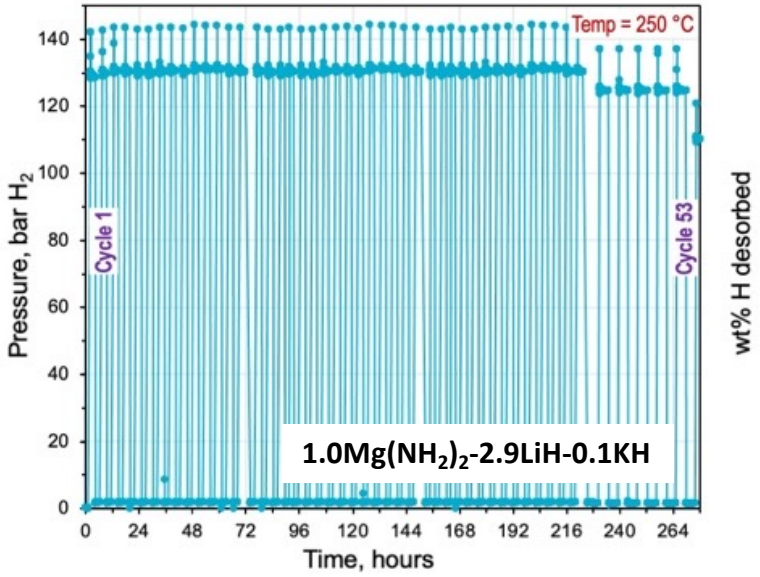
**Equilibrium model (last year)*; others are kinetic model

More active and selective hydrogenation catalysts are needed to reduce the LCOS for BDO/GBL.

Accomplishment Task 2/metal hydrides: Composites of Li-Mg-N amides exhibit robust cycling and rapid desorption, pointing to several possible use cases

Goal: demonstrate the durability of the material during extended cycling periods and optimize strategies to lower desorption temperature and increase desorption kinetics.

- The KH-doped material possesses a **volumetric capacity ≥ 350 bar** of pressurized gas (25 gH_2/L) .
- The material is **robust***:* completed **>80 reversible (5.6 wt%H_2) desorption-uptake cycles** with minimal loss in capacity and kinetics.
- Dehydrogenation is rapid:[2] → meets or exceeds the H_2 rate requirement for several use cases (see table).[1]
- **Scale up of the synthesis initiated** to enable application-specific tests to be conducted.



Use Case	H_2 rate req'd (kg/h)	Storage mat'l required (kg)[6]
Telecom Backup (72 hrs)	0.14[1]	274
Seasonal Microgrid (130 days)	1.6[1]	1.36E+05
Long-haul truck (11 hrs)	5.4[1]	1613[2]
Rail locomotive tender (20 hrs)	74[5]	8961[3,4]

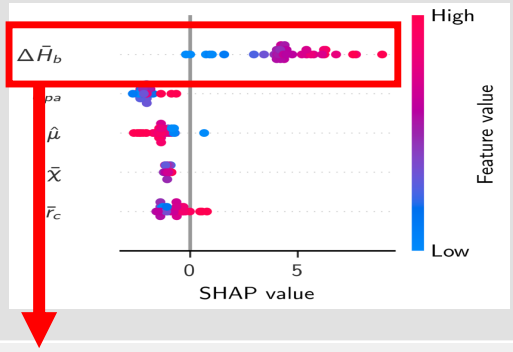
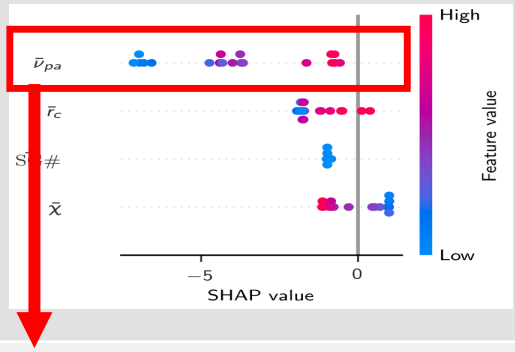
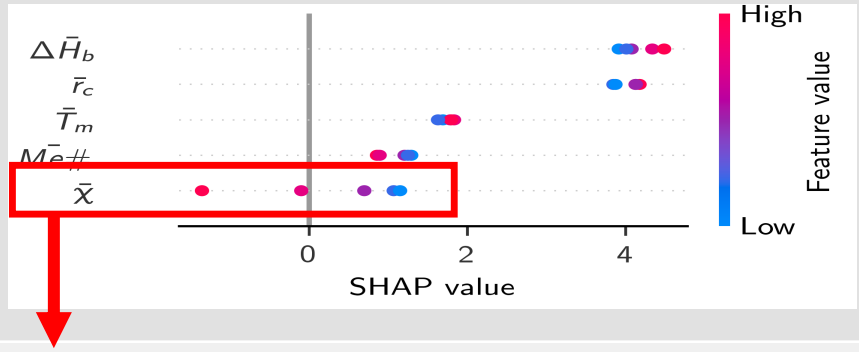
[1] Allendorf, Bowden, et. al., *Nature Chemistry*, **2022**, 14, 1214
[2] Allendorf, Horton, Stavila, Witman *Sandia Nat'l Labs* report SAND2023-05851 (2023).
[3] Allendorf, Klebanoff, Stavila, Witman *Sandia Nat'l Labs* report SAND2023-13180 (2023).

[4] Equivalent to 700 bar pressurized gas; meets weight limit requirement.
[5] Estimate assuming same efficiency as HDV.
[6] 1.0$Mg(NH_2)_2$-2.1LiH-0.1KH

Next step: scale up synthesis and characterize changes in material performance

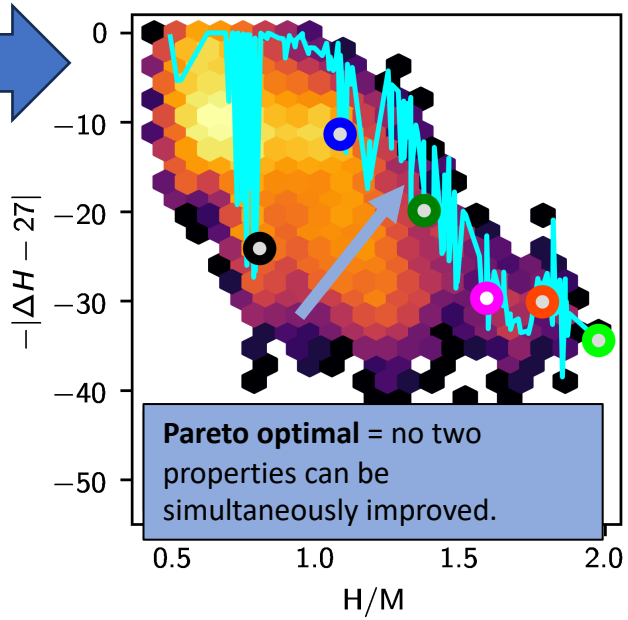
Accomplishment/Task 2 Metal Hydrides: established design rules using explainable machine learning allow us to rapidly identify metal hydrides optimized for specific use cases

- These design rules correlate **composition** with **thermodynamics** for **specific interstitial hydride classes**

MH class:	AB | e.g., TiFeX	AB2 | e.g., (TiZr)(FeNiMnCr)	BCC → FCC | e.g., Ti(VNb)X
SHAP analysis reveals the compositional feature(s) that differentiate MH stability within a given MH class:			
Differentiating feature:	$\Delta\bar{H}_b$- binary hydride ΔH	$\bar{v}_{pa}$- volume per atom	$\bar{\chi}$ – Pauling electronegativity

- **Design rules** + **Pareto optimization** target optimal modifications of existing MH (AB, AB2, and BCC → FCC)[1-3]

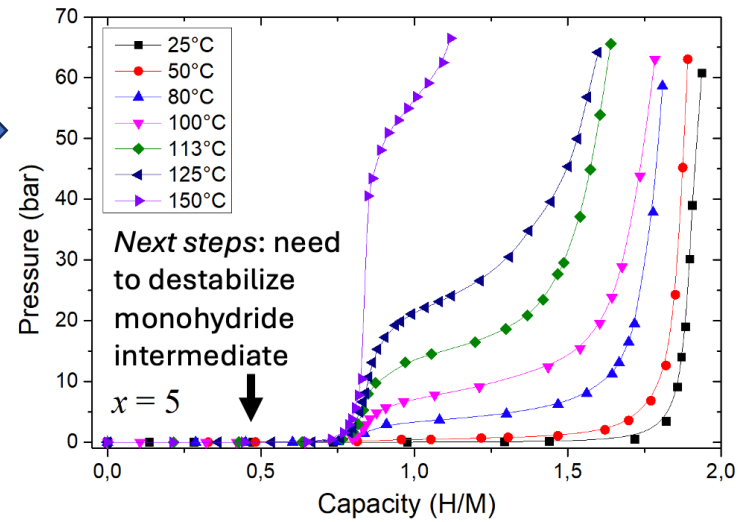
- **DFT + ML** for **PCT isotherm prediction** to facilitate alloy screening + TEA[4]



Example: **High H/M, "low" ΔH** BCC->FCC MH via **earth-abundant (Fe)** substitution

