SAND2021-12628PE

Energy & Homeland Security

SNL Hydrogen Program Overview

Kristin Hertz, Hydrogen Program Manager

Sandia National Laboratories, September 29, 2021

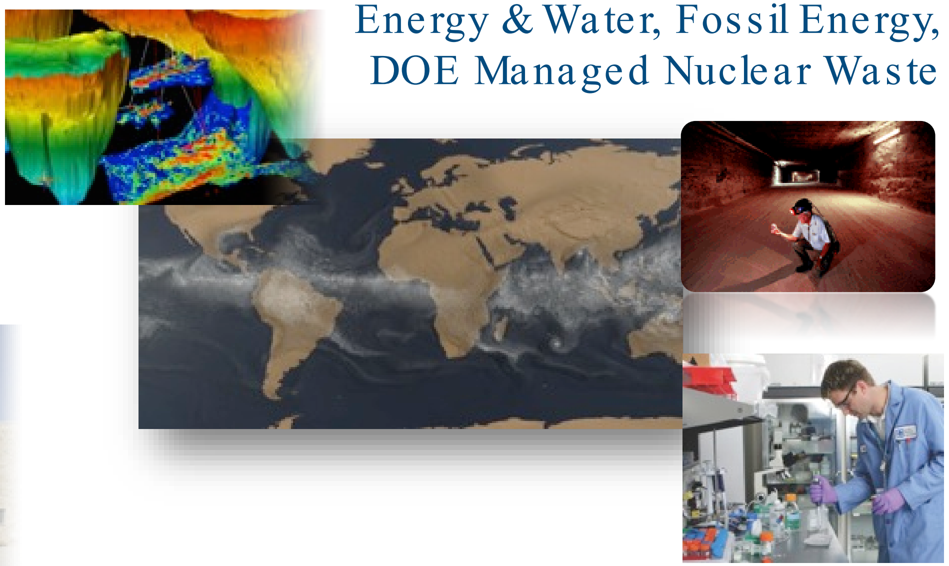
SANDIA'S ENERGY PROGRAM INTEGRATES GENERATION AND APPLICATIONS

Nuclear Energy & Fuel Cycle

Commercial Nuclear Power Generation, Nuclear Energy Safety & Security

Engineered Earth Systems

Energy & Water, Fossil Energy, DOE Managed Nuclear Waste



Fundamental Energy Research

Chemical, Geological, Biological, Materials, Computational, and Nano Sciences

Renewable Power & Energy Infrastructure

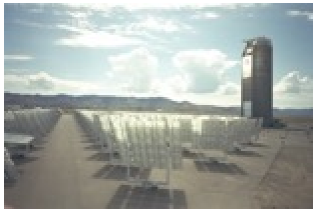
Renewable Energy, Energy Efficiency, and Grid Modernization

Sustainable Transportation

Vehicle Technologies, Bioenergy, Hydrogen & Fuel Cell Technology

SANDIA'S HYDROGEN PROGRAM BUILDS ON EXPERTISE IN MATERIALS AND SAFETY

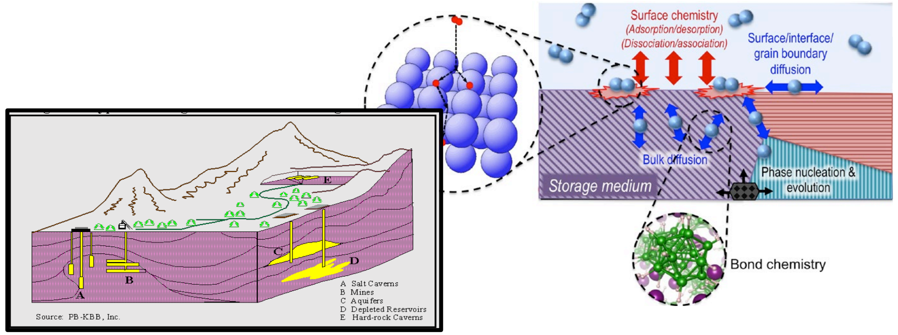
Hydrogen Production



Water-splitting materials
for large-scale hydrogen production

Hydrogen Storage

Discovering the behavior of solid storage materials and advancing subsurface storage technologies

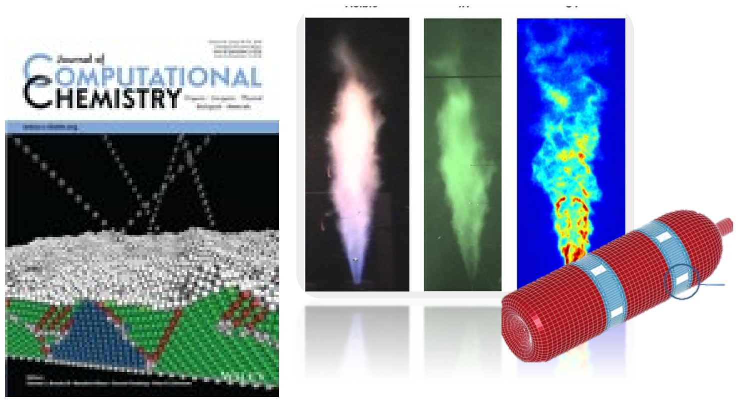


Hydrogen Delivery

Materials compatibility for hydrogen in natural gas pipelines

Safety Codes and Standards

Structural material selection for production, storage and utilization



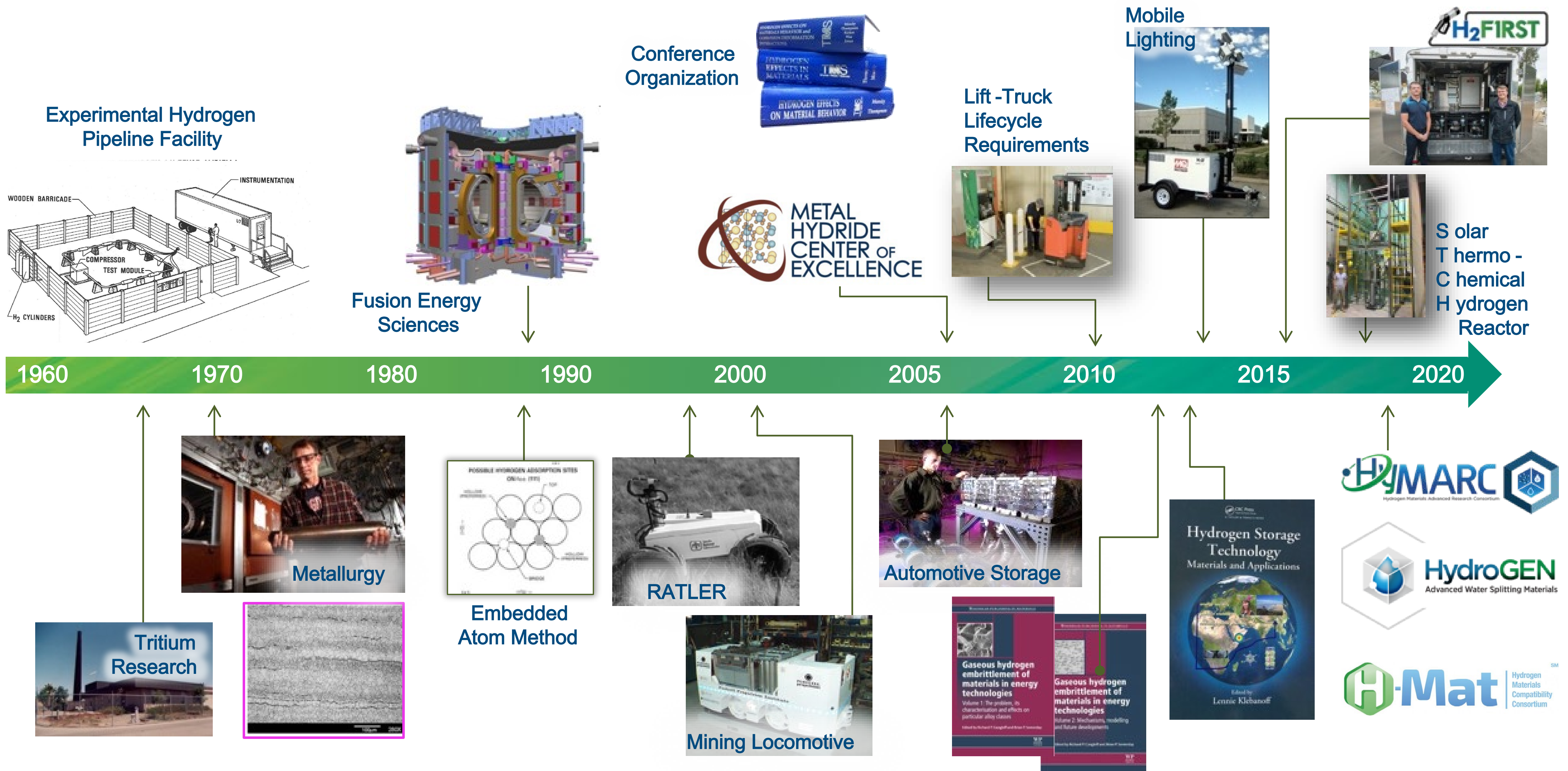
Systems Engineering

Demonstrate innovative engineering solutions to harness clean energy technologies

Fuel Cells

Develop synthesis toolbox and membrane chemistry for enhanced electrochemical performance

PARTNERSHIPS AND CONSORTIA ARE CRITICAL TO SANDIA'S HYDROGEN PROGRAMS



Metal Hydride Research at Sandia-CA

Mark D. Allendorf, Vitalie Stavila, Terry A. Johnson

September 29, 2021

HyMARC: Hydrogen Materials Advanced Research Consortium

The overall goals of HyMARC are to:

- Discover new storage materials for both transportation and stationary applications
- Double the energy density of compressed-gas storage
- Provide foundational understanding to accelerate materials discovery
- Develop metrics for hydrogen carriers and match with applications
- Serve as a gateway to access National Lab facilities

www.hymarc.org

HyMARC is an interdisciplinary team employing state-of-the-art synthesis, cutting-edge diagnostics, and high-performance computing to achieve these goals

