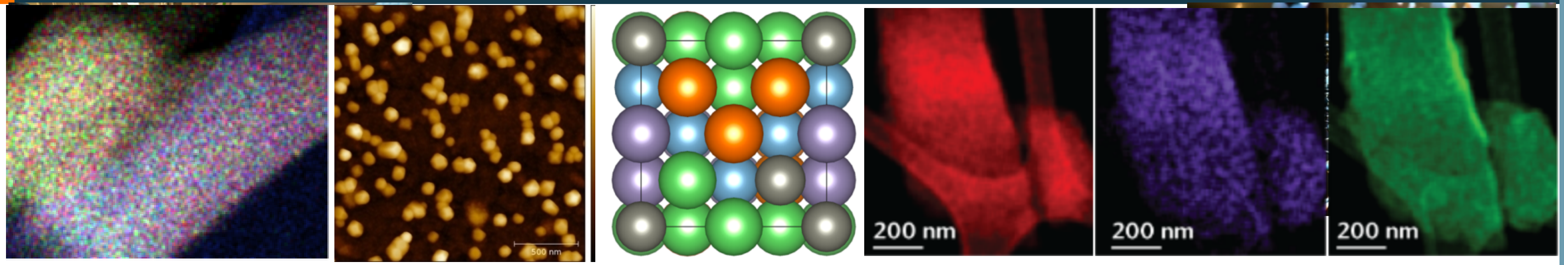
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2023-03163C

Discovery of High-Entropy Hydrides Inspired by Machine Learning



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Energy Nanomaterials Department

Sandia National Laboratories, Livermore, CA

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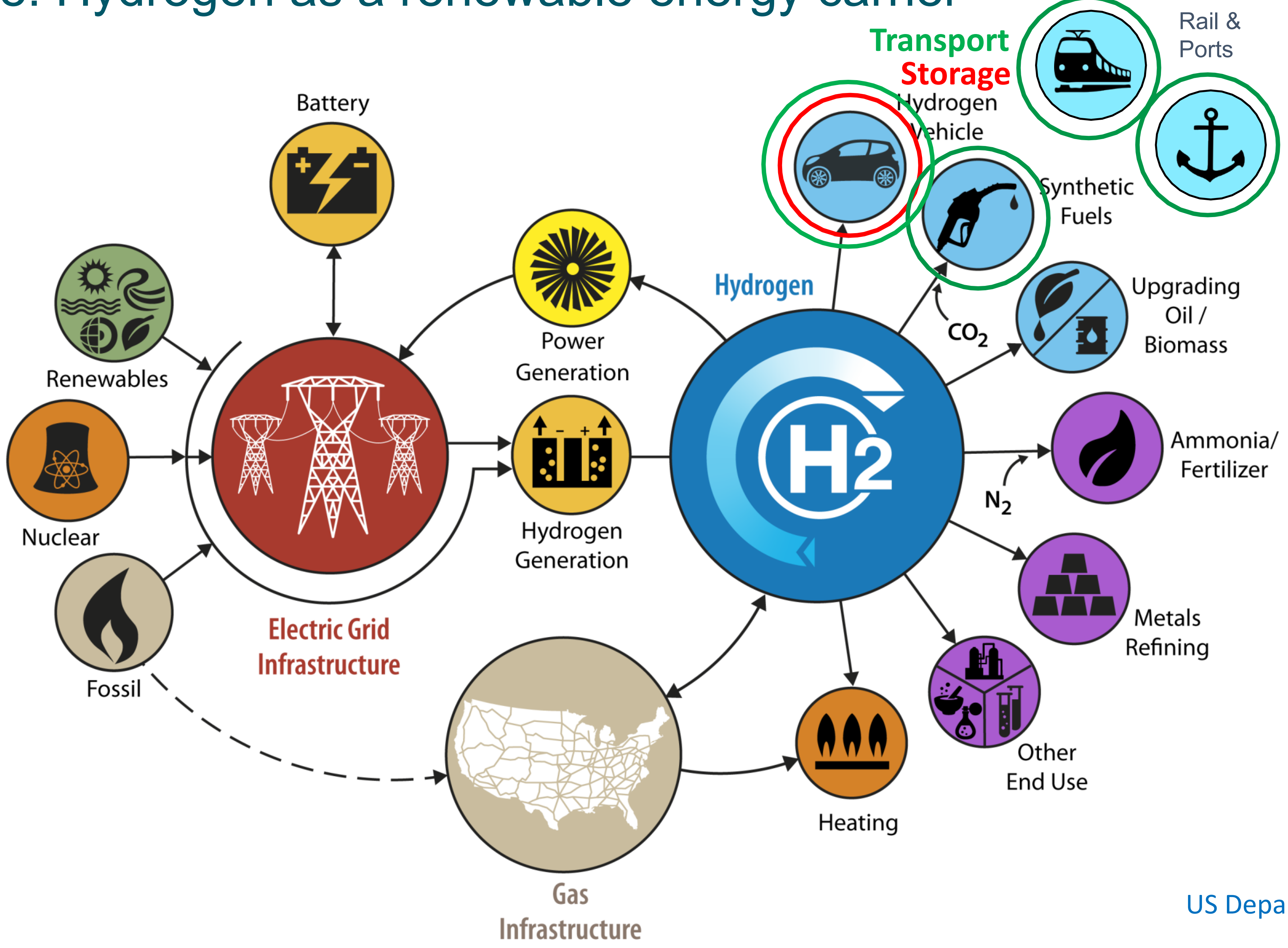
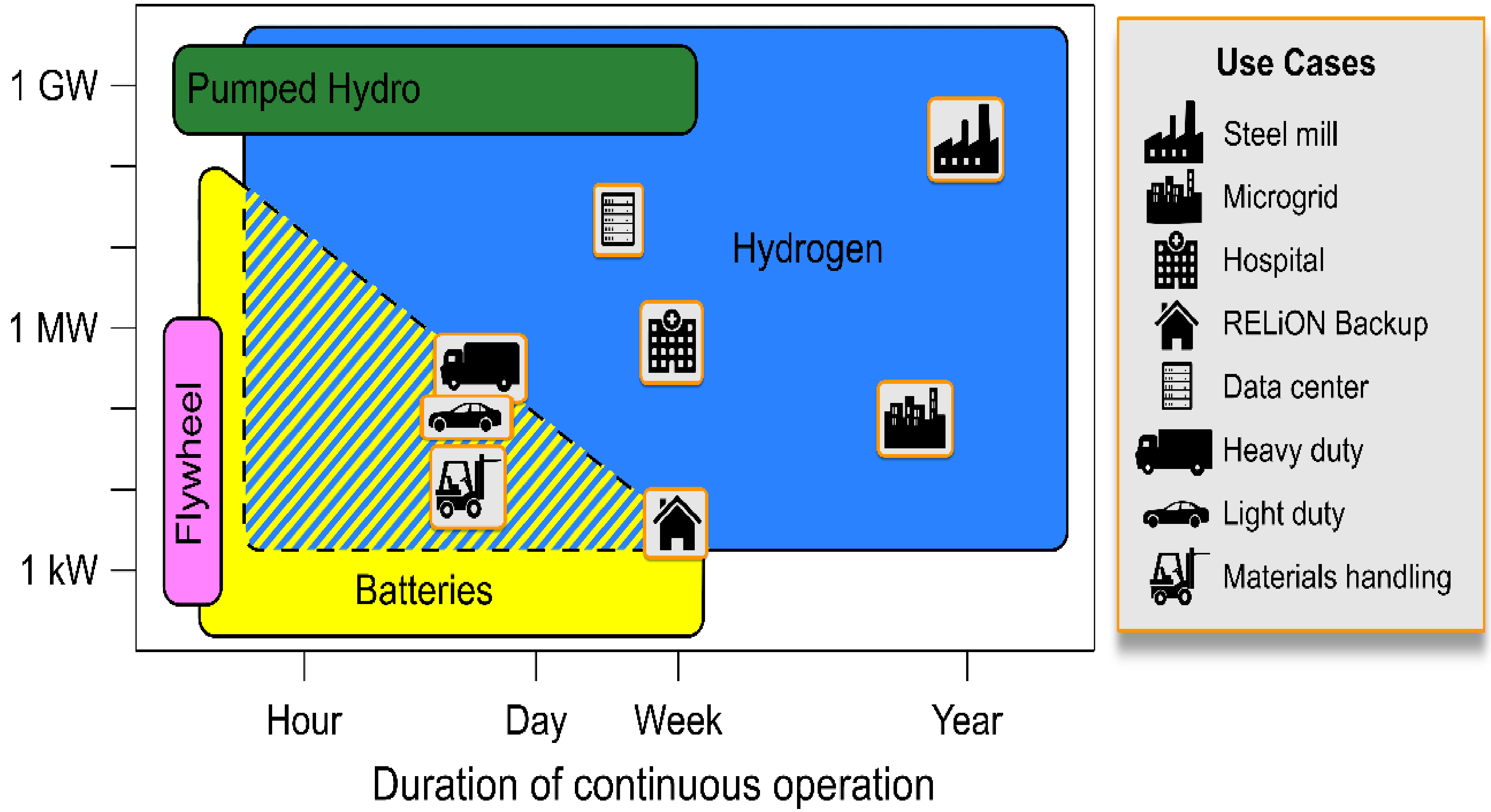
H_2@Scale: Hydrogen as a renewable energy carrier