- Total H/M ~ 2x of TiFe
- Reversible H/M > TiFe @ 40 kJ/mol H_2

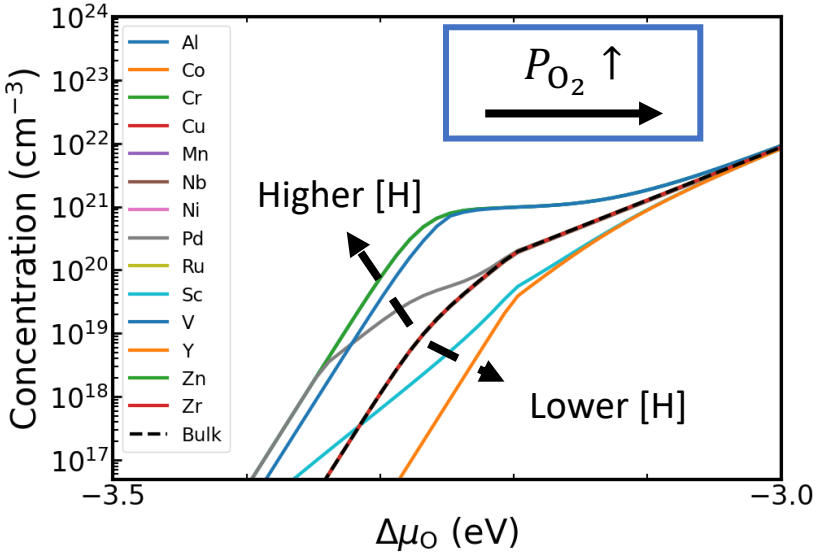
x=5 in $(TiVNb)_{75}Cr_{25-x}Fe_x$



[1] Witman et al. *J Mater Chem A*, **2023**
[2] Strozi, et al. *ACS Appl. Mater. & Int.* **2023**
[3] Pineda-Romero et al. *ACS Appl. Mater. & Int*. **2023**
[4] Witman, et al. *J. Phys. Chem Lett*, **2024**

Accomplishment/Task 2 Metal Hydrides: theory predicts efficiency and activation of TiFe(X) under scalable operation to guide composition and processing modifications

Composition variation for milder activation conditions

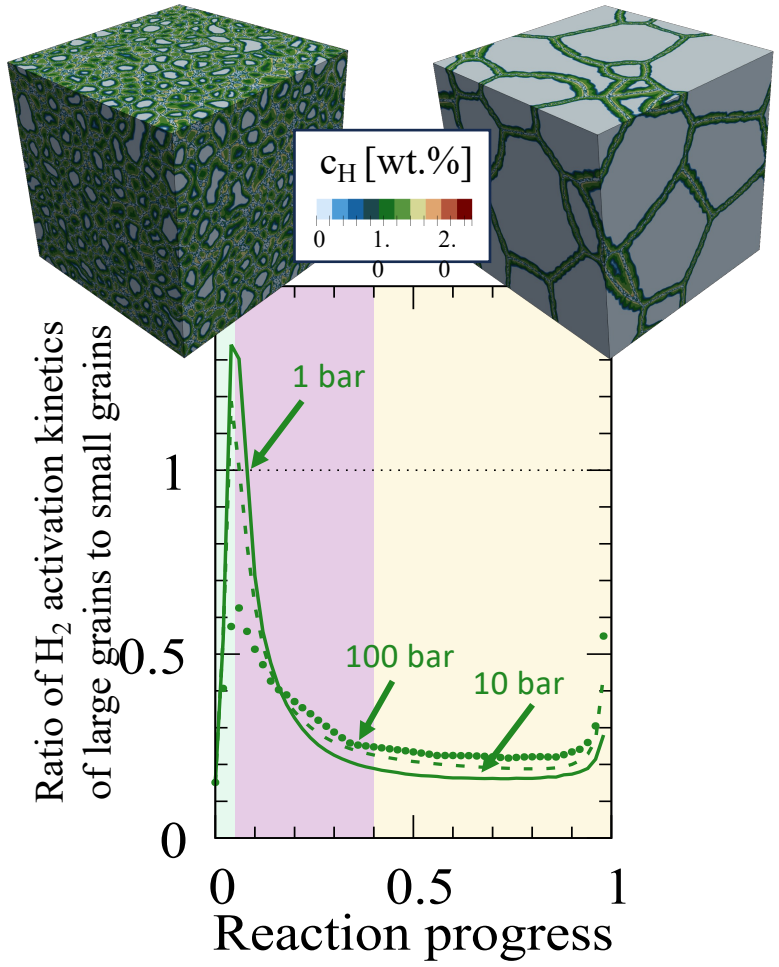


Predicted H accumulation in $TiFeO_3$ surface oxide during activation

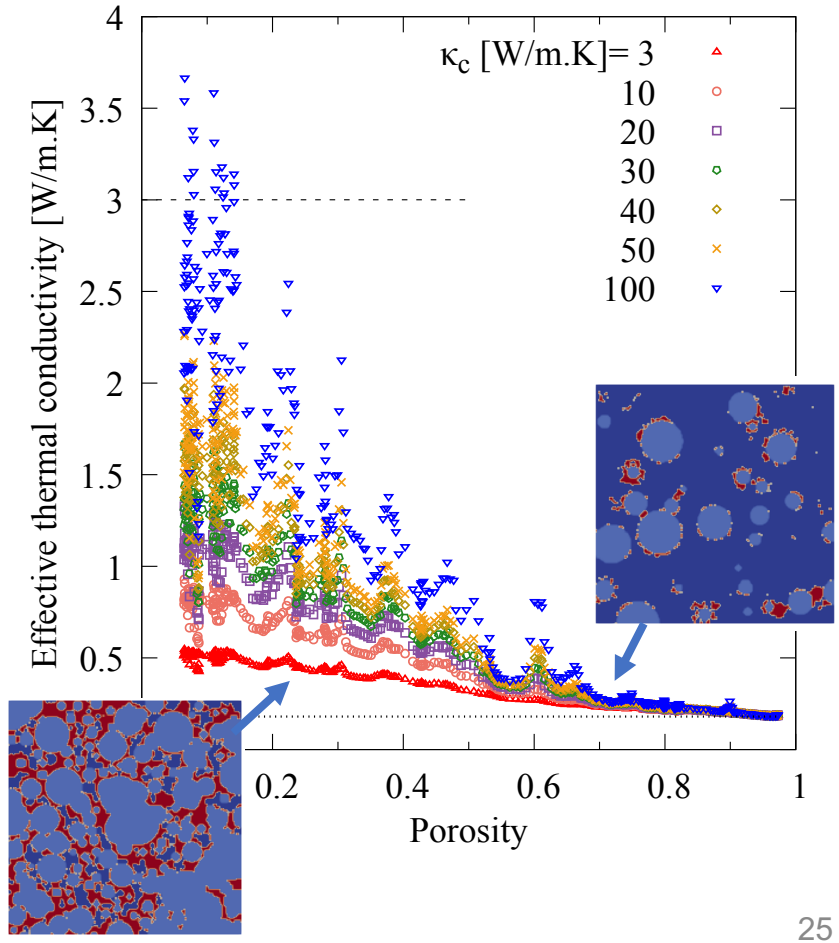
Impact of pre-process annealing of surface oxide on activation

Small-grain (ball-milled)

Large-grain (pre-annealed)



Processing guidance to avoid emergent heat management issues



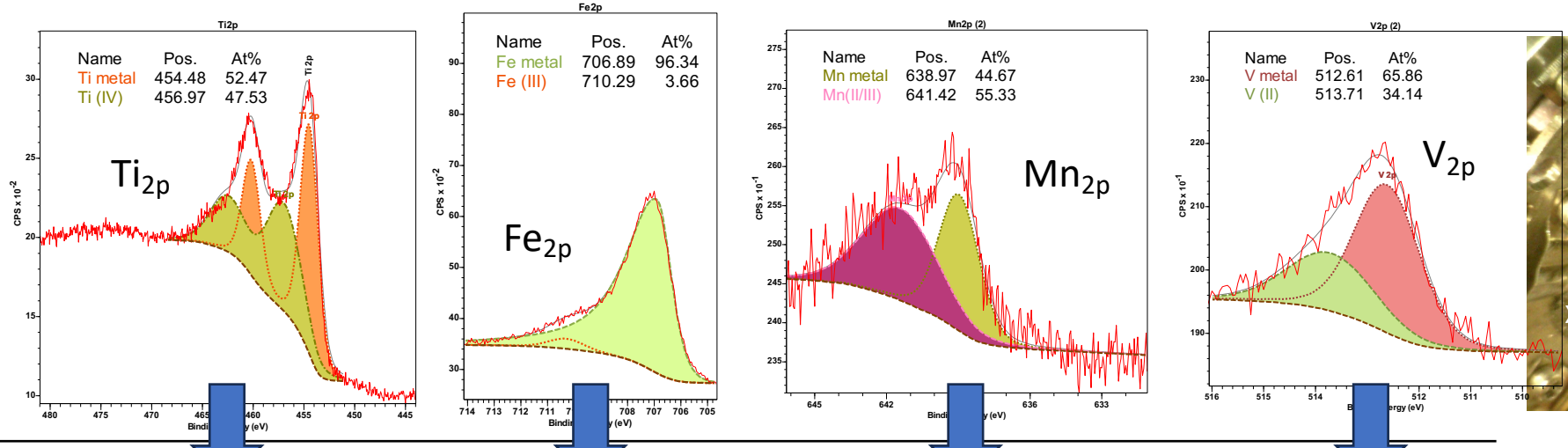
Accomplishment/Task 2 Metal Hydrides: Accomplishment: Understanding emergent phenomena at scale to design better activation strategies for interstitial metal hydrides