We are delivering high-impact outcomes including:

- Storage materials to exceed those of 700 bar pressurized gas
- Revolutionizing material discovery/development by co-design using:
  - Machine learning and data science
  - System models
  - Techno-economic analysis
- Databases of fundamental material properties
- Documented results in high-impact publications
- Network of international collaborations

Relevance: pressurized gas and liquid-phase hydrogen cannot meet the storage requirements of all applications

Criteria—Long Duration and High Power

- Applications where batteries are too expensive
- > 2 weeks where LH2 boil-off significant
- Lower pressure and smaller volume than GH2

Stationary use cases under consideration:

Seasonal Microgrid Storage

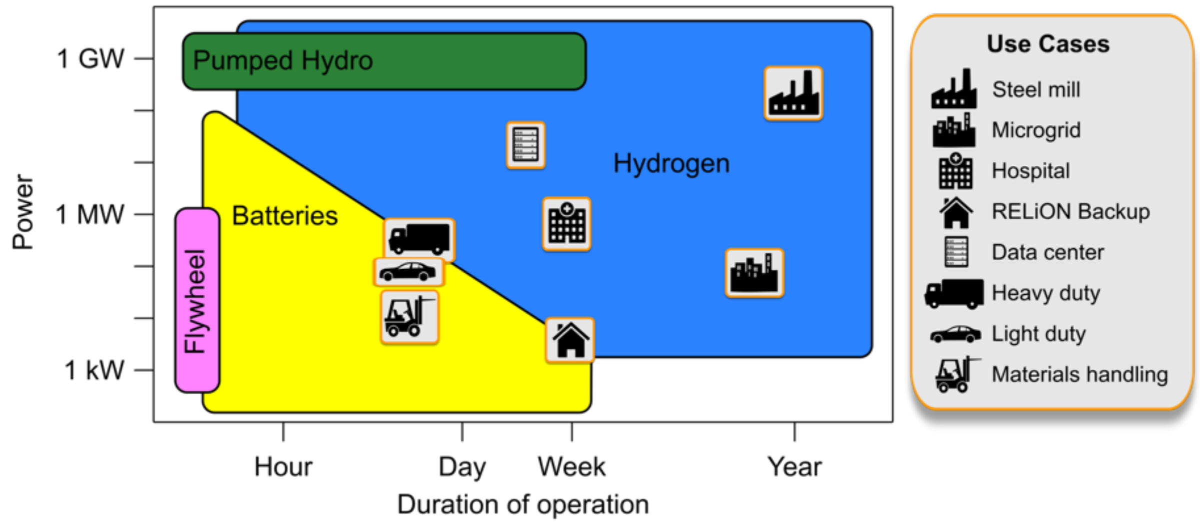
- Long term storage
- Low power/energy
- 3 Months, 5000 kg H_2, 50 kW

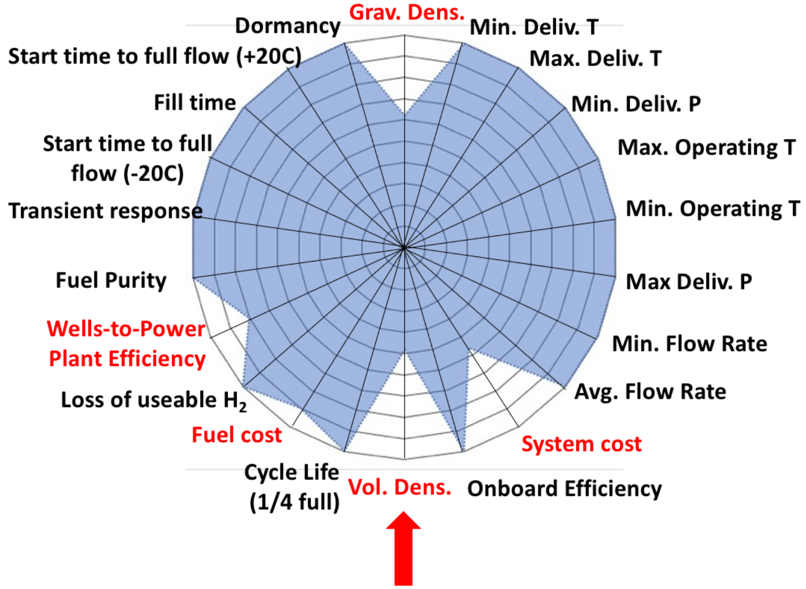
Data Center Backup Power

- Long term storage
- High power/energy
- 3 Days, 45000 kg H_2, 10,000 kW

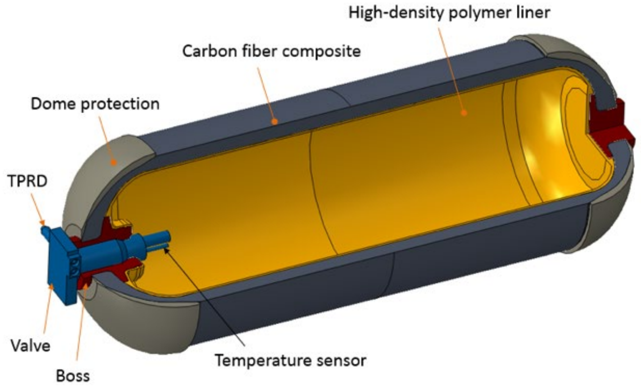
Transportation applications:

- LDV: compressed H_2 gas storage falls short of several DOE targets
- HDV: storage system cost, volume, and weight must be minimized
- Carriers needed for efficient transport





Unachievable using 700 bar

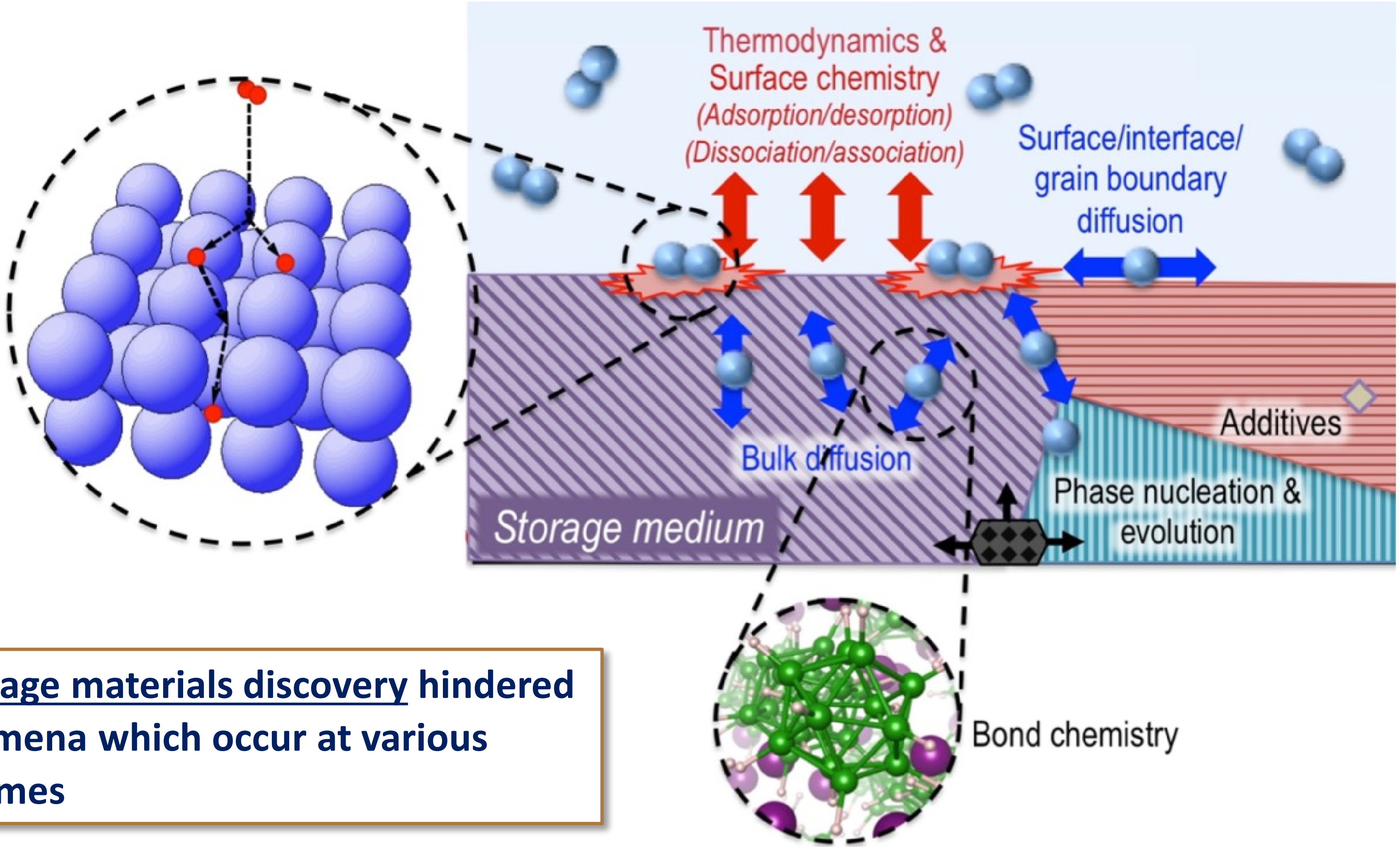


TPRD = Thermally Activated Pressure Relief Device
Credit: Process Modeling Group, Nuclear Engineering Division. Argonne National Laboratory (ANL)

Complex phenomena provide opportunities to design new materials

Effective thermal energy for H_2 release: $\Delta H(T) = \Delta H^{\circ}(T) + E_a$

Thermodynamics | Kinetics



⇒ **New hydrogen storage materials discovery hindered by complex phenomena which occur at various length and timeframes**

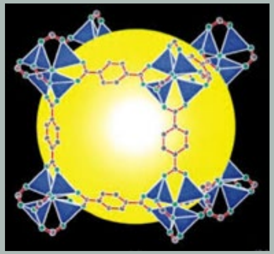
Mitigate problematic physical phenomena

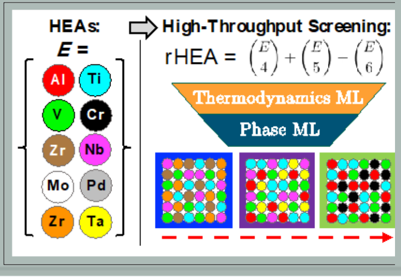
Energetics

How can we control ΔH and ΔS of hydrogen adsorption and desorption in sorbents and metal hydrides to enable near-r.t. hydrogen storage?