US Department of Energy

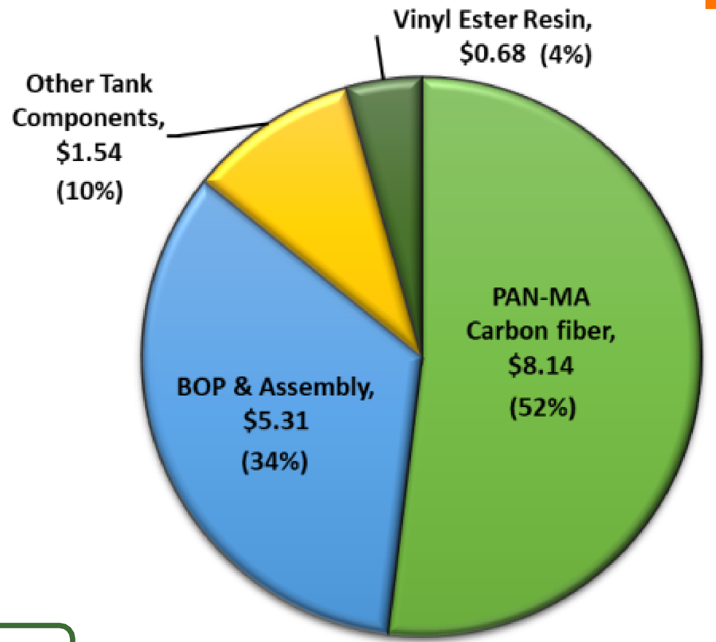
Hydrogen use cases



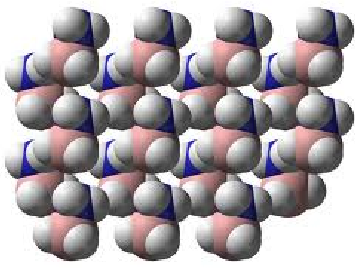
Nature Chemistry, volume 14, pages 1214–1223 (**2022**)

Potential for materials-based hydrogen storage

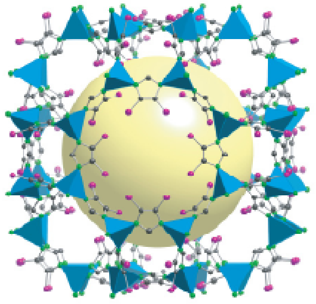
- Increased capacities to meet technical targets
- Materials-based options would allow for lower pressure storage, meaning the potential for all-metal Type I tanks
- Potential for 100 bar refueling = significant cost and energy savings for infrastructure