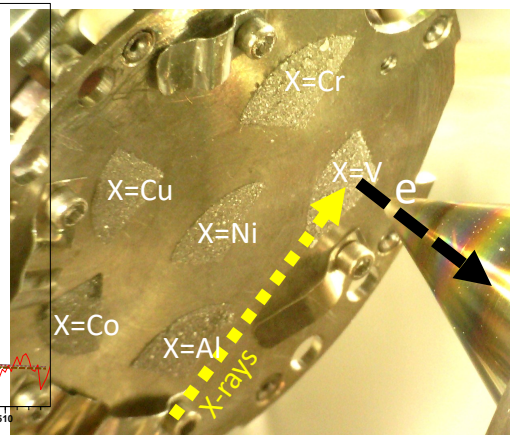
Quantifying the onset oxidation mechanism for $TiFe_{0.8}Mn_{0.1}V_{0.1}$ using X-ray Photoelectron Spectroscopy (XPS)

- TiFe-based intermetallic alloys quickly form an inert surface oxide layer that is very hard to prevent in large-scale settings
- Activation by high temperature chemical reduction is required to remove the oxide but is costly energetically
- O*perando* XPS allows us to identify the oxides and understand how the surface evolves in time
- Goal: design a tailored activation strategy that allows the material to be activated faster and at lower temperature

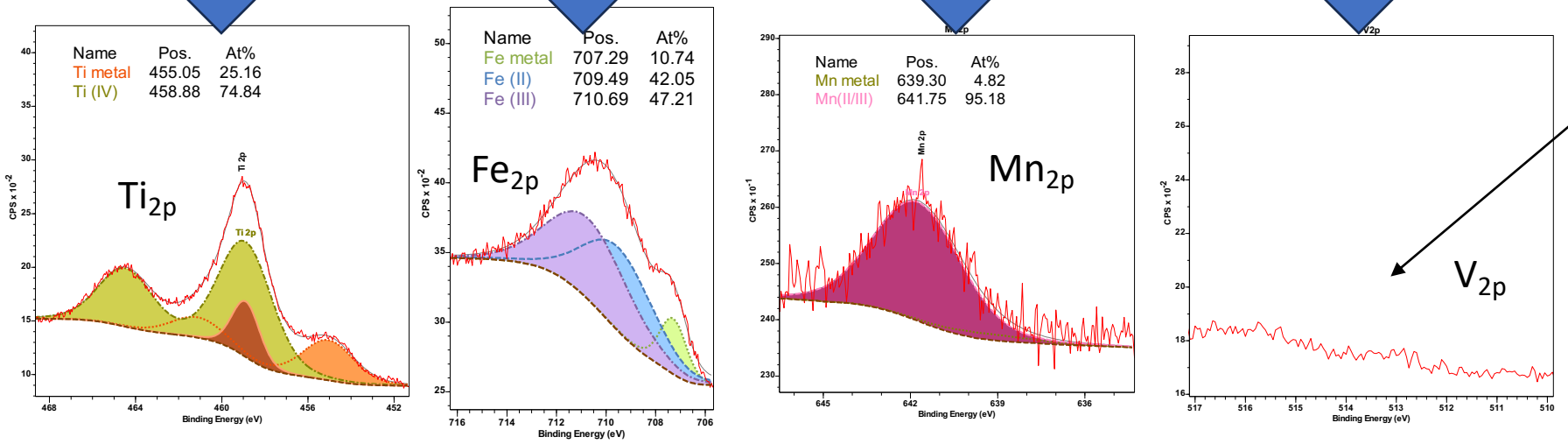
$TiFe_{0.8}Mn_{0.1}X_{0.1}$
X = Al, V, Cr, Co, Ni, Cu

Sputter clean Surface: oxides of Ti, Mn, and V exist >100 nm deep into the bulk





Onset oxidation: exposing to pure oxygen at room temperature for 3 min. dramatically changes the surface



Surprisingly, surface rearrangement during exposure to oxygen removes V from the surface, preventing its participation in surface reactions.

Progress/Task 3 (New Concepts): determining performance limits for Plasmonic Dehydrogenation of LOHCs

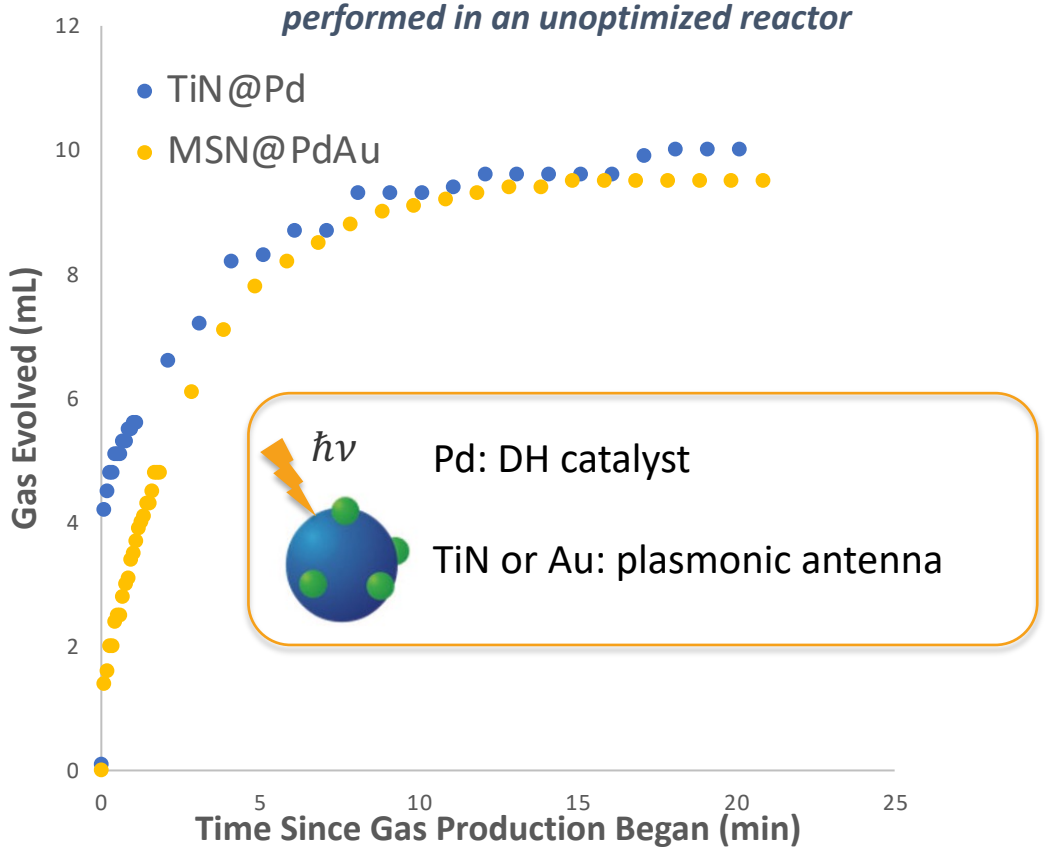
Motivation:

- Dehydrogenation (DH) of LOHCs is associated with high desorption enthalpies and is thus energy-intensive
- LOHC dehydrogenation can also have low selectivity

Potential Impact of Plasmonic DH:

- Reduce the energy input by minimizing bulk heating through local heating
- Compatible with renewable electricity
- Can be scaled up to medium and large scales
- Plasmonic chemistry is often highly selective

Volume of gas evolved upon illumination of PdAu@MSN10 (GRP0404) and Pd@TiN as a function of time. Light source: white LED. Experiments performed in an unoptimized reactor



The TiN plasmonic antenna system evolves as much gas from formic acid DH as Au and the kinetics may be faster. Switching to TiN from Au could reduce material cost as much as 500x.

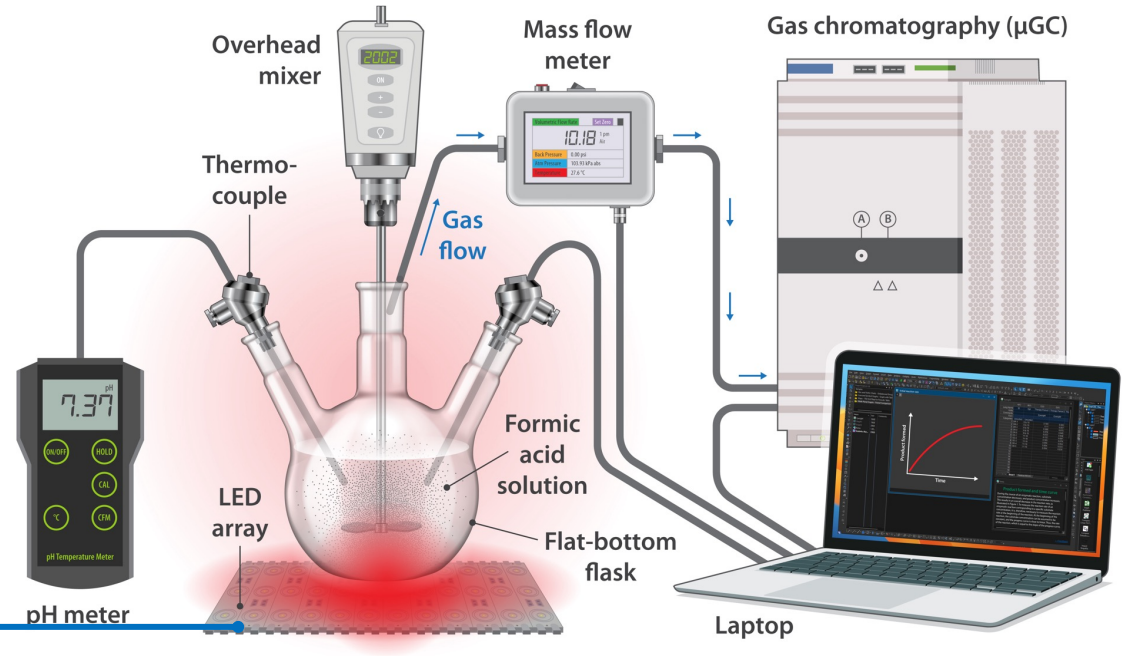
Progress/Task 3 (New Concepts): assembled new bench-scale plasmonic reactor for energy-efficient LOHC dehydrogenation