Sorbents:
- Polarizable groups
- Flexibility, gate-opening phenomena
- Open coordination sites

Metal hydrides:
- Nanostructuring and host effects
- Multicomponent systems



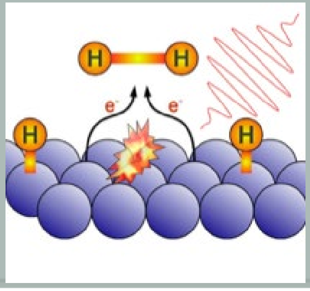


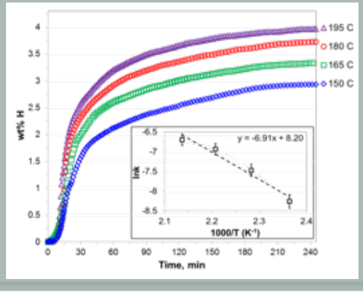
Kinetics

How can we identify mechanisms by which surfaces and strain effects accelerate reaction rates in reversible metal hydrides?

Metal hydrides:
- Surface modifications to promote H_2 activation
- phase nucleation and interfaces
- Confinement and strain effects

Hydrogen carriers:
- Heterogenous catalysts for reversible H_2 storage in LOHC



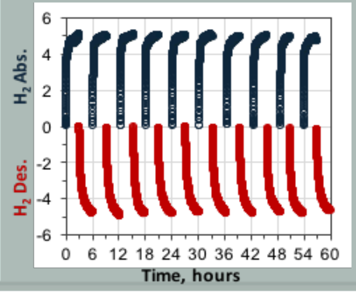


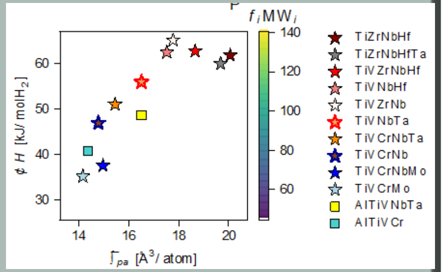
Reversibility

How can we improve the reversibility and cycle-life of metal hydrides and sorbents under realistic conditions of H_2 cycling?

Metal hydrides:
- Nanoconfinement and nanostrain to improve capacity, reversibility and cycle-life

Sorbents
- Flexibility in framework materials, non-porous to porous phase transitions





NREL NATIONAL RENEWABLE ENERGY LABORATORY | Sandia National Laboratories | Lawrence Livermore National Laboratory | BERKELEY LAB | Pacific Northwest NATIONAL LABORATORY | NIST | SLAC NATIONAL ACCELERATOR LABORATORY

Nanoscale metal hydrides

Nanoscale metal amides

Objective

Demonstrate metal amides with optimized thermodynamic, kinetic, and heat transport properties can provide sufficiently fast H_2 desorption at ≤ 200 °C, enabling low-cost, light-weight aluminum storage tanks to be used.

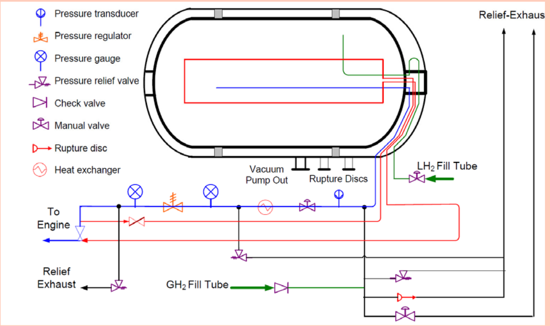
Research Strategy

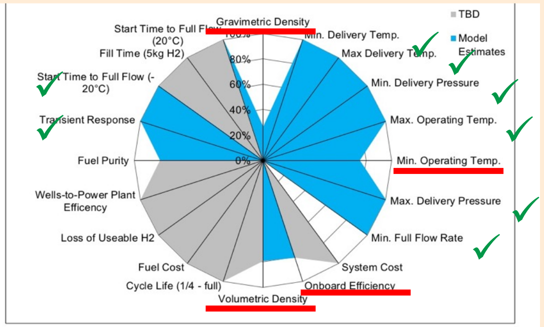
Implement a ”Co-design” strategy to accelerate material development:

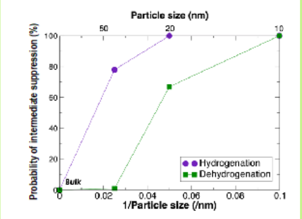
Interacting models inform each other and are not optimized independently

co-optimization

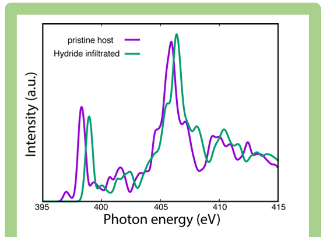
Systems model ⟷ **Materials model**



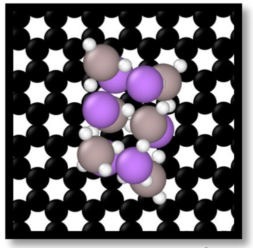




Nano-scaling thermodynamics



Spectroscopy of host interactions

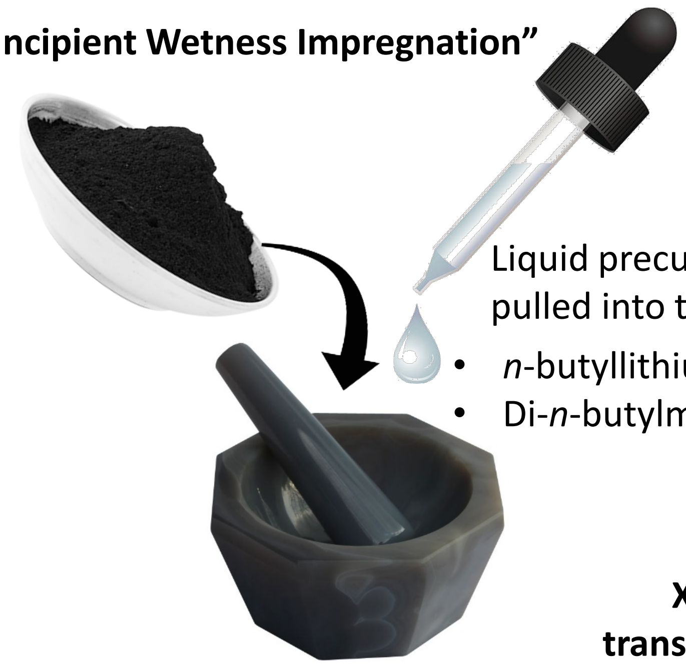


Dynamics & specific heat capacity

Accomplishments: New synthesis method for nano-amides

- To develop a nanoscale material, we can infiltrate a porous carbon host with precursors
- After drying, treatments convert the precursors to metal hydrides/amides within the pores

"Incipient Wetness Impregnation"



Liquid precursors are pulled into the pores, e.g.

- *n*-butyllithium (BuLi)
- Di-*n*-butylmagnesium (Bu_2Mg)