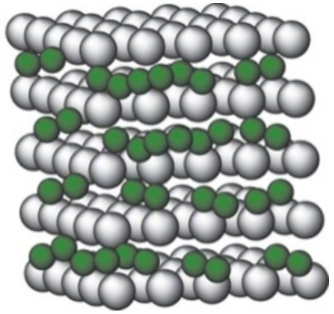
Current technology
p (H_2) = 700 bar, 25 g H_2/L



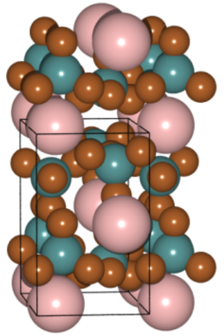
chemical storage
~70-150 g H_2/L
(NH_3BH_3)



sorbents
≤ 70 g H_2/L
(MOFs/activated C)



interstitial hydrides
~100-150 g H_2/L
($LaNi_5$)

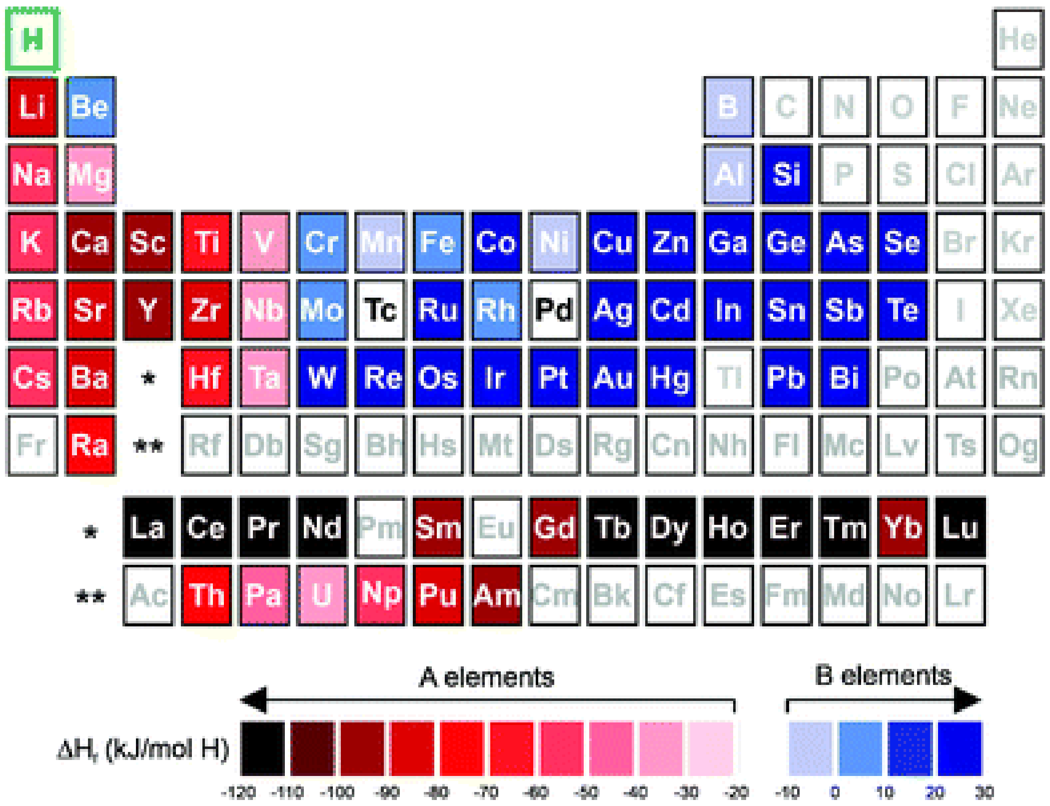


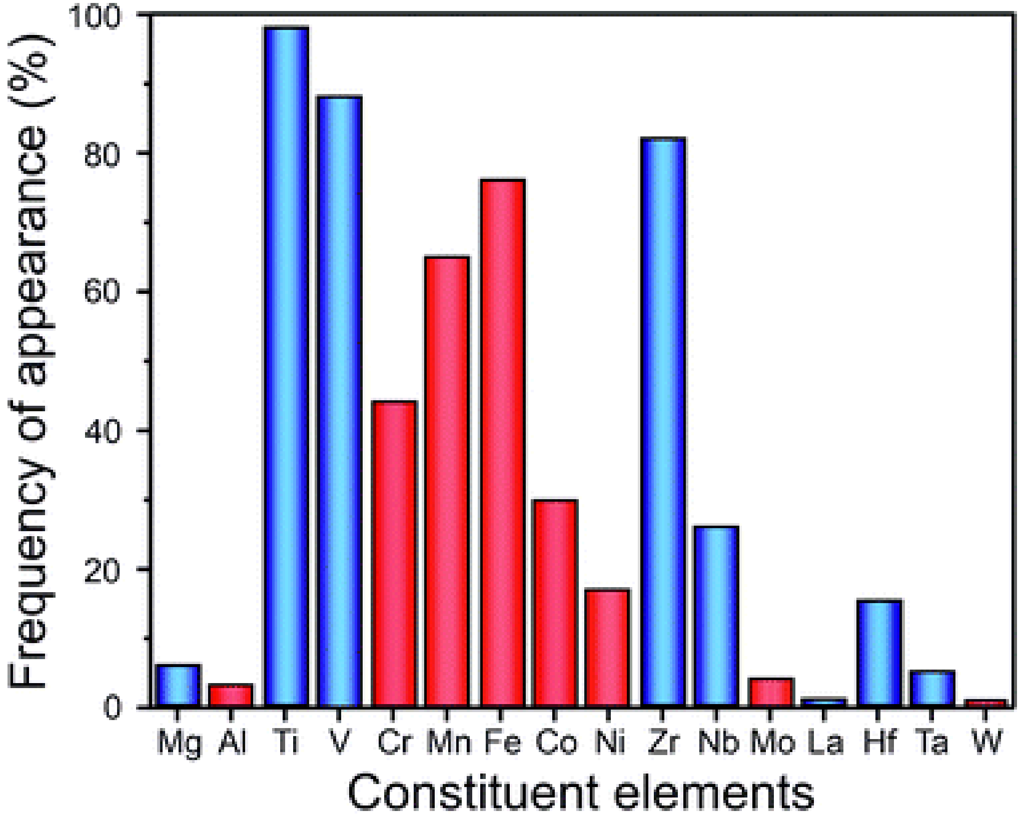
complex hydrides
~70-150 g H_2/L
(MgB_2 <-> $Mg(BH_4)_2$)