Replaced bulk heat by leveraging photo-induced plasmonic heat at <μm level:

- Formic acid (FA) as a case study for LOHCs
- Goal: Understand process limitations to design reactor
- Synthesize antenna-reactor plasmonic catalyst systems

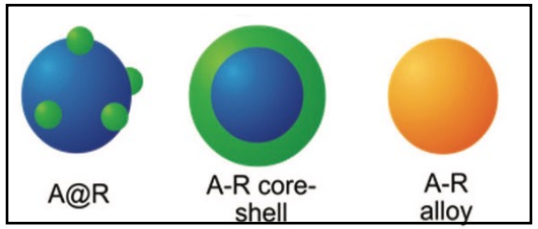
- **Supported plasmonic systems**
  - Synthesized various Pd-Au systems supported onto various supports
  - Alloyed PdAu
- **Free-standing decorated NPs**
  - Au@Pd
  - TiN@Pd → for cost optimization

Air-free reactor for plasmonically driven reactions



Flexible system allows the reaction vessel and light source to be easily changed or modified

Suspended plasmonic catalyst



***Status as of March 2024*: system integration complete except for micro-GC**

Approach/Task 4 (Characterization & Validation): Inter-laboratory isosteric heat study

Interlaboratory study to understand sources and extent of qST inconsistency within the research community

Multiple laboratories measure capacities isotherms for a **standard MOF sample** and determine Δq_{st} according to their own best practices.

↓

Results and methods reported to NREL

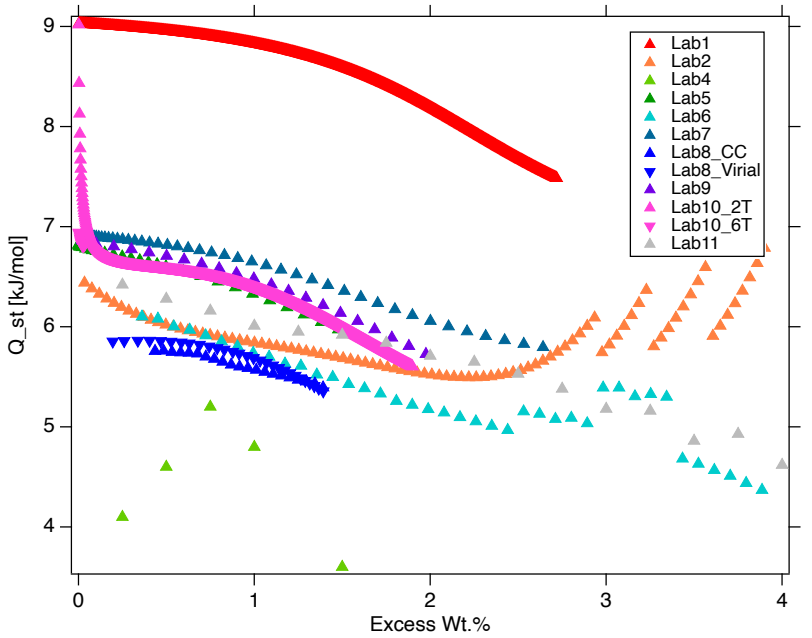
↓

Analysis of all results to correlate discrepancies in Δq_{st} with deviations in isotherm results, data processing, and methods for using the CC-equation

The isosteric heat of sorption (Δq_{st}) is a widely used metric for evaluating hydrogen storage materials.

- Δq_{st} often determined from capacity isotherms via the Clausius-Clapeyron
- Inconsistent results across research community:
- Errors in isotherm measurement result in disproportionately large errors in Δq_{st}.
- Seemingly innocuous decisions made when processing the isotherm data impact Δq_{st}.

Δq_{st} for HKUST-1 as determined from multiple labs all pressures



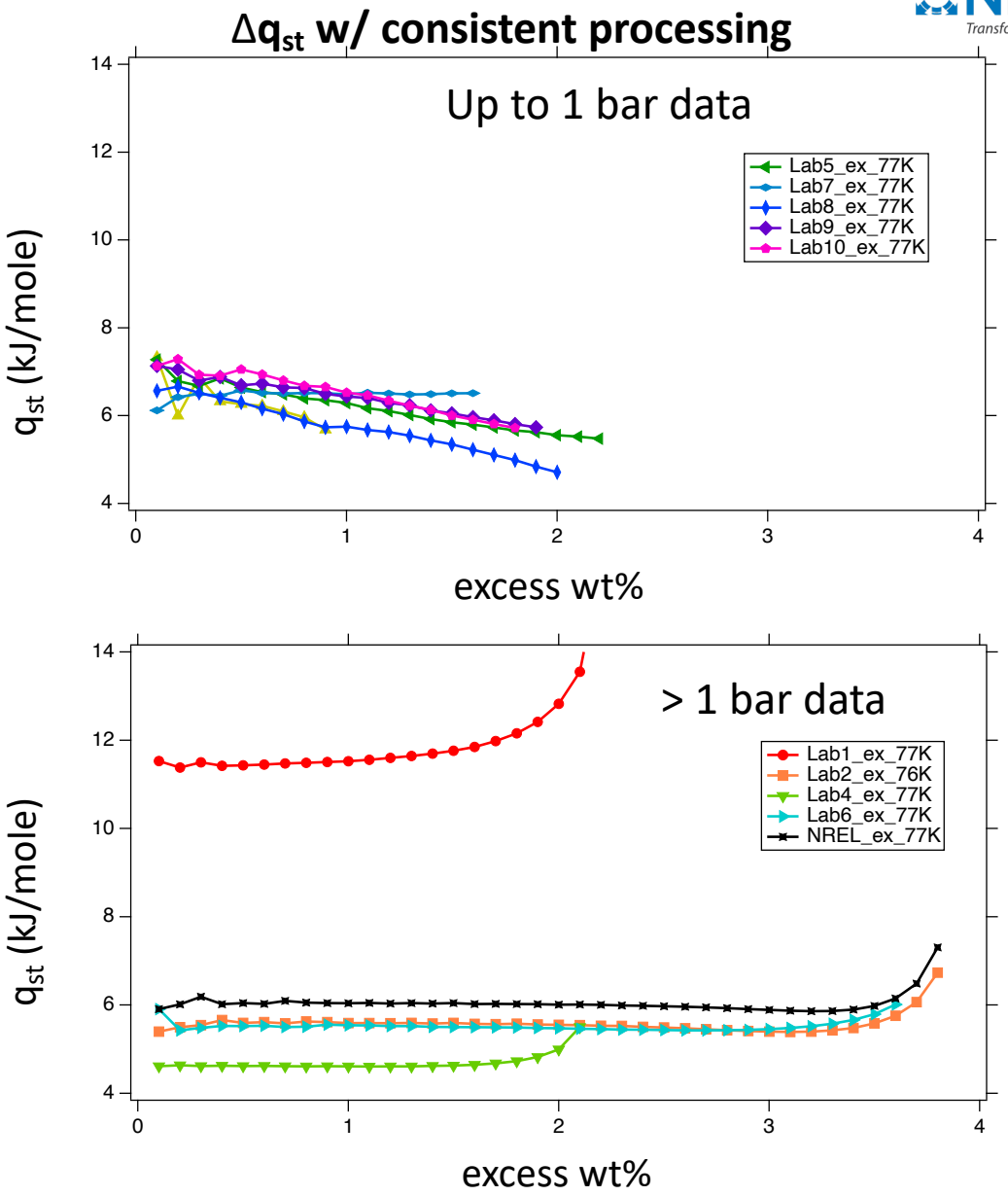
The research community needs to understand sources of inconsistencies and expected error.

Accomplishment/Task 4 (Characterization & Validation): Inter-laboratory isosteric heat study completed

All data from participating labs collected and data analysis completed.