New Synthesis Routes

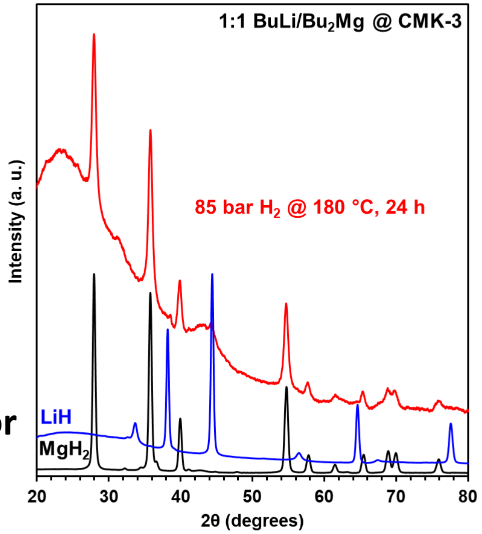
$BuLi + Bu_2Mg$

↓ Heat under H_2

$LiH + MgH_2 + C_4H_{10}$

↓

XRD analysis shows transformation of precursor



$BuLi + Bu_2Mg$

↓ Heat under H_2

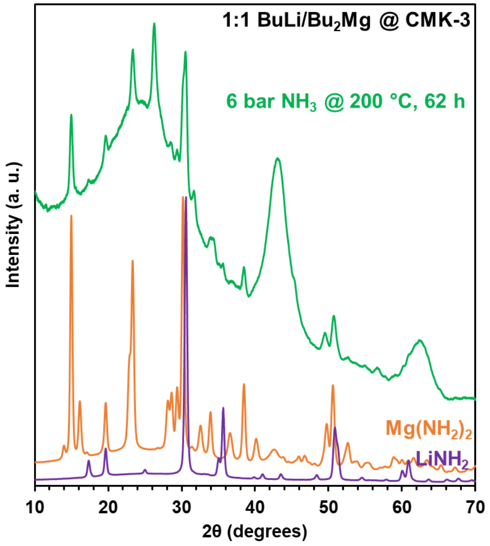
$LiH + MgH_2 + C_4H_{10}$

↓ Heat under NH_3

$LiNH_2 + Mg(NH_2)_2 + H_2$

↓ Desorb under vacuum

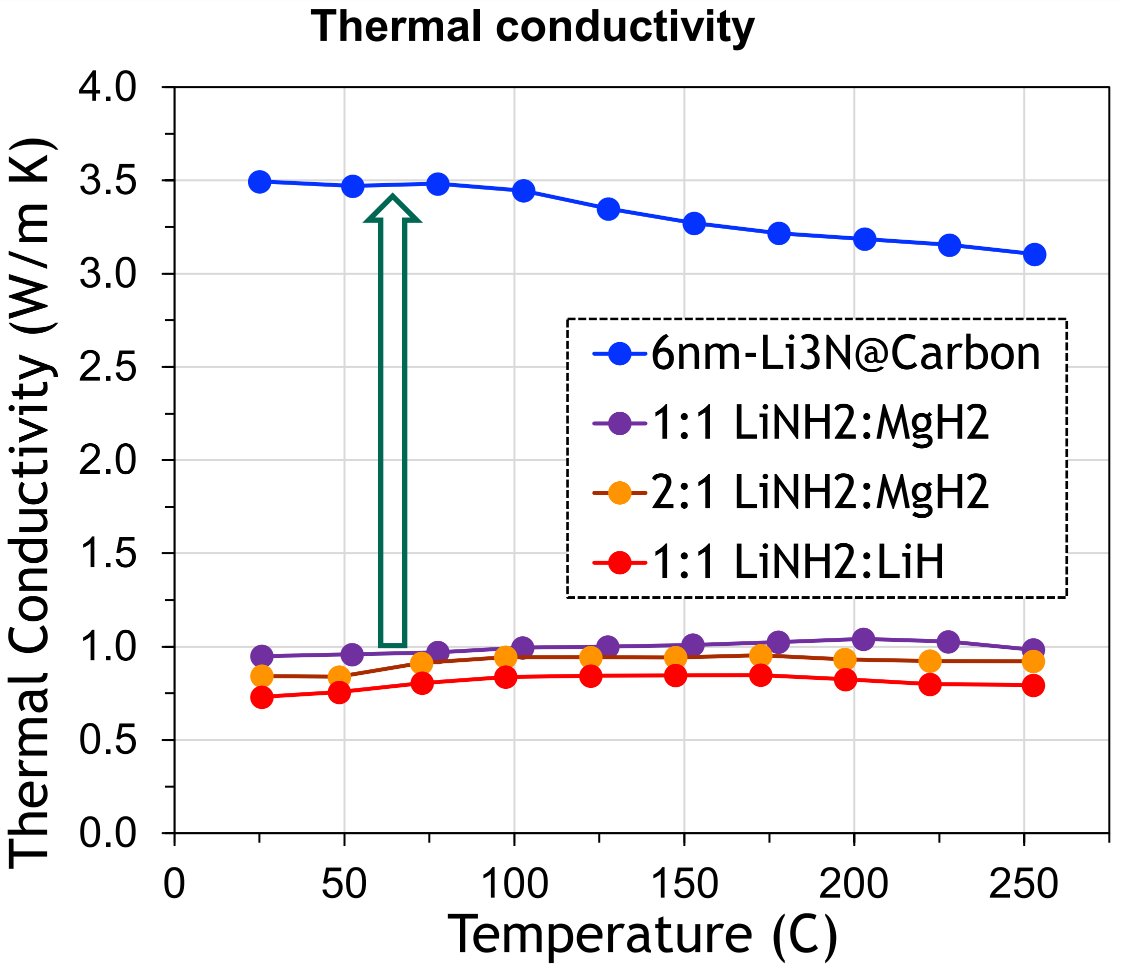
$Li_2Mg(NH)_2 + NH_3 + 2H_2$



⇒ **Successfully infiltrated both Li and Mg organometallic precursors into carbons and demonstrated conversion into the mixed metal amide phases under mild conditions of pressure and temperature**

Accomplishments: Thermal conductivity of nano- vs bulk amides

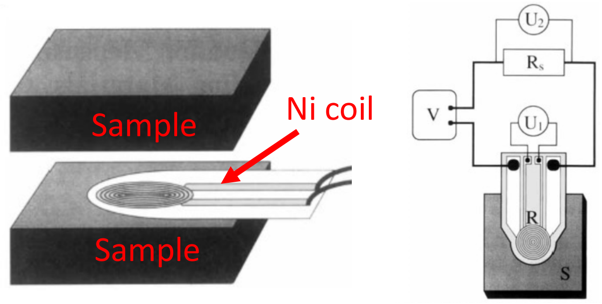
Sandia National Laboratories NREL



Transient Plane Source (TPS) Technique

Hot Disk Transient Plane Source: A validated method for testing low to high thermal conductivity materials, where the thermal conductivity is directly (or independently) measured.

- A nickel coil with a known temperature coefficient of resistance (TCR) is heated between two homogenous samples.
- Measure resistance of nickel coil during a transient heat wave.
- Compute temperature from the TCR of the sensor. The resulting temperature depends how well the sample can conduct heat away from the sensor.
- The temperature-time response can be fit to determine the thermal conductivity of the sample.
- Samples: pressed into disks at 10,000 psi in an argon glove-box



$$\Delta T_{ave}(\tau) + \Delta T_i = \frac{1}{\alpha} \cdot \left(\frac{R(t)}{R_0} - 1 \right)$$

$$\Delta T(\mathrm{t}) = \frac{P}{\pi^{3/2} \cdot r \cdot k} D(t)$$

$$\tau = \sqrt{\frac{t}{\theta}} \text{ and } \theta = \frac{r^2}{\alpha_r}$$

P = power
r = sensor radius
k = thermal conductivity
α = thermal diffusivity
ρc_p = volumetric specific heat

Thermal conductivity is increased by factor of 3.0-3.5 going from bulk to nano.

Approach: Framework for materials co-design

Storage system modeling tool workflow
(developed by the DOE Hydrogen Storage Engineering Center of Excellence)

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

→ **Tankinator** →

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

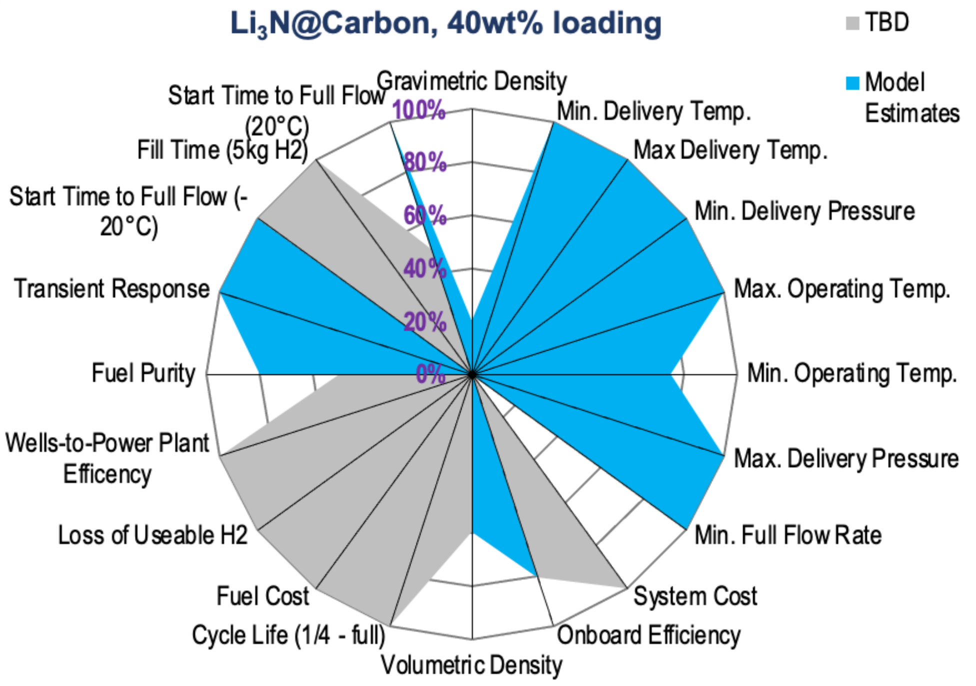
H-capacity, enthalpy, entropy, heat capacity, packing density, thermal conductivity, rates of hydrogen uptake and release

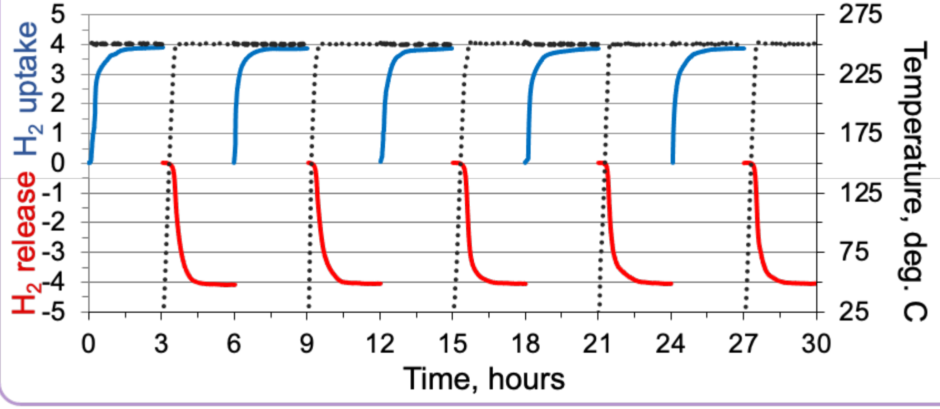
DOE Vehicle framework model evaluates proposed storage system w/drive cycle

Inputs
Tankinator inputs
Tankinator outputs
Heat capacity
Kinetics of reaction

→ **Vehicle Framework** →

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





○ <u>Coupling materials development with systems co-design</u> **provides guidance on tradeoffs and properties needing improvement**