Key is finding the right material to reversibly absorb and desorb H_2

High-entropy hydrides

By mixing multiple elements in near equiatomic proportion, the configurational entropy is increased to the level sufficient to overcome the enthalpies of intermetallics formation





Energy Environ. Sci., **2021**, *14*, 5191-5227

High-entropy hydrides for H_2 storage[1-6]

Key concepts:

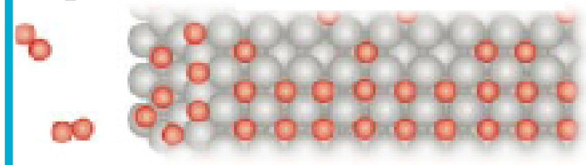
- Compositional ML models can predict critical hydride properties
- High-throughput screening and synthesis of destabilized high entropy alloy hydrides
- Can target multi-dimensional Pareto optimal materials for experiments

[1]Witman, Ling, Grant, Walker, Agarwal, Stavila, Allendorf. *J. Phys. Chem. Lett.*, 11 (1), **2020**
[2]Witman, Ek, Ling, Chames, Agarwal, Wong, Allendorf, Sahlberg, Stavila. *Chem. Mater.* 30 (11), **2021**
[3]Ek, Nygard, Pavan, Montero, Henry, Sorby, Witman, et al. *Inorg. Chem.*, 60 (2), **2021**
[4]Witman, Stavila. *Submitted Patent*, **2022**
[5]Pineda-Romero, Witman, Stavila, Zlotea, *Intermetallics,* **2022**
[6]Witman, Stavila, Allendorf, et al. *submitted*

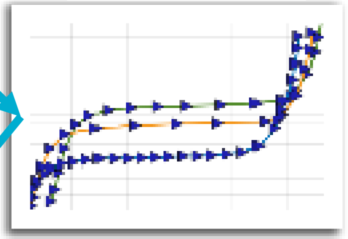
Explainable machine learning models

(1) $\ln(P^o_{eq}/P_o)$ target property

H$_2$ Metal Hydride



PCT curves



$$\ln\left(P^o_{eq}/P_o\right) = -\frac{\Delta H}{R(25^oC)} + \frac{\Delta S}{R}$$

- Data manually accumulated from experimental literature in HydPARK database (pre "ML days")
- Large effort to clean, remove errors, etc.
- ***Only*** 400 / 2500 examples usable for ML training

(2) Featurization for compositional ML model

Magpie features[1] -> (mean, stddev., etc) on elemental properties and their at.%

$TiFe_{0.92}Nb_{0.08} \rightarrow$

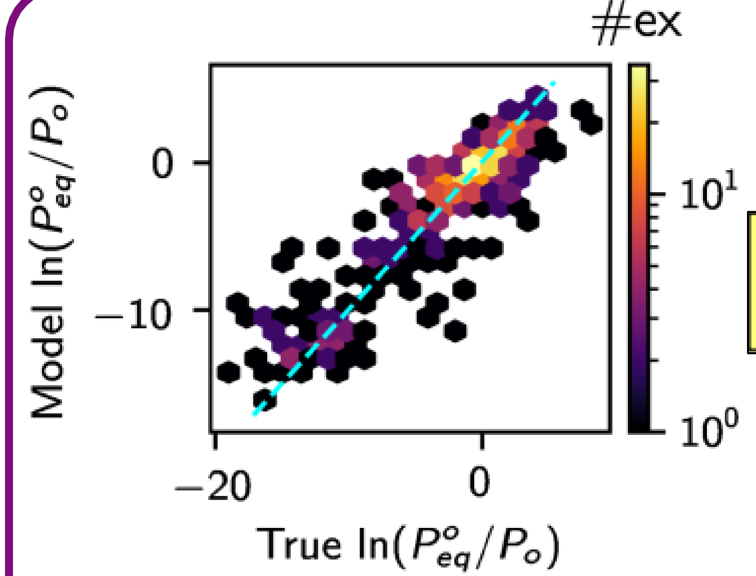
$$\boldsymbol{x} = \{\bar{v}_{pa}, \bar{r}_{cov}, \bar{\chi}, \dots\} \in \mathbb{R}^{145}$$

$\bar{v}_{pa} = \sum_i f_i v_i$

$v_i \equiv$ ground state vol. per atom

$f_i \equiv$ composition frac. of element i

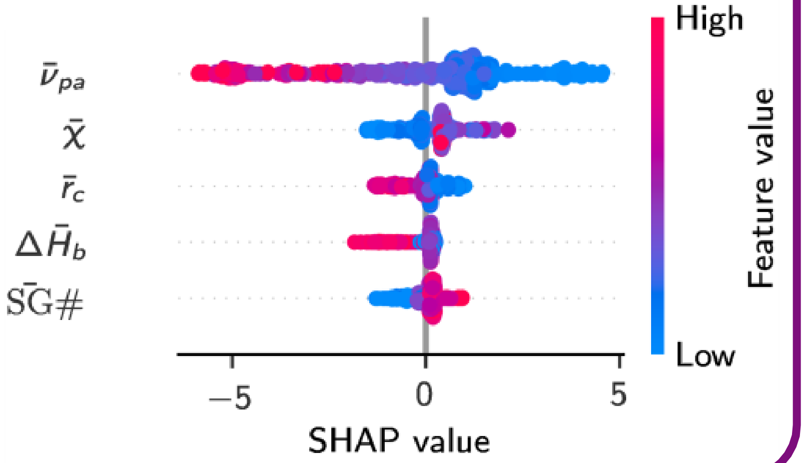
(3) Gradient boosting regression (GBR) model validation and explainability



GBR model predicts $\ln(P^o_{eq}/P_o)$ with K-fold expected MAE = 1.5

~ linear correlation with $\bar{v}_{pa}$:

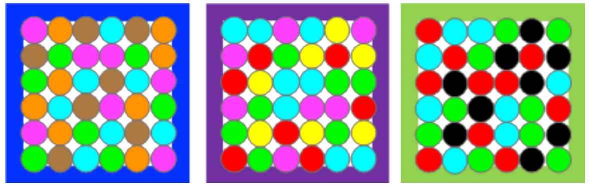
$$\ln\left(\frac{P^o_{eq}}{P_o}\right) \approx -m\,\bar{v}_{pa} + b$$



[1]Ward, et al. *Comp. Mat. Sci.* 2018, 152, 60-69

ML predicts destabilization of high entropy hydrides

(1) Expanded refractory HEA search space overview:

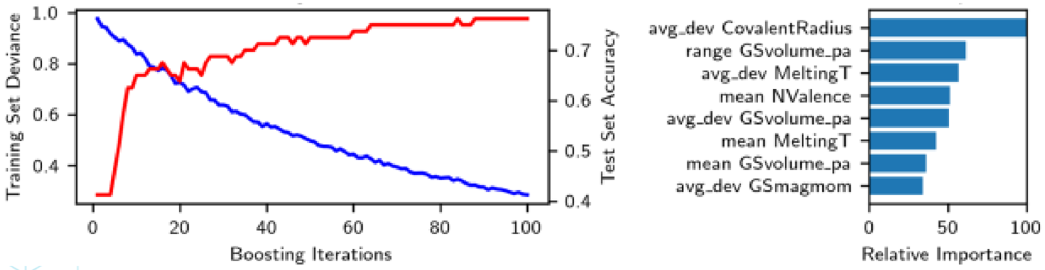


- >4 elements, approx. equimolar, defined lattice type
- Solid solution character -> compositional ML model
- Target HEA space, E = {Al,Ti,V,Cr,Zr,Nb,Mo,Pd,Hf,Ta}

$\binom{E}{4} + \binom{E}{5} + \binom{E}{6}$ = 672 compositions, model needed!

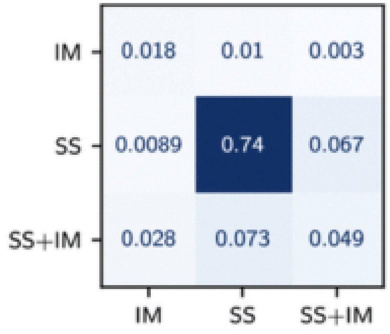
(2) Solid Solution gradient boosting classifier model

- {SS, IM, SS+IM} experimental data from Senkov
- ~75% class-weighted accuracy on {SS, IM, SS+IM}



- Filter candidates based on synthesizability metric

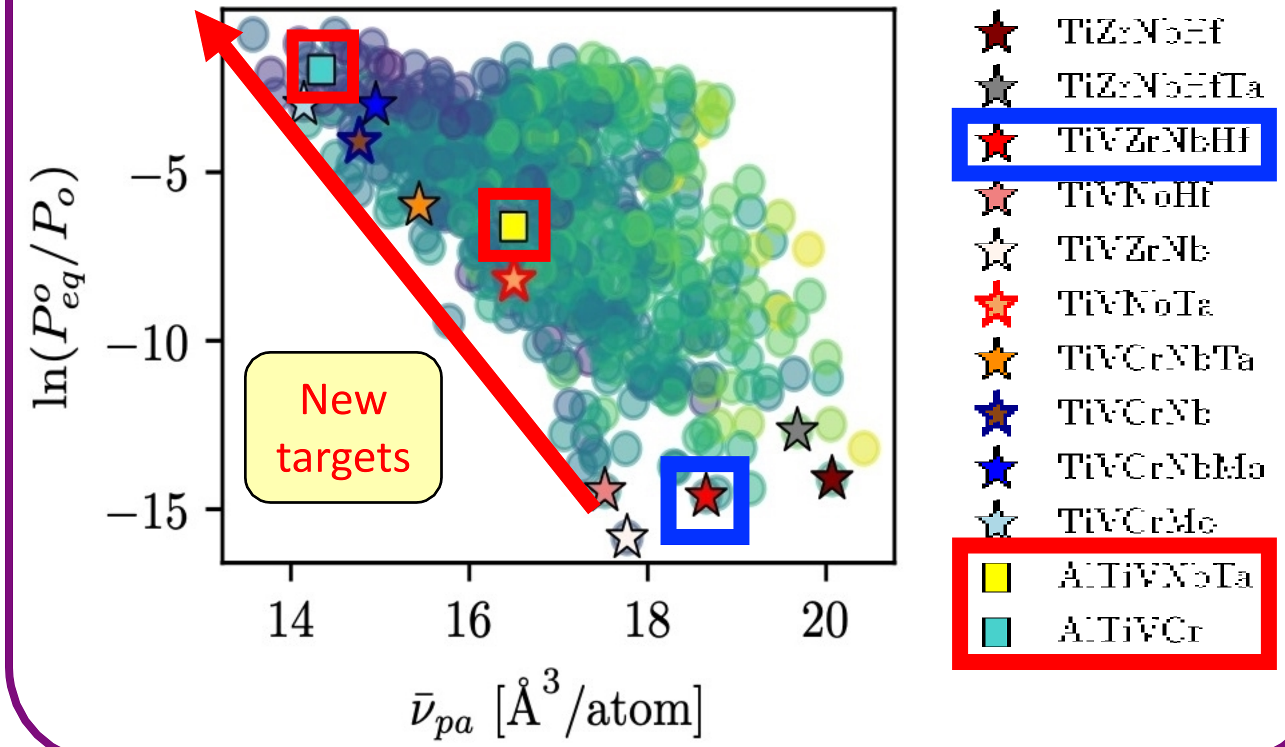
(3) Screening expanded refractory HEA space