- Δq_{st} results are highly sensitive to isotherm shape (systematic errors in isotherm measurements are less significant).
- Model selected for fitting isotherm data impacts resultant isosteric heat values and shape when plotted as function of hydrogen loading.
- Following same analysis protocol for all data collected resulted in ~20% spread in isosteric heats except for one series.
- Data fit using temperature-dependent double site Langmuir equation for 77K-100K isotherms
- Isosteric heats extracted using discretized Clausius-Clapeyron equation on 77K-87K isotherm pairs

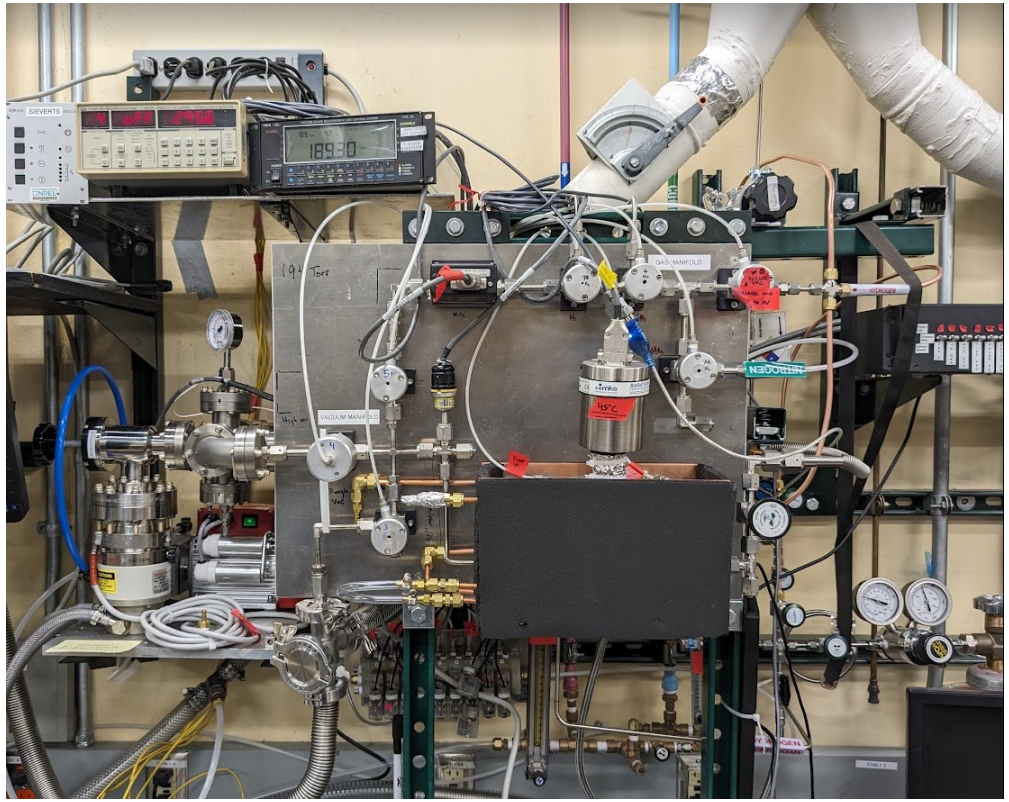
Publication planned summer 2024



Accomplishments/Task 4 (Characterization & Validation): Low-pressure Sieverts apparatus completed

Low-pressure Sieverts instrument: High resolution hydrogen capacity data at 0-5 bar

- Evaluation of hydrides and sorbents for low pressure hydrogen storage applications
- Instrument design, build, & validation complete.
- Automated python software with user GUI for running experiments complete.
- Modified design to control both flow and temperature of Hydrogen gas (similar system for high pressure PCT will come on-line in summer 2024)



Task 6 Accomplishments: Community Benefits / DEIA Plan/ Successes

- ***Plan Specifics:*** Collaboration with Metropolitan State University of Denver, a Hispanic Serving Institution (HSI) near NREL
  - **Part 1. Two Bridge Experiences with first-in-the-nation models for students from Underrepresented/Minoritized (URM) groups**
    - Bridge-to-Graduate School and Bridge-to-Career Program
    - Tailored Coursework + Research Experience with HyMARC researcher
    - Tiered Mentorship with Trained Mentors
    - Networking and Community Engagement Opportunities
    - Tuition free, $50K/yr (Living + Housing) Stipend, free Health Insurance
  - **Part 2. Summer Internships for students from URM groups**
    - 10-week internships with HyMARC researchers at NREL
    - $23/hr wage plus holistic support

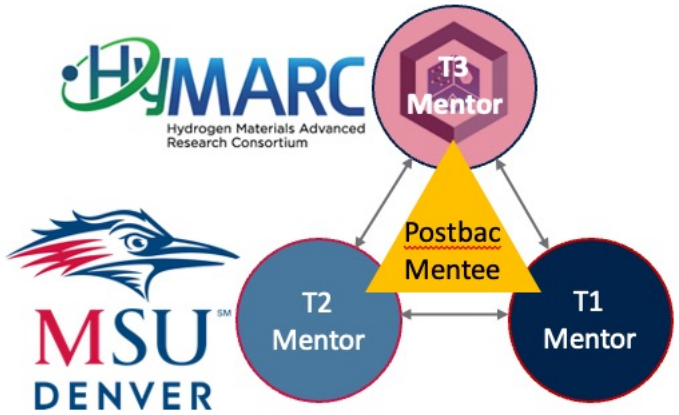


Figure 1. Mentorship Structure of MSU Denver's Postbac bridge programs with HyMARC

- ***Progress:***
  - **Part 1. Bridge Programs**
    - 2024 Bridge Partner with the American Chemical Society Bridge Program
    - Three Oral Presentations
    - HyMARC support helped garner >$2.25M in additional grant funding
    - On schedule for initial cohort to start in Fall 2024
  - **Part 2. Summer Internships**
    - Two student interns in SU2023
    - Two scientific manuscripts from student work (one published, one submitted)

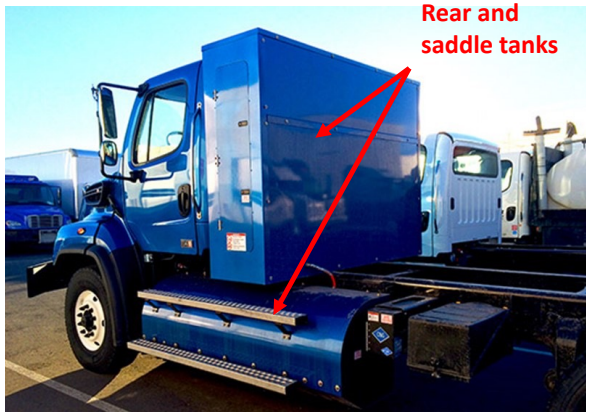
- ***Challenges:***
  - **Part 2. Summer Internships**
    - Administrative barriers with finalizing MSU Denver subcontract
    - Impacted timeliness of design/implementation of student support structures

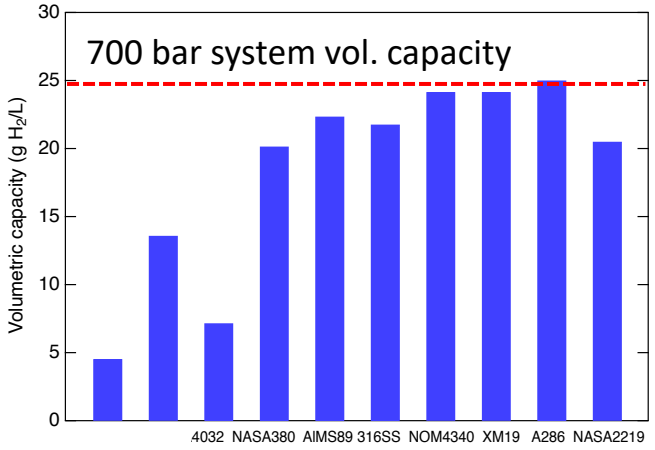
Task 7: Industrial Advisory Board established

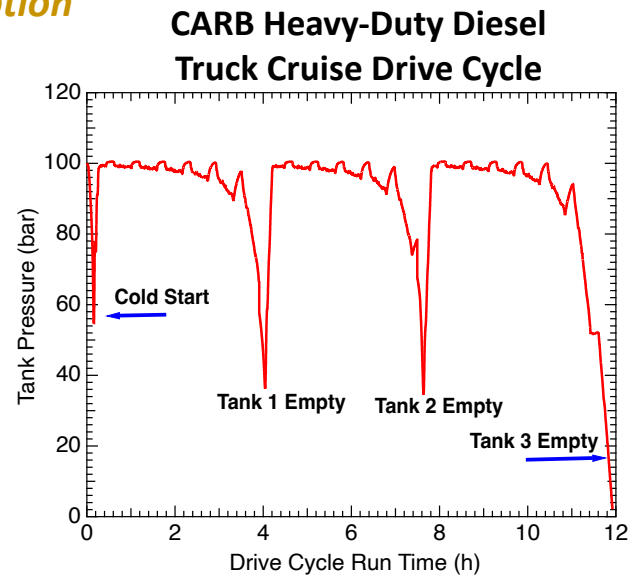
- Purpose: to provide a forum for information exchange between the HyMARC team and current and potential users of hydrogen storage technology
- Up to 10 members representing organizations actively engaged in developing hydrogen as an energy carrier for stationary, transportation, or industrial use.
- Meetings are virtual and occur ~2X per year
- First meeting occurred October 2023
- Current members:
  - Ammobia, Baker Hughes, BST Systems, Chevron, HGmotiv, GKN, Numat, SoCalGas, US Army

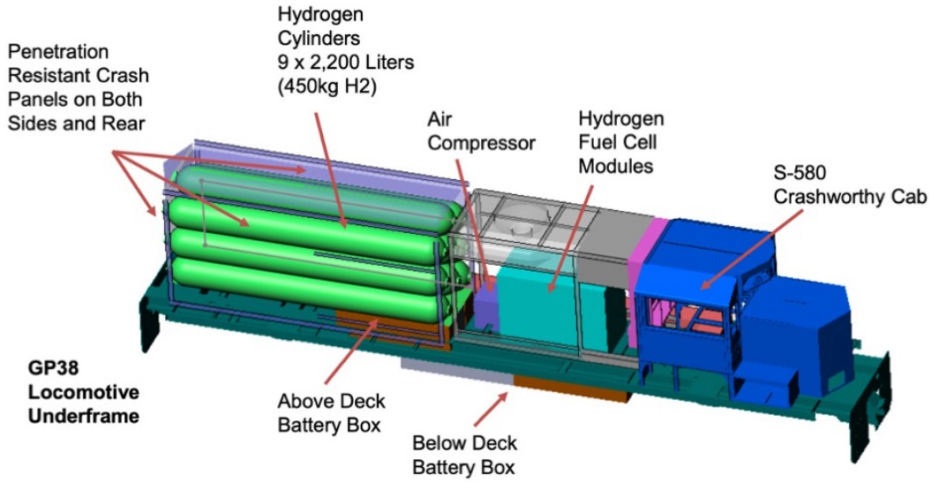
Externally funded projects: completed projects funded by SoCalGas to assess viability of materials based storage for HDV and rail