Accomplishments: Sensitivity analysis on system volumetric capacity

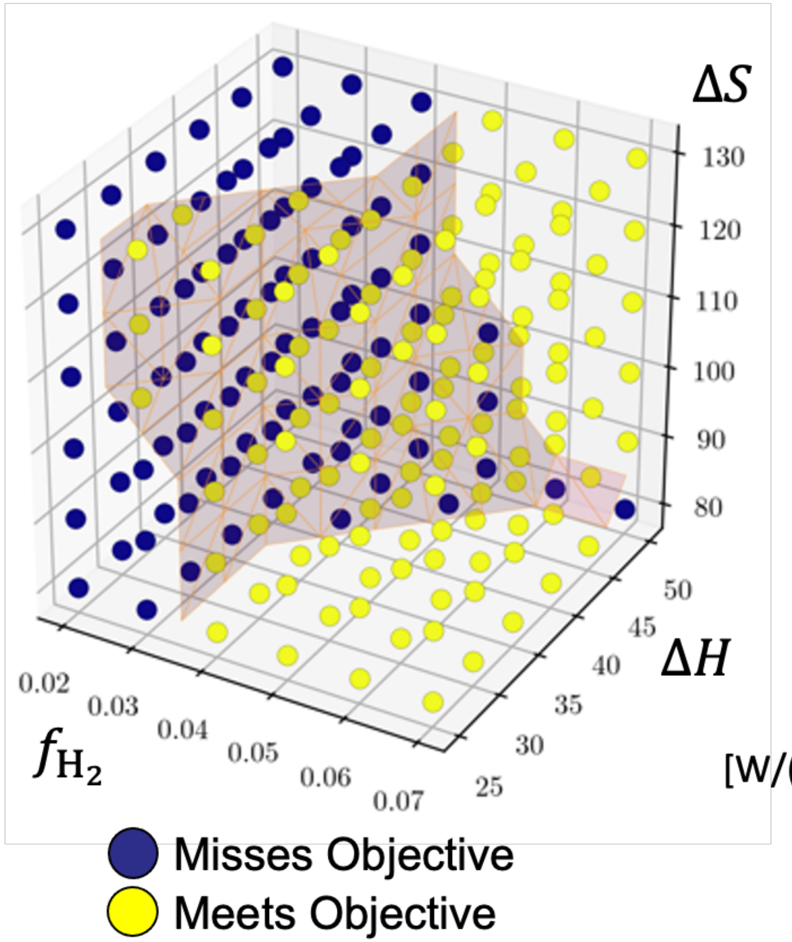
Sandia National Laboratories | Pacific Northwest National Laboratory

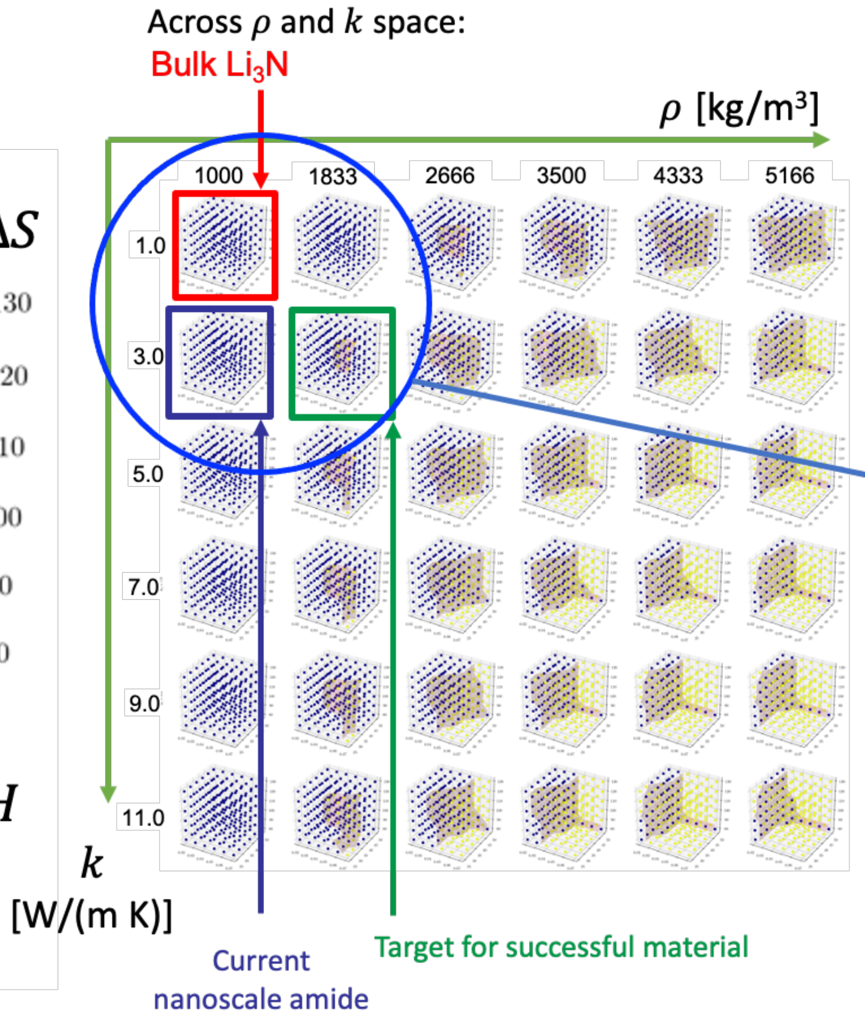
Objective: %Vol 2025 Target > 60 (i.e. better than 700 bar compressed H_2)

We developed algorithms to automatically perform a large number of Tankinator calculations across a wide parameter space

Example: P_{max} = 100 bar H_2

6-D $(\Delta H, \Delta S, f_{H_2}, \rho, k, P_{max})$ sensitivity analysis

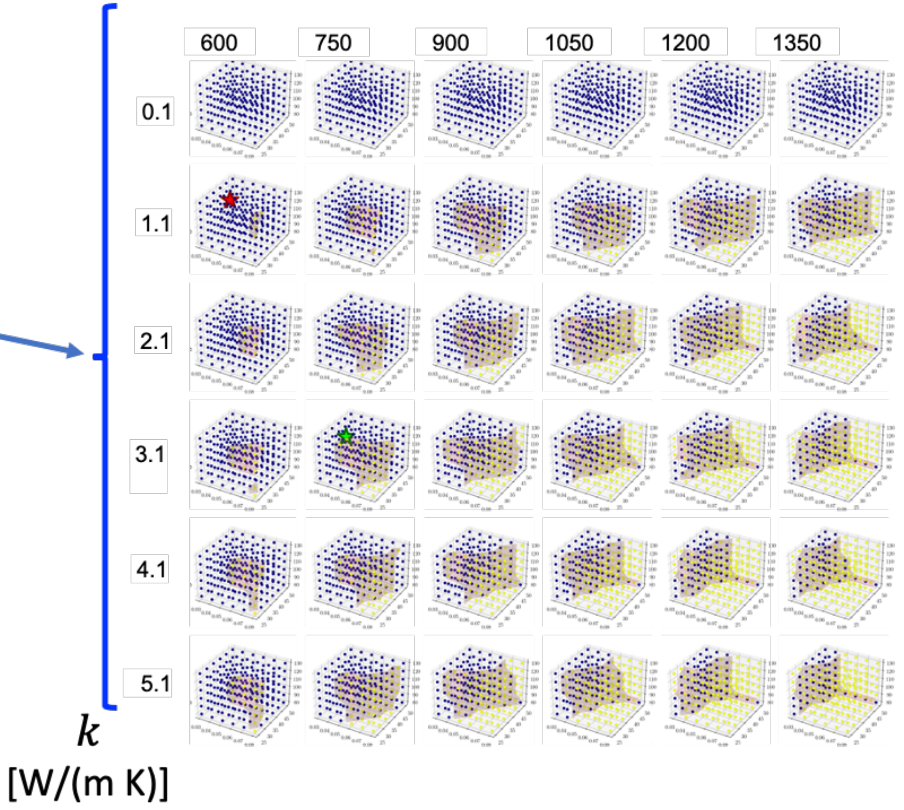




ρ ≡ bed density [kg/m³]

k ≡ thermal conductivity [W/(mK)]

P_{max} ≡ max operating pressure [atm]



Technology transfer activities

Joint industry project with SoCalGas focused on HDV

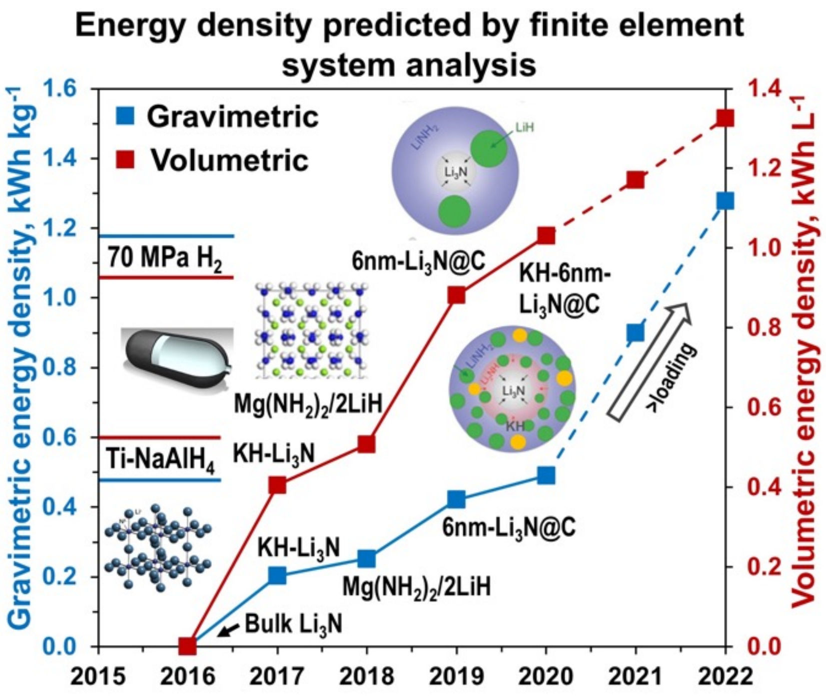
Project objective: Evaluate metal hydride composites as a materials-based storage medium to replace high-pressure hydrogen gas on Class 7 or 8 tractor FCEV