- Choose from candidates with ~75% agreement between SS classifiers

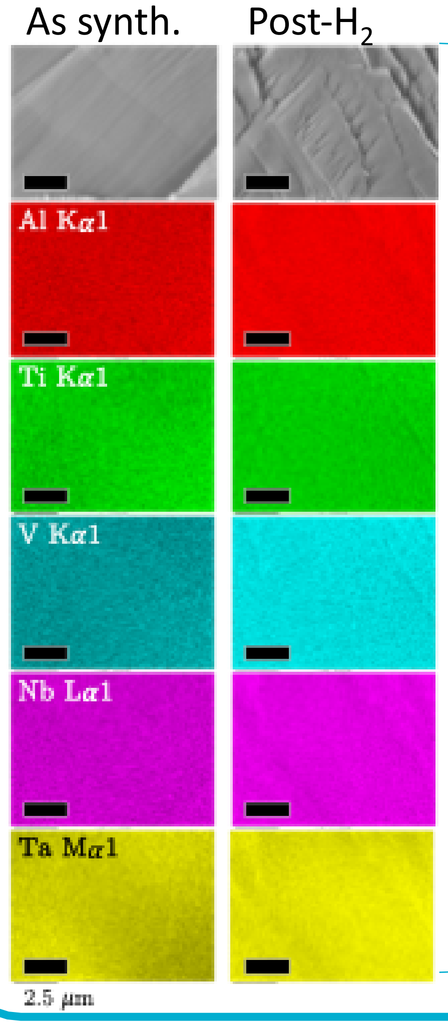
… and…

- Desired hydriding thermodynamics



Experimental validation of destabilized high-entropy hydrides

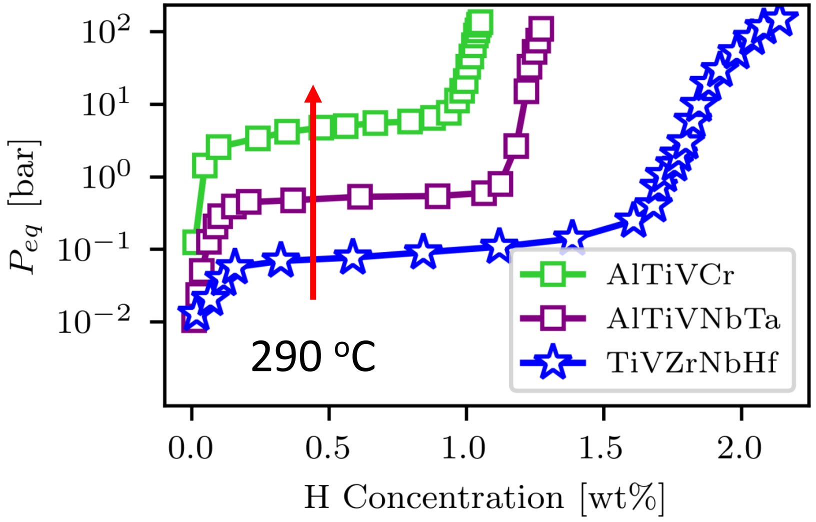
AlTiVNbTa & AlTiVCr synthesis

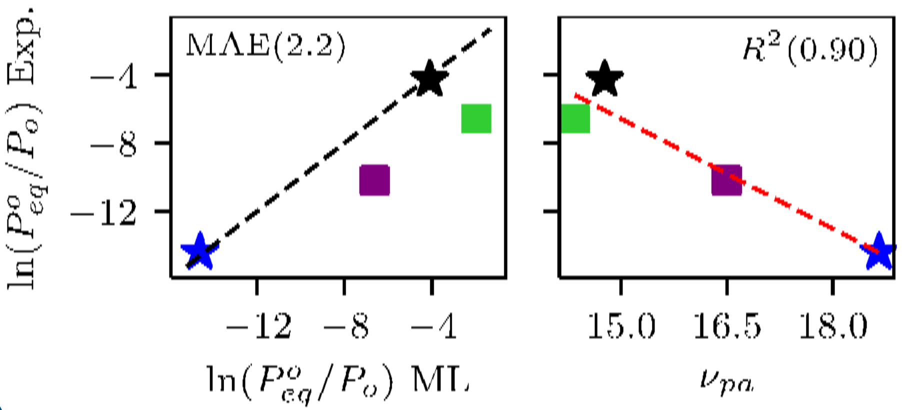


No elemental segregation

ML model & design rule confirmed by PCT experiments

Successfully targeted destabilized hydrides (increase in P_{eq})





Validated ML model & design rule

M. Witman, V. Stavila, M.D. Allendorf, *et al*. *Chemistry of Materials*, **2021**, *33*, 4067–4076

From an expanding training dataset and increased elemental search space, determine the Pareto optimal front of high-entropy hydrides

(1) Begin augmenting training data with most up-to-date HEA hydride literature

Composition	ΔH	ΔS	$\ln\left(P_{eq}^{o}/P_{o}\right)$	Hwt.%	H/M	T	Reference
NbTiVZrHf	61.8	88.0	-14.35	2.2	2.06	315.0	Ref. 4
VTiZrNb	67.6	90.3	-16.41	1.5	1.07	311.0	Ref. 5
$NbTiV_{0.5}ZrHf$	59.1	87.4	-13.33	1.8	1.76	326.0	Ref. 5
VTiAlCr	42.7	88.4	-6.59	1.1	0.49	311.0	Ref. 6
VTiAlTaNb	56.1	92.1	-11.55	1.25	1.0	301.0	Ref. 6
TiVCrNb	47.1	122.0	-4.33	3.0	1.87	100.0	Ref. 7
$Ti_{0.2833}V_{0.2833}Nb_{0.2833}Cr_{0.15}$	68.0	156.0	-8.67	3.2	2.04	160.0	Ref. 8
$Ti_{0.3176}V_{0.3176}Nb_{0.3176}Co_{0.047}$	64.0	143.0	-8.62	3.1	2.02	160.0	Ref. 8
$Ti_{0.321}V_{0.321}Nb_{0.321}Ni_{0.038}$	70.0	152.0	-9.96	3.1	2.02	160.0	Ref. 8
TiVNb	67.0	157.0	-8.14	3.1	2.03	220.0	Ref. 9
$Al_{0.1}Ti_{0.3}V_{0.3}Nb_{0.3}$	48.6	154.0	-1.08	2.6	1.59	62.5	Ref. 9