Tanks for Class 8 trucks and locomotive tenders fabricated from light-weight, high-performance alloys would enable operation at elevated temperatures needed for fast hydrogen desorption







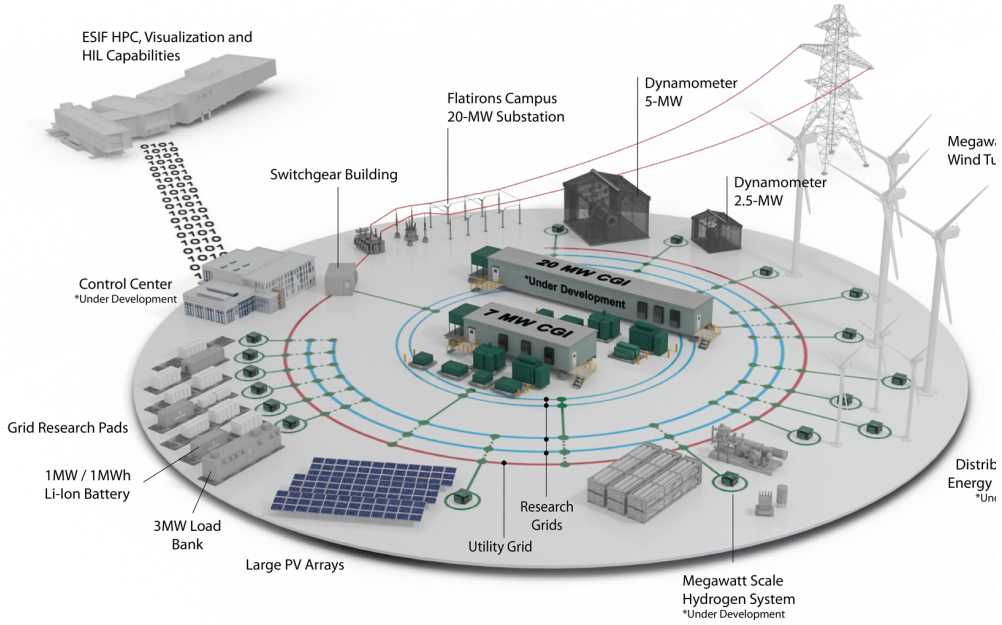


Picture credit: P. Sanchez, HGmotive

	MgH_2	Li-Mg-N[1]	$NaAlH_4$	LaN_5H_6	$LiFeH_2$
Tot. hydride mass (kg)	11622	8961	10358	55678	53572
GHC[2] (g H2/kg system)	27.9	25	21.2	10.3	12
VHC[3] (g H2/L system)	35.2	25.6	23.8	44.9	50.7
% of 700 bar systems w/ Type 3 tank (25.5 g/L)	138	100.4	93.3	176.2	198.7

[1] $1.0Mg(NH_2)_2$-2.1LiH-0.1KH with 10wt% carbon nanoworms. [2] Gravimetric hydrogen capacity (system). [3] Volumetric hydrogen capacity (system).

Accomplishments/Externally funded projects: High Efficacy Validation of Hydride MEga Tanks at the ARIES Lab (HEVHY METAL)



TMS Container

2x MEGA 2.0

520 kg H_2
17.2 MWh

- **Demonstrate how two HY2MEGA subsystems are installed with MW–scale green H_2 infrastructure**
- **Validate performance: Rates, capacity, efficiency**
- **Investigate supply, demand side techno-economics**
- **Identify potential deployment pathways**

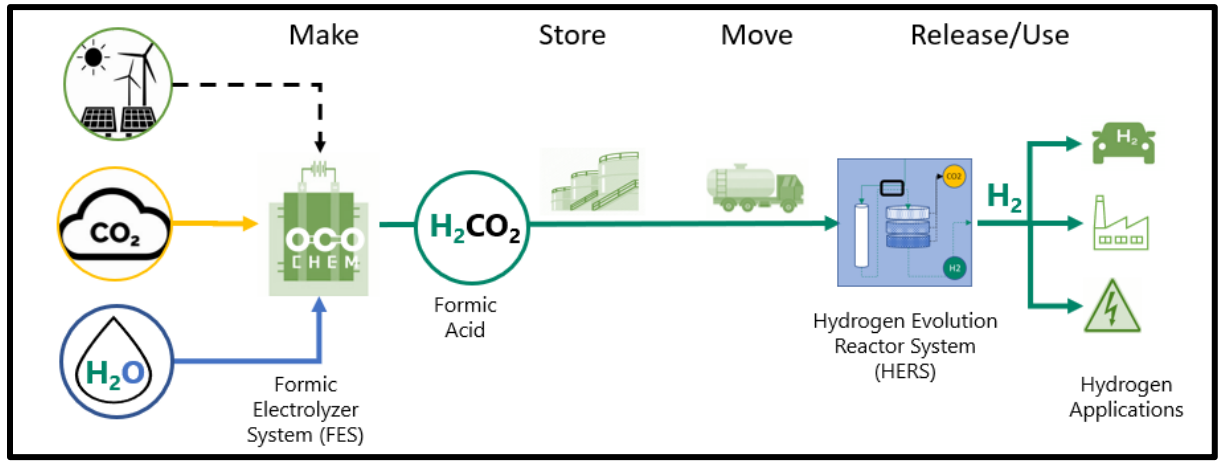
PI: Katie Hurst

Accomplishments/Externally funded projects: collaborations to develop hydrogen production/storage/distribution systems

HyMARC Hydrogen Materials Advanced Research Consortium

PNNL

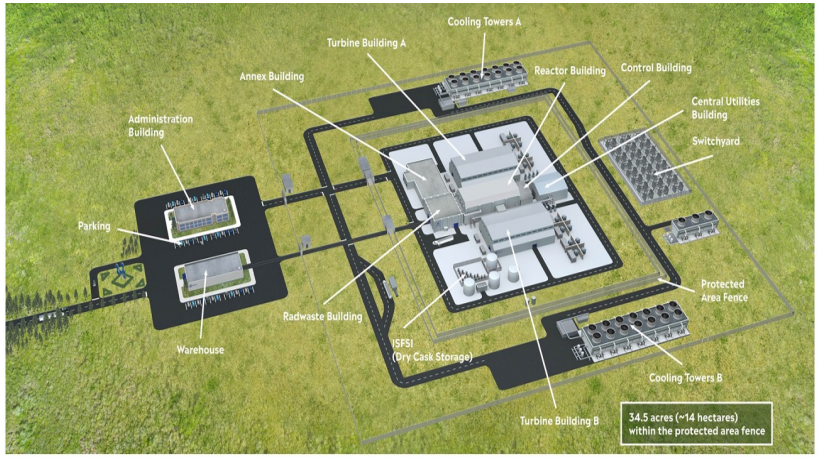
Formic Acid-Based Hydrogen Energy Production and Distribution System



Demonstration project to:

- Electrochemically synthesize formic acid at a rate of 200 kg/day
- Catalytically release H_2 at 1 kg/h from stored formic acid
- Purify H_2 from the 50/50 H_2/CO_2 mix and feed to a fuel cell

NuScale VOYGR Power Station – 12 Small Modular Reactors Total 924 MWe



NuScale-funded project to investigate the utilization of Small Modular Reactor to generate hydrogen as an energy carrier and a storage mechanism

- Utilizes formate salts
- Addresses emergency backup power

Accomplishments/Externally funded projects: Material-based H_2 storage for H_2-powered UAVs

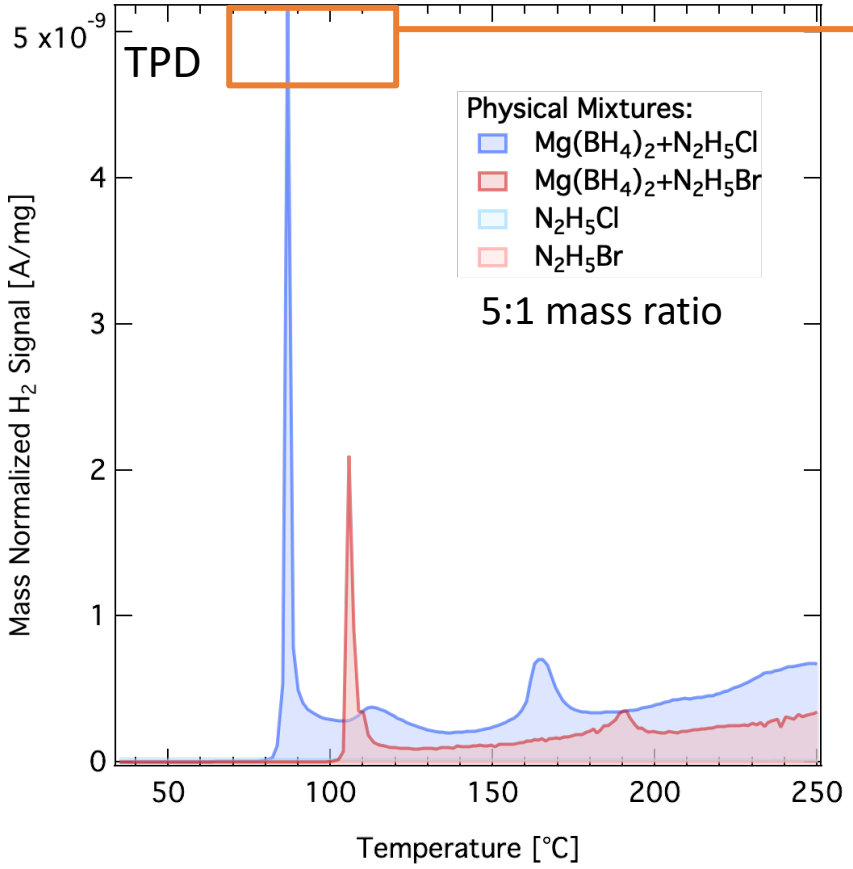
Technology Commercialization Fund | U.S. DEPARTMENT OF ENERGY | OFFICE OF Technology Transitions