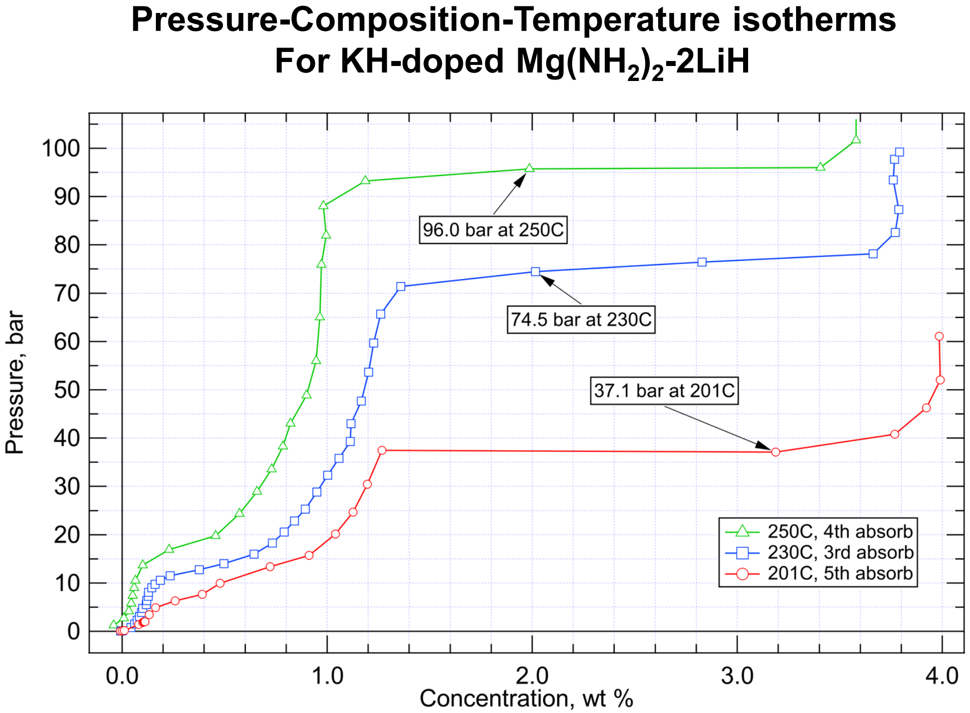
Duration: 18-month project initiated in November, 2020

Funding: funds in to Sandia from SoCalGas, $350K/year

SoCalGas

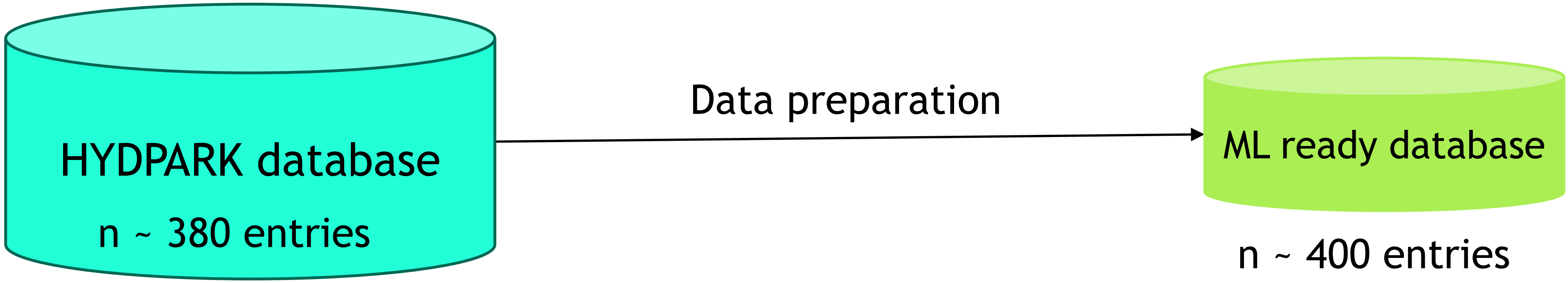
Nikola class 8 FCEV truck, 80 kg H_2 on board





Explainable Machine Learning

ML database assembly and feature selection



- Filter database for duplicates and missing data
- Create initial features using Magpie
- Compute $\Delta S = R\ln P_{eq} + \frac{\Delta H}{T}$
- Compute $\ln P_{eq}^{o} = -\frac{\Delta H}{R(25\,°C)} + \frac{\Delta S}{R}$

Features (Magpie):

Structurally agnostic features describe each composition

$$\text{“LaNi}_5\text{”} \equiv \{v_{pa}^{Magpie}, \text{Feat\#2}, \ldots, \text{Feat\#145}\}$$

$$v_{pa}^{Magpie} = \sum_i f_i v_i$$

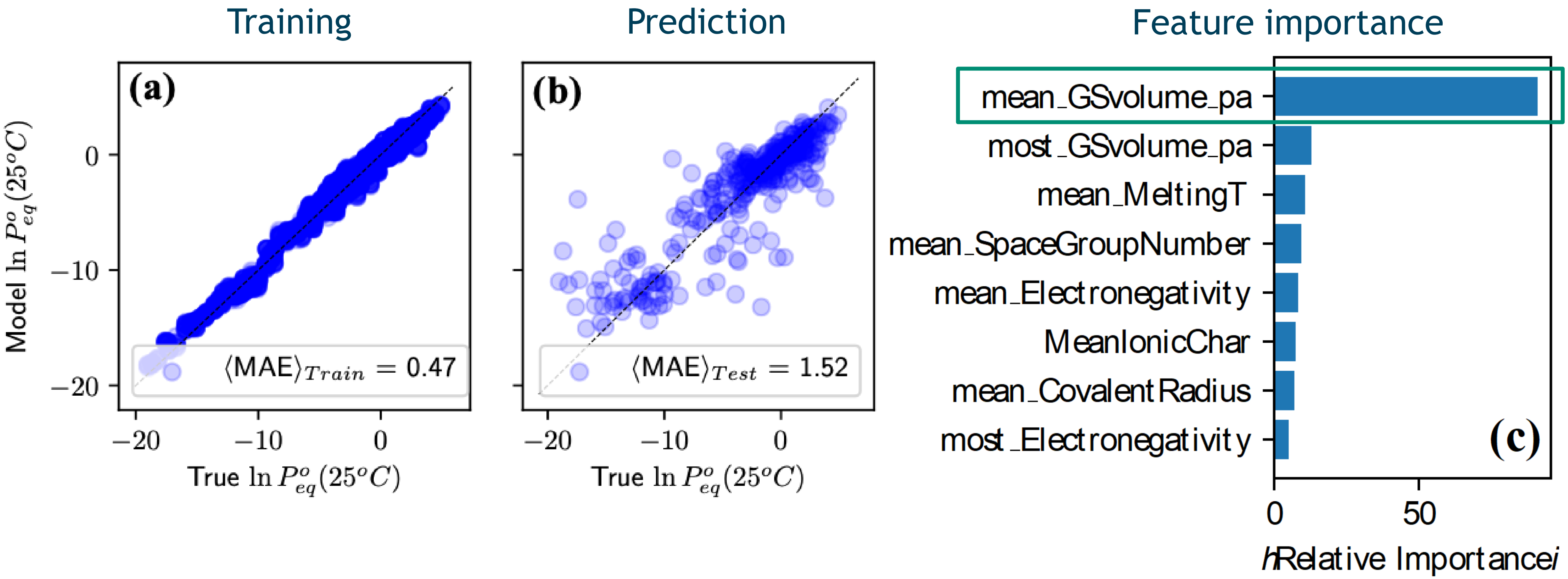
$f_i \equiv$ composition fraction of element *i*

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

Started collaborations for additional data sources

- DFT with Prof. Sanliang Ling (U. Nottingham)
  - Crystal structure for complex features
- Hydrogen diffusion data from Prof. Dallas Trinkle (University of Illinois at Urbana Champaign)

ML accurately predicts H_2 equilibrium P_{eq} in metal hydrides

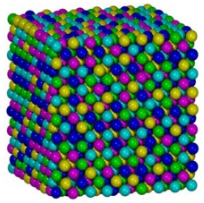


⇒ Our explainable ML model accurately predicts thermodynamics and indicates that the average atomic volume is the best predictor of hydrogen equilibrium pressure

M. Whitman, V. Stavila et al. *J.Phys. Chem. Lett.* (2020) 11, 40-48.

Accomplishments: ML discovery of high-entropy alloy metal hydrides

High-entropy alloys (HEAs) are alloys formed by mixing equal or relatively large proportions of four or more elements