(2) Screen a more expansive HEA space

E = {Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Pd, Hf, Ta}

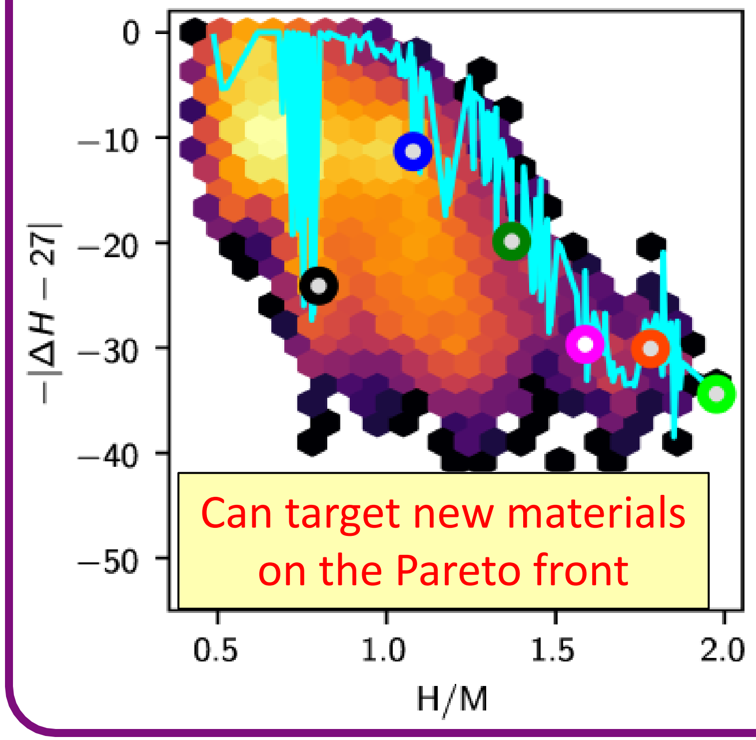
$$\binom{E}{4} + \binom{E}{5} + \binom{E}{6} \rightarrow 20,944 \text{ compositions}$$

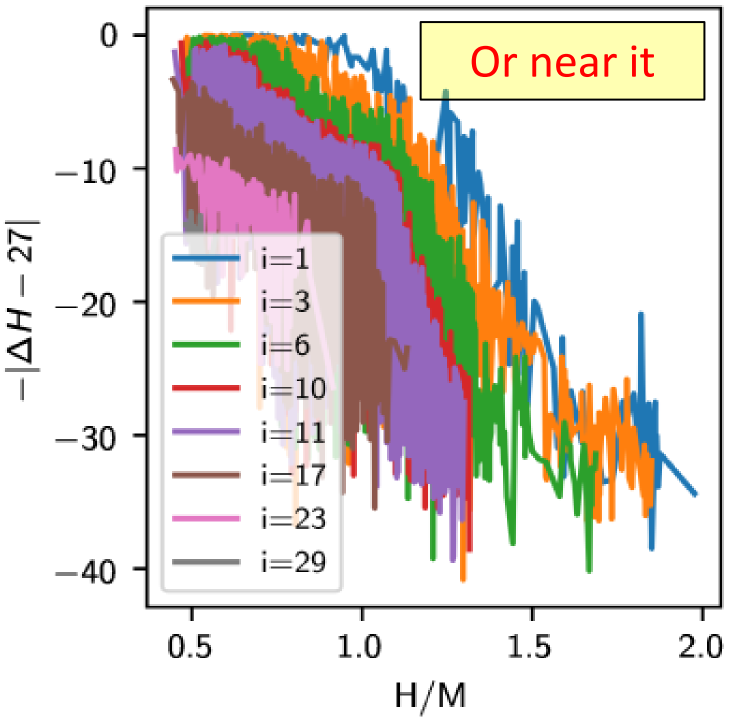
An interesting challenge: no Mg containing HEAs in training data

(2) Identification of ~100 Pareto optimal materials

Define objectives / quantities to maximize:

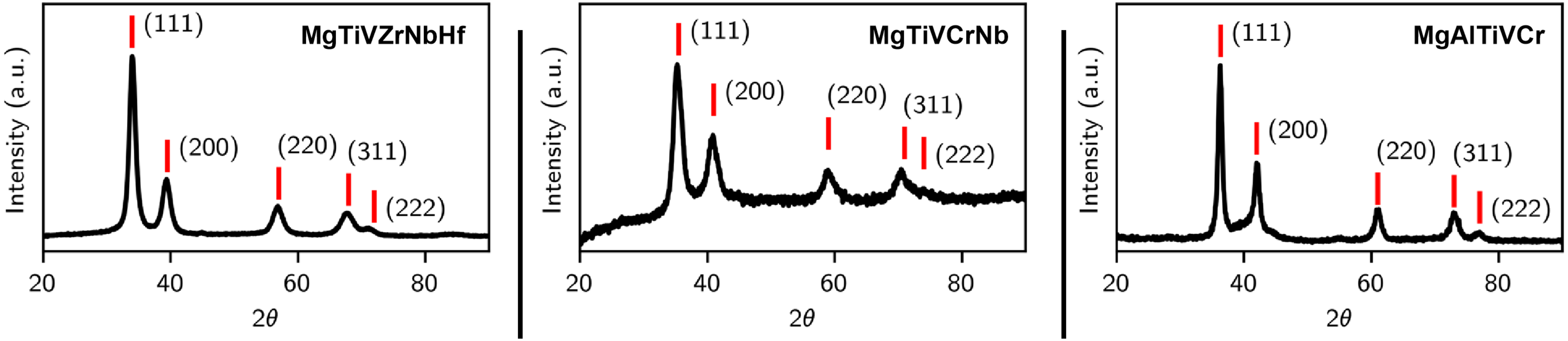
- Optimal thermodynamics -> $-|\Delta H - 27|$
- High volumetric capacity -> H/M
- High gravimetric capacity -> Hwt%
- - Raw material cost