HyMARC Hydrogen Materials Advanced Research Consortium

Honeywell THE POWER OF CONNECTED

NREL NATIONAL RENEWABLE ENERGY LABORATORY

6-8 wt% H_2 released

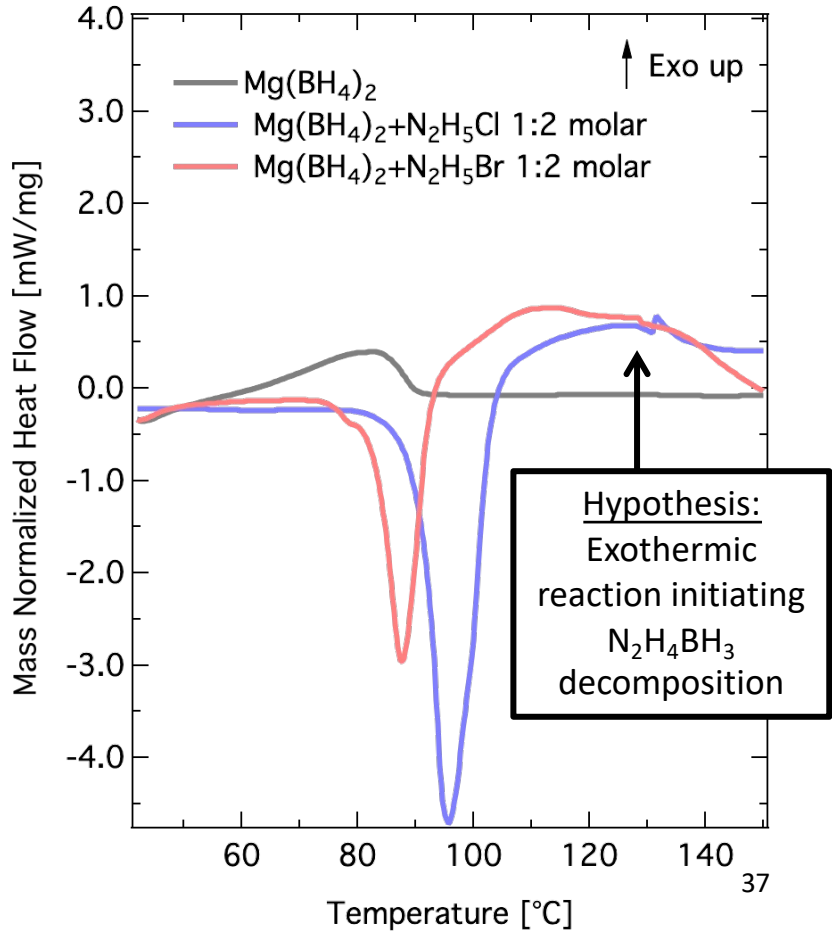


Proposed mechanism: $Mg(BH_4)_2$ + N_2H_5Br Thermolysis

$$Mg(BH_4)_2 \cdot 2\,N_2H_5Br \xrightarrow{\Delta} MgBr_2 + 2\,N_2H_4BH_3 + 2\,H_2$$

This material discovery has led to a TCF project in which fuel formulation is being optimized for H_2-powered unmanned aerial vehicles (UAVs).

DSC



Patents:

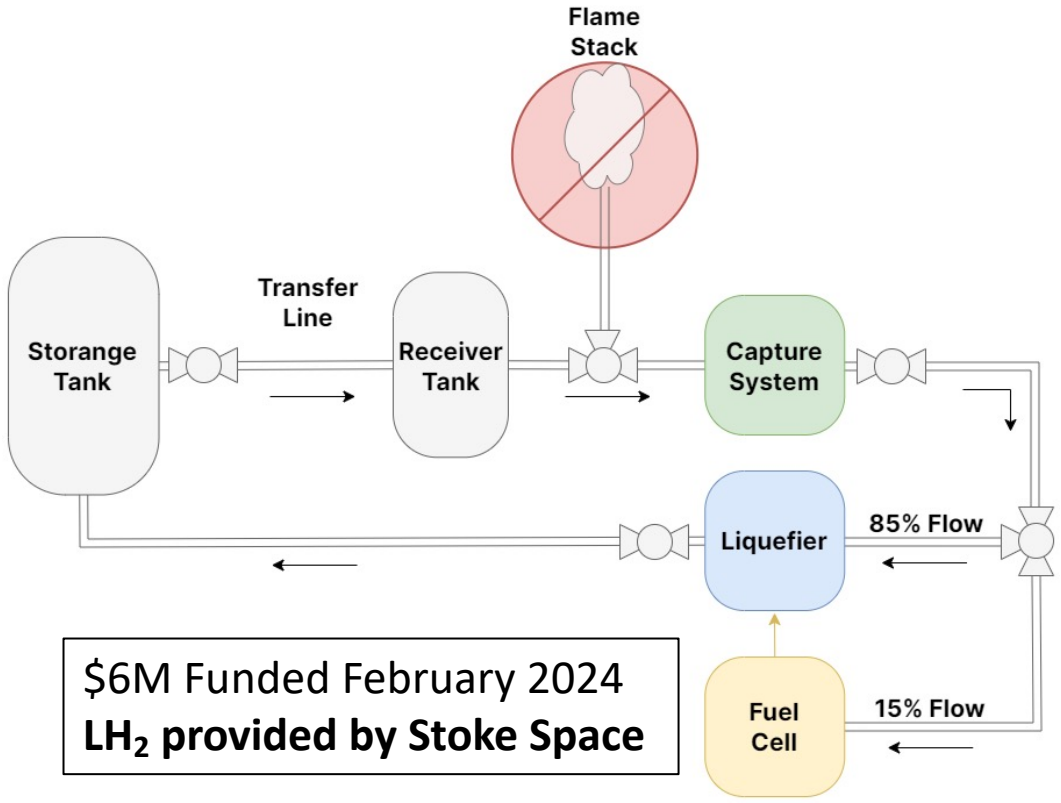
Nanostructured composite metal hydrides, by S. Christensen, T. Gennett, N. Marius, K. Gross, U.S. Patent No.: US 10,751,795 B2 – Aug. 25th, 2020

Fuel additives for storage and rapid generation of hydrogen, by S. Christensen, N. Strange, Van Allsburg, US 2022/0298011 A1 – Sept. 22th, 2022

PI: Forrest Harrington

Accomplishments/Externally funded projects: solid-state-based hydrogen loss recovery during LH_2 transfer

Boil-off losses throughout high-flow LH_2 transfer have significant financial and environmental impacts. We propose to ***engineer and deploy*** a materials-based recovery system prototype.



$6M Funded February 2024
LH_2 provided by Stoke Space

Outcomes

- TEA analysis
- Evaluation of multiple materials for H_2 recovery system
- **Prototype recovery system integrated into LH_2 infrastructure at Stoke Space**

Community benefits: 2-year intensive training for UMR students pursuing national lab/industry career or graduate school through accredited post-bachelor program.

Key Personnel

NREL/CSM (Prime): Tom Gennett, Project lead, DEI, Materials
NREL: Sarah Shulda, Characterization & lab-scale prototype lead
Stoke Space: David Buckley, on-site prototype lead
Airbus Americas: Sean Jones, LH_2 for aviation infrastructure lead
LBNL: Hanna Breunig, TEA lead

New Seedling Projects

Seven new Seedling projects were launched in FY2024. HyMARC staff are engaged with designated points of contact to facilitiate access to our capabilities and expertise.