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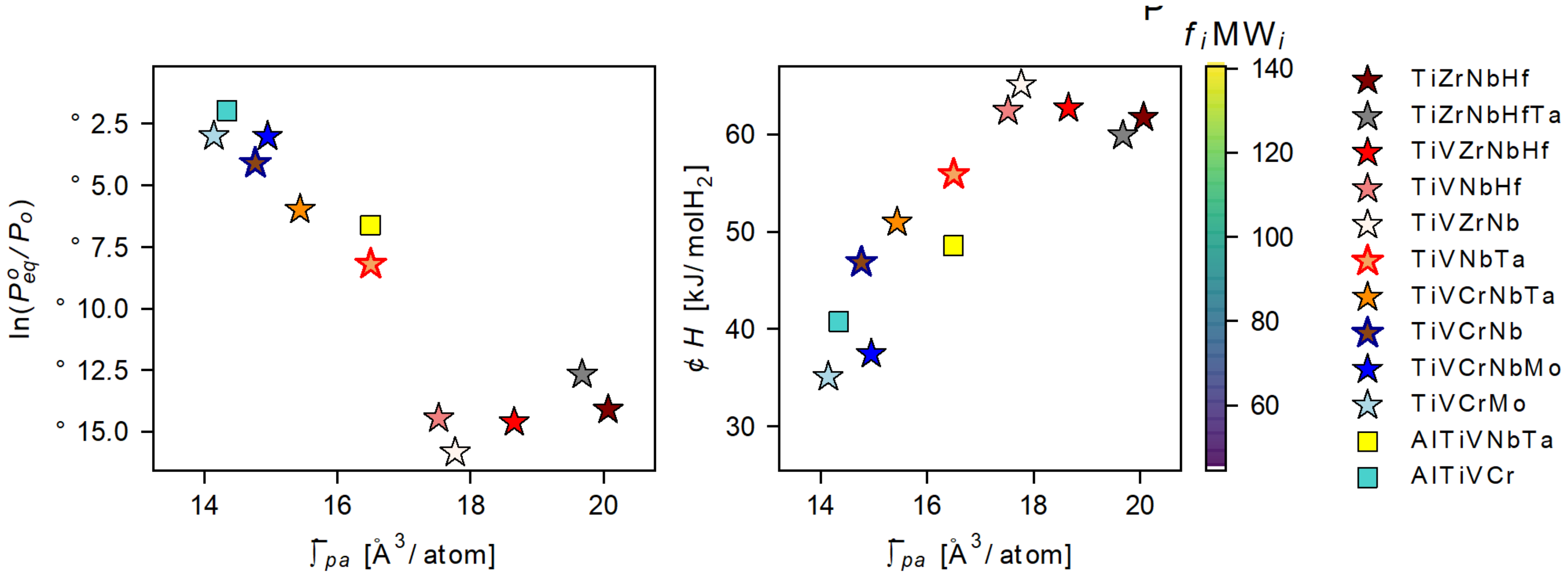
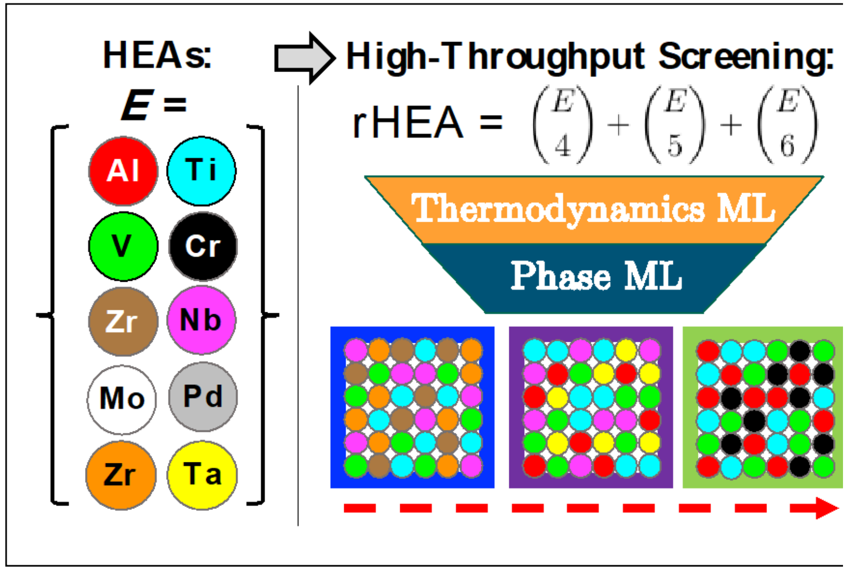


- Used 10 elements {Al, Ti, V, Cr, Zr, Nb, Mo, Pd, Hf, Ta} which provides 672 new compositions for H_2 storage
- Predicted the thermodynamics properties for all compositions and identified 12 HEAs to be synthesized

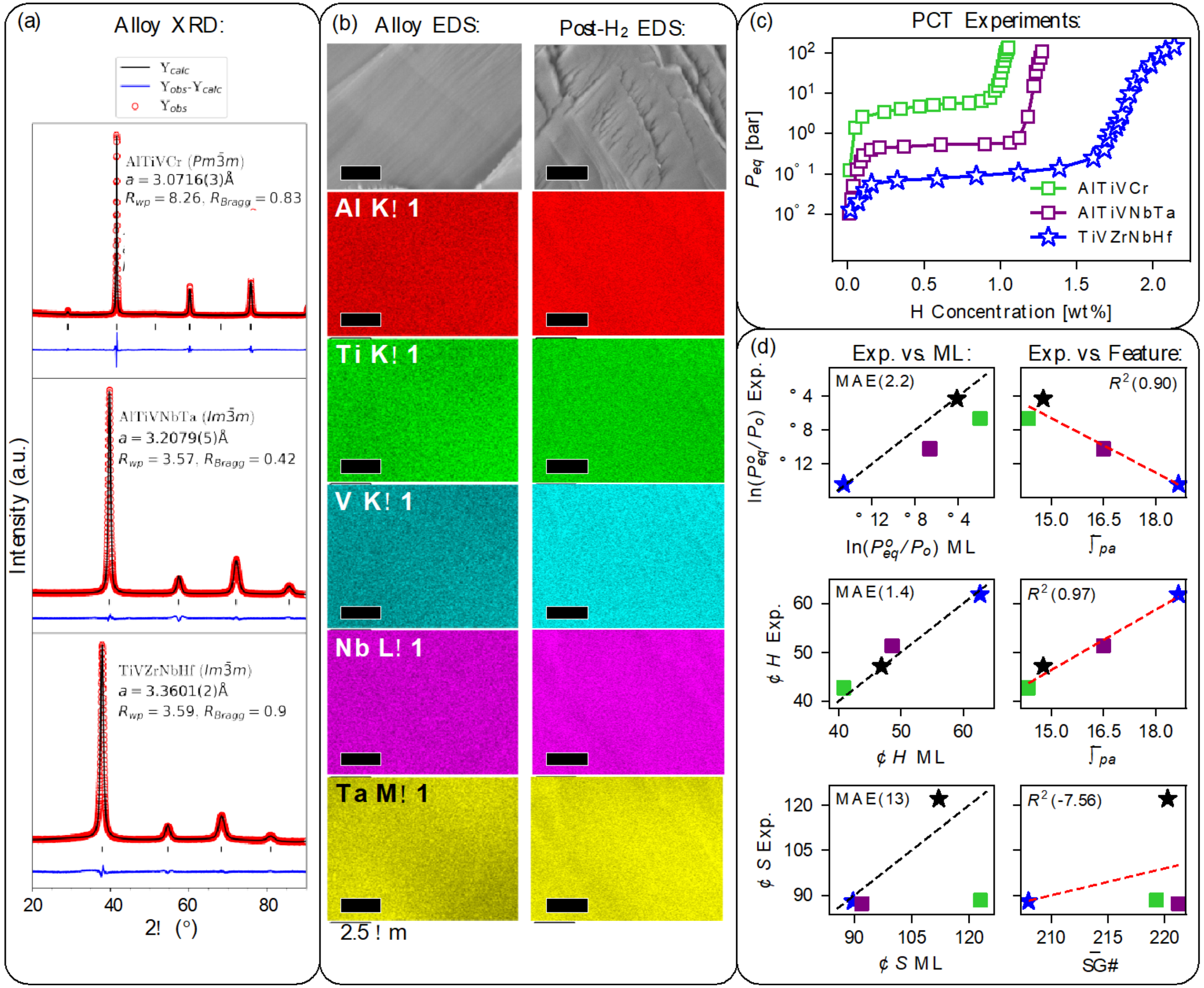
M. Witman, *et al. Chemistry of Materials*, **2021**, *33*, 4067–4076 (Journal Front Cover)

Accomplishments: Synthesis of high-entropy alloy hydrides

Synthesis and characterization



- **Successfully synthesized 12 new HEA hydrides which cover >11 orders of magnitude of H_2 plateau pressures**
- **The EML model accurately predicts the crystal structures and the thermodynamic properties of hydrogen release from HEA hydrides**



M. Witman, *et al*. *Chemistry of Materials*, **2021**, *33*, 4067–4076 (Journal Front Cover)

Metal Hydride Compressor

Metal hydride-based compressor

A metal hydride compressor has potentially significant advantages over current technology

- Greatly reduced operating costs
  - Requires little or no maintenance
  - Can be powered by waste heat rather than electricity
- More Reliable: Simple design and operation with no moving parts
- High purity H_2 delivery: Oil free operation

Characterization of multiple alloys for low and high pressure stages resulted in several options for 875 bar compression

System-level analysis using final bed design and measured hydride properties demonstrates 875 bar H_2 delivery at reasonably achievable temperatures

Prototype compressor and test facility designed and assembled to demonstrate proof-of-concept performance

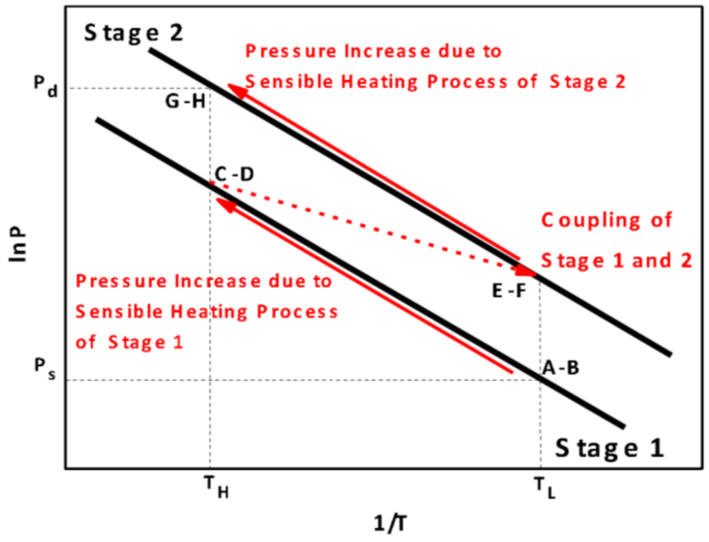
Approach: Two-stage Metal Hydride Compressor