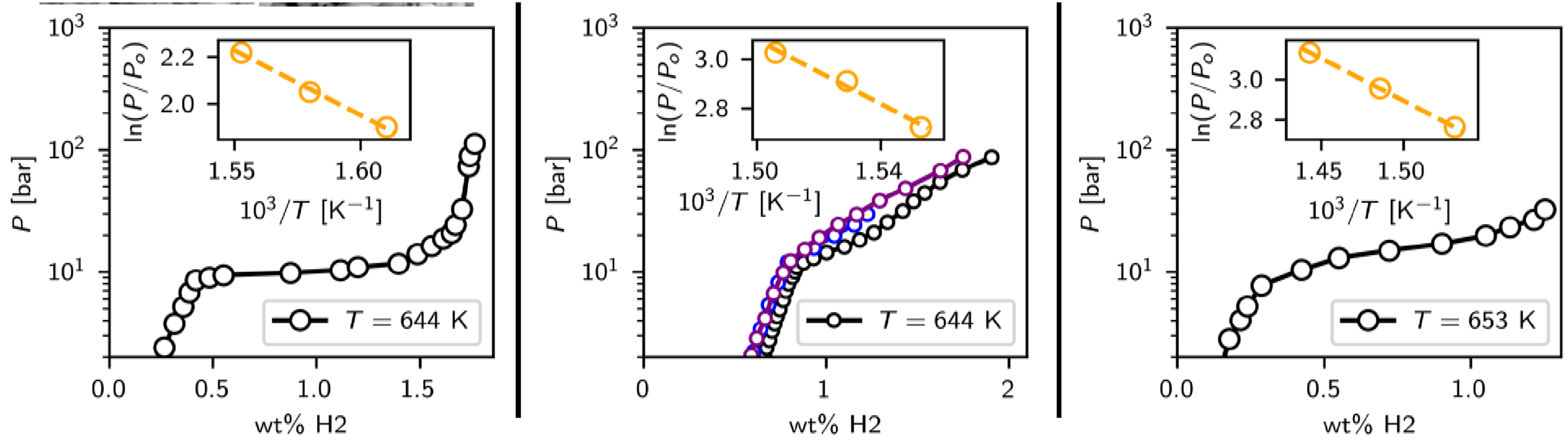


Magnesium-containing high-entropy hydrides

XRD patterns of fcc hydrides



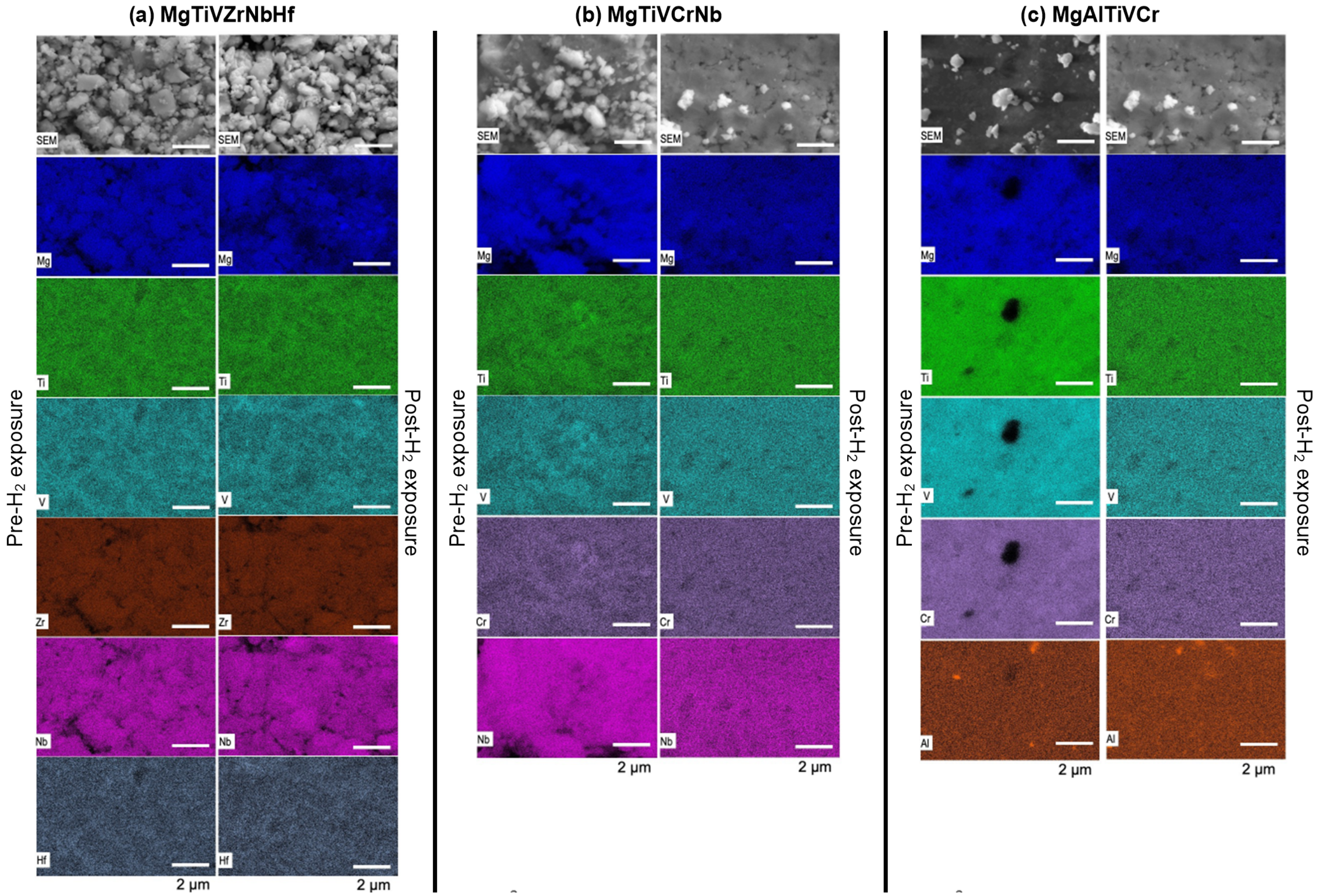
PCT isotherms for Mg-containing high-entropy hydrides