Affiliation	Title	PI	HyMARC POC
Univ. Tennessee Knoxville	Highly Active Hexagonal Boron Nitride Catalysts for the Dehydrogenation of Liquid Organic Hydrogen Carriers	Sheng Dai	T. Autrey/PNNL
Johns Hopkins Univ.	Efficient Ammonia Decomposition Using PGM-Free High-Entropy Alloy Catalysts	Chao Wang	M. Witman/SNL
Washington State Univ.	Developing a New Liquid Organic Hydrogen Carrier (LOHC) Technology for Hydrogen Storage in the Sustainable Aviation Fuels (SAFs)-Lignin Jet Fuel (LJF)	Bin Yang	J. Su/LBNL
Louisiana State Univ.	Enabling Formate-Based Hydrogen Storage and Generation via Multimetallic Alloy Catalysts	Ye Xu	M. Bowden/PNNL
Colo. School of Mines	SCALABALE, LOW-COST HYDROGEN DELIVERY SYSTEMS	C. Wolden	R. Bell/NREL
USC	Chemical Hydrogen Storage Media with Value-Added Co-Products	T. Williams	H. Breunig/LBNL
Rice Univ.	Plasmonic Photocatalysis for LOHC-Based Hydrogen on Demand	N. Halas	N. Leick/NREL

Collaboration and Coordination

- **Industrial Collaborators**
  - Immaterial
  - Microsoft
  - Airbus USA
  - Honeywell
  - Stoke Space
  - OCOchem
  - NuScale
  - Amogy
  - SoCAL

National Lab Collaborators

- Argonne National Laboratory
- Oak Ridge National Laboratory

- **Academic Collaborators (non-seedlings)**
  - Washington State University (Hongfei Lin)
  - University of Southern California (Travis Williams)
  - University of Rostock, Germany (Karsten Mueller)
  - Korean Institute of Science and Technology (Hyangsoo Jeong, Eun Seon Cho)
  - Aarhaus University, (Torbin Jensen)
  - University of Nottingham (Sanliang Ling, David Grant, Gacvin Walker)
  - Uppsala University (Martin Sahlberg
  - CRNS Paris-Sud, (Claudia Zlotea
  - Max-Planck-Institut Festkoerperforschung (Bettina Lotsch, Hendrik Schlomberg)
  - Helmholtz Zentrum Hereon – Paul Jerabek and Claudio Pistidda
- **International Coordination**
  - IEA Task 40

Proposed Future Work (remainder FY24 – first half of FY25)

Overall priorities for future work

- **Use system-level analysis to guide materials property focus for highest-impact design guidelines and LCOS**
- **Match individual material classes (sorbents, hydrides, carriers) to optimize performance of most relevant stationary or mobile applications**
- **Scale up material quantities to identify emergent phenomena, provide data on aging/degradation for systems modeling, and increase TEA**

Systems analysis/TEA

- Complete metal hydride systems analysis tool
- Improve stationary storage models with the inclusion of additional **material properties such as durability and stability** based on degrading mechanisms.
- Develop **multi-criteria screening capabilities** (i.e., energy density, safety considerations, etc.)

Experimental, characterization, and modelling/simulation for material co-design

- Employ scale-up reactors to evaluate long-term effects and emergent phenomena at scale
- Develop and validate kinetic and thermodynamic models for the performance of carriers and storage materials
- Employ high-pressure differential scanning calorimetry (DSC) to evaluate heat flow during adsorption-desorption cycles
- Assess the effect of impurities: perform cycling PCT experiments with lower grade H_2
- Understand reversibility ("refueling"): perform hydrogenation studies and provide data for LCOS calculations
- Assess microstructure and packing impacts on mass/heat transport and degradation: validate current models with experiments

Best practices, IAB, DEI

- Complete and distribute report on best practices for TEA and LCOS within HyMARC and with IAB
- DEI: place DEI interns within consortium laboratories and engage local MSI's to address barriers to workforce diversification in STEM

Proposed future work is subject to change based on funding levels

Project Summary (High Level)

Identify and develop materials, targeted for specific use cases, that exceed the capabilities of physical storage at reduced cost and meet DOE targets established for various applications

- **Sorbents: automated pairing of materials with end uses**
- **Sorbents: Combined machine learning with TEA to screen material databases and operation conditions**
- **Metal hydrides: developed model for stationary power and formulated a research roadmap**
- **Metal hydrides: demonstrated long-term reversible cycling of a Li-Mg-N complex hydride; used system modeling to match with use cases**
- **Metal hydrides: established design rules for interstitial hydride classes**
- **LOHCs: Established multi-lab collaboration to improve modelling of MCH/toluene for GW-scale electrolyzer applications**
- **LOHCs: Identified operations that dominate the levelized cost of storage (LCOS) for the BDO/GBL H_2 carrier system**
- **Scale-up: Initiated design, assembly, and/or testing of three reactors/demo systems**
  - **1) High-pressure hydride reactor; 2) catalytic flow reactor; 3) MOF tank**
- **Scale-up: Assessed effects of surface oxide formation on activation process for Ti-Fe-M alloys**
- **Characterization & validation: determined new best practices for measurement of isosteric heats**
- **Communications: established Industrial Advisory Board**
- **DEI: Initiated the pilot program in Summer 2023, new mentor training and expansion of intern numbers underway**

FY23-24 Milestone status

FY23 Milestones

- **Q4** Year 1 GNGs:
  (a) Demonstrate one composite hydride material with experimental data showing reversibility (50 cycles) and volumetric capacity $\geq$ 350 bar compressed gas **(100% complete)**
  (b) Demonstrate a full cycle of hydrogenation and dehydrogenation of potassium formate (5 M solution using water-soluble Ir-based catalyst. Hydrogenation at 30 °C and 30 bar H_2 with 95% conversion. Dehydrogenation at 80 °C and 1 bar H_2 with 85% conversion **(100% complete)**

FY24 Milestones

- **Q1** Seedling project engagement: Engage with 7 new FY23 seedling projects on construction and calibration of validation apparatuses for hydrogen conversion and release experiments for ammonia, plasmonic catalysts, and other carrier technologies **(100% complete)**
- **Q2** Metal hydride system model: Preliminary TEA and systems analysis of a metal hydride system model, identifying 2 quantitative metrics of importance, specific to stationary applications to outperform traditional liquid and compressed storage options **(75% complete)**
- **Q3** Kinetics of carriers: Measurement of the intrinsic rates for hydrogen release from 4 M formate at 3 different stages of conversion and 3 temperatures with 3 different catalyst formulations, (i) Pd/C, (ii) Pd/C/CeO3, (iii) Pd/N-doped C, to assist with LBNL system modeling efforts for hydrogen carriers. **(50% complete)**
- **Q3** Adsorbent-based tank system: Complete the design for an adsorbent-based (100 g scale) tank system to feed H2 to a FC setup for initial demonstration. The system will target operation for initial experiments at up to 100 bar and room temperature, with future upgrades to 170 bar and temperatures as low as -50 C **(75% complete)**

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

THANK YOU

Response to Reviewer's Comments

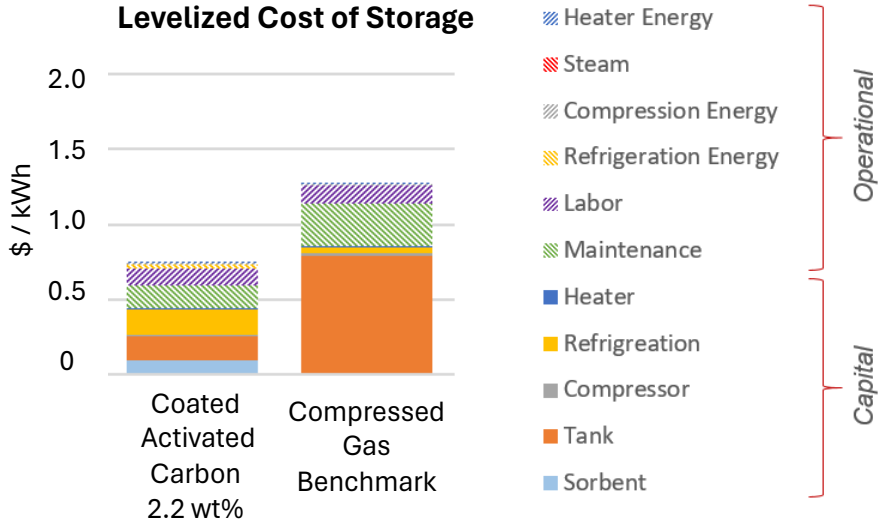
Question 2: Accomplishments and progress (P 186/187)

"The overall impact and importance of the work on polymer-coated framework materials, MXenes, and plasmonic materials for liquid organic hydrogen carrier (LOHC) dehydrogenation remain questionable. Apart from some general comments about potential advantages, compelling data were not provided to adequately support a case for continued work in those areas. For example, polymer-coated framework materials currently have a capacity of ~1.5% w/w. A well- defined pathway to achieving a capacity competitive with 350 bar compressed hydrogen (~2.5% w/w) was not provided.

Response: Because polymer coated sorbent materials provide advantages in terms of cost savings when it comes to increasing useable H_2 relative to uncoated sorbents, reducing refrigeration capex and opex, addressing challenges associated with thermal management, etc., comparing levelized cost of storage across these different technologies is arguably the more important metric.

For example, recent TEA conducted by LBNL highlighted that the levelized cost of storage for a polymer-coated activated carbon sorbent, capable of storing 2.2 wt% H_2 at 50 bar and 180 K, was found to be 40% lower than storing 170 bar of compressed H_2 at room temperature.

We are currently working with an activated carbon boasting a BET surface area of 3500 m^2/g. Preliminary results suggest a 2.2 wt% capacity on a coated material is feasible at the mg scale. Efforts are underway to scale up these procedures using synthetical techniques conducive to industry.



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Response: The need for alternative energy sources to overcome the high enthalpy of desorption for most LOHC is guaranteed. Based on deployed gas-phase chemistry, photon-coupling using plasmonic catalysts provides a very attractive pathway, with ~70% energy efficiency. (link to press release)

However, preliminary data (obtained by the HyMARC scientists) using the same TiN-based plasmonic material on physisorbed CO_2 and low-energy LEDs has demonstrated the tremendous opportunity of plasmonic catalysts (see Figure to the right where the amount of photo-desorbed CO_2 exceeds thermal desorption). The same team has also successfully demonstrated methanation reactions using this approach with ~100% selectivity and conversion.

Applying the same concept to the liquid-phase chemistry adds additional challenges, such as pH and mass transport, impacting yields and overall efficiency. Addressing these limitations is at the core of this research, and needed a robust reactor which is now available (see slides on Accomplishments).