Two-stage metal hydride compressor

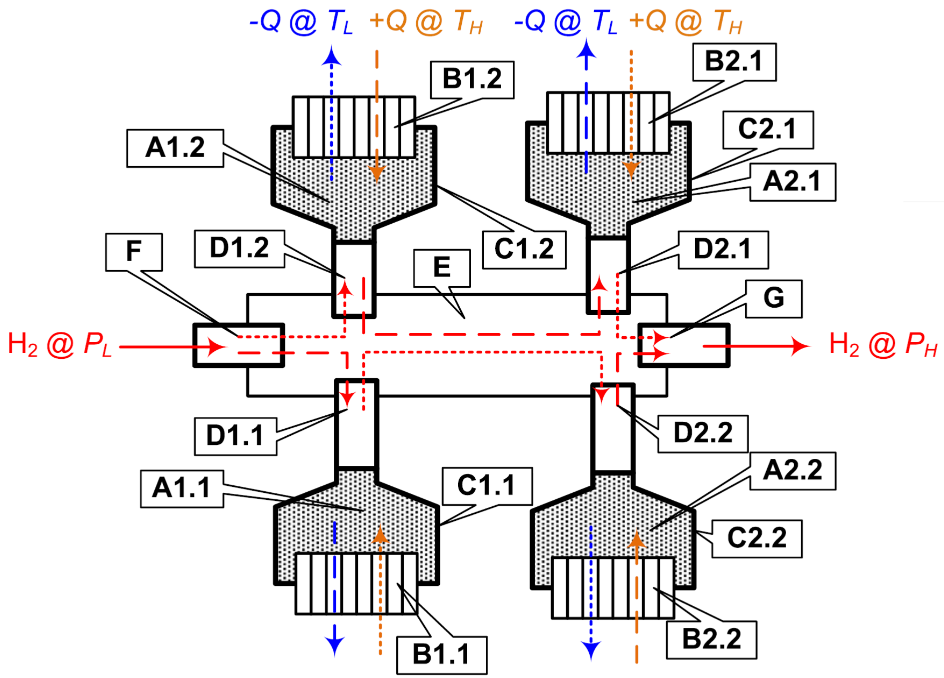
- Feed pressure 50-100 bar
- Outlet pressure ≥ 875 bar
- High purity H_2 gas

Optimized material for each stage

- 2-3 candidates per stage will be characterized (thermodynamics, kinetics, and hydrogen capacities) to determine optimum design



- Each stage consists of multiple (2-3) hydride beds
  - synchronized hydrogenation & dehydrogenation cycles
  - size and number of beds optimized for continuous pumping at desired pressure with minimal heat input



M.V. Lototskyy, Y.A.Yartys, B.G. Pollet, R.C. Bowman Jr., "Metal hydride hydrogen compressors: A review." Int J. Hydrogen Energy **39** (2014) 5818

Prototype compressor system design

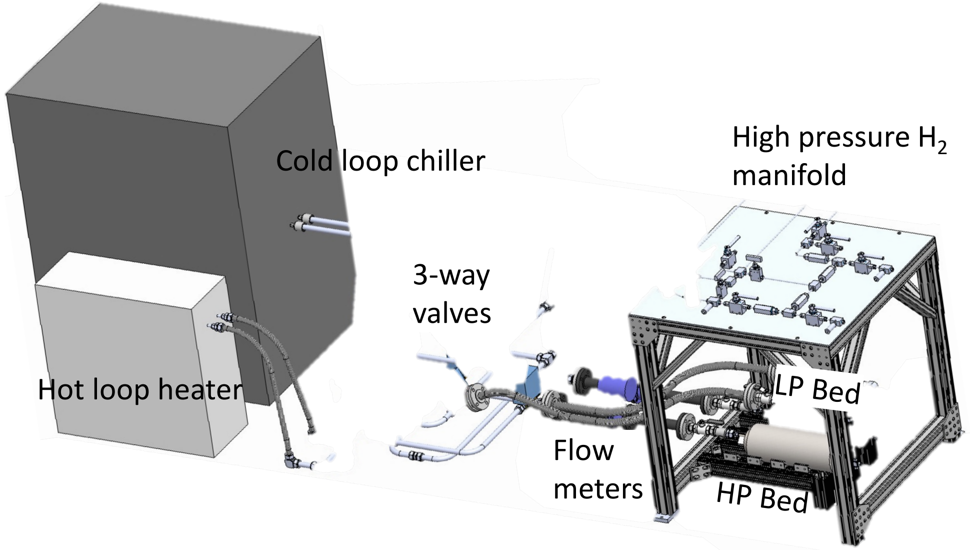
2 stage; 1 bed per stage

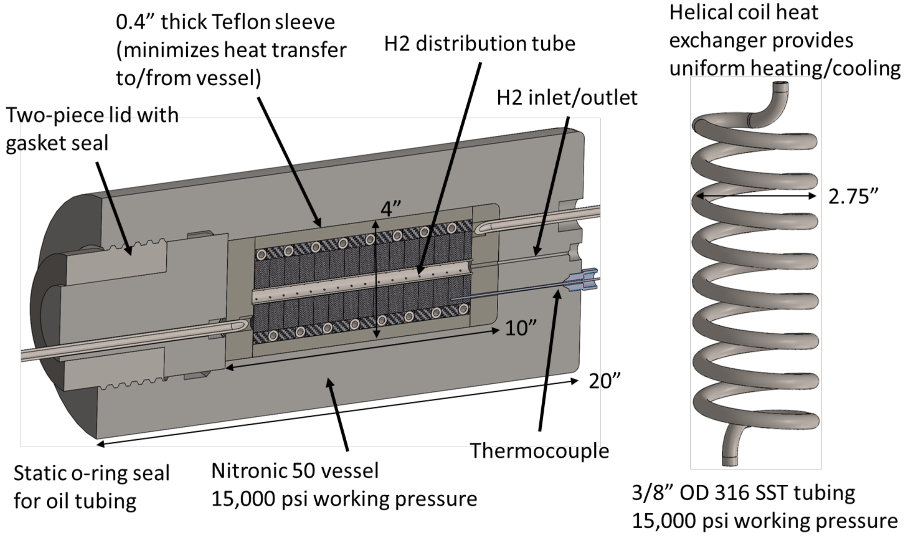
- 2.4 kg hydride per bed
- 20”L X 8”OD; 220 lbs
- Self-contained oil recirculation systems

Stage 1 = $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$

Stage 2 = $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$

Target: 150 bar to 875 bar compression with temperatures of 20℃ - 150℃





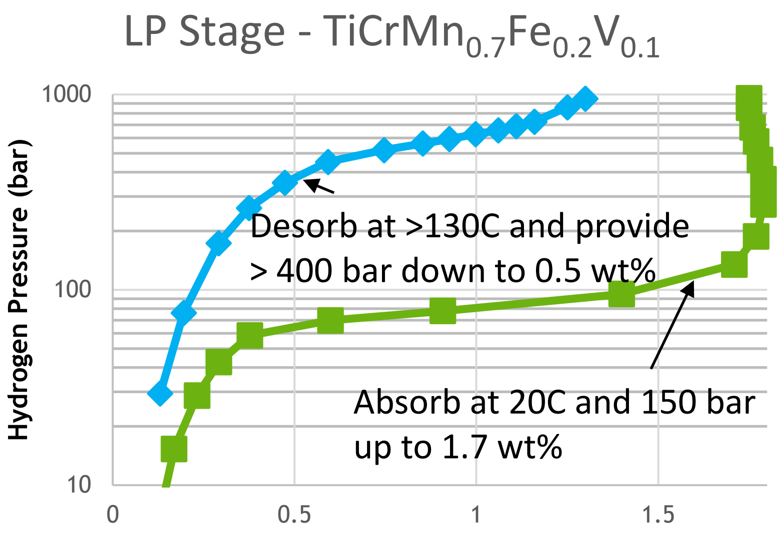
Dynamic system model predicts performance using measured alloy properties

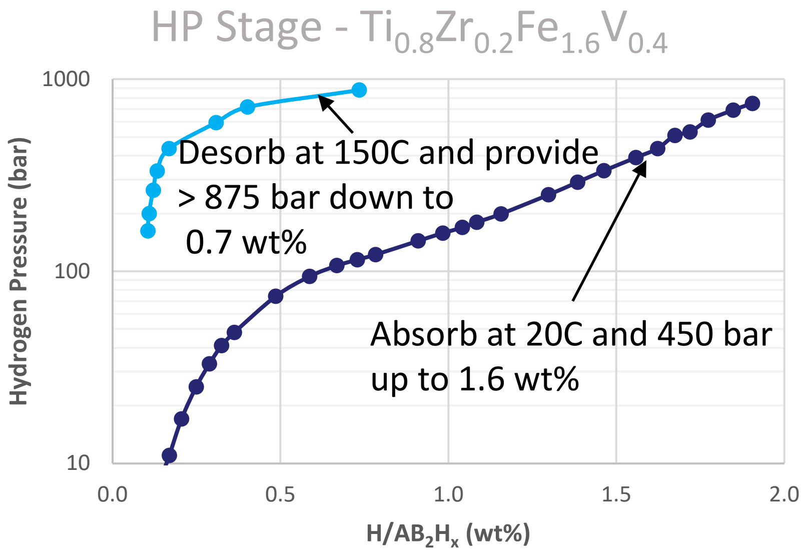
Configuration:

- 2.5 kg of LP hydride ($TiCrMn_{0.7}Fe_{0.2}V_{0.1}$)
- 2.2 kg of HP hydride ($Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$)
- 15 minute half cycles
- 150 to 875 bar compression
- Heating/cooling of beds
  - Cold loop temperature set to 20 ℃
  - Hot loop temperature set to 160 ℃

Results:

- Utilization = 54% for all beds
  - $Utilization = \frac{Hydrogen\ delivered}{Storage\ capacity}$
- **90 g/hr average flow rate**
- **Energy usage for heating 10.9 kWh/kg H_2**





Realized prototype system performance

The low-pressure stage has demonstrated compression from 133 bar to 450 bar over the operating temperature range of the system, but with lower capacity than expected. Better capacity performance was demonstrated compressing up to 400 bar with a capacity of up to 0.67 wt% in 20 minute cycles.

The high-pressure stage of the prototype has limited capacity to deliver hydrogen above about 700 bar. The best capacity at this delivery pressure demonstrated to date has been about 0.43 wt% with a 20-minute cycles which translates to 30.6 g/hr.

Thank you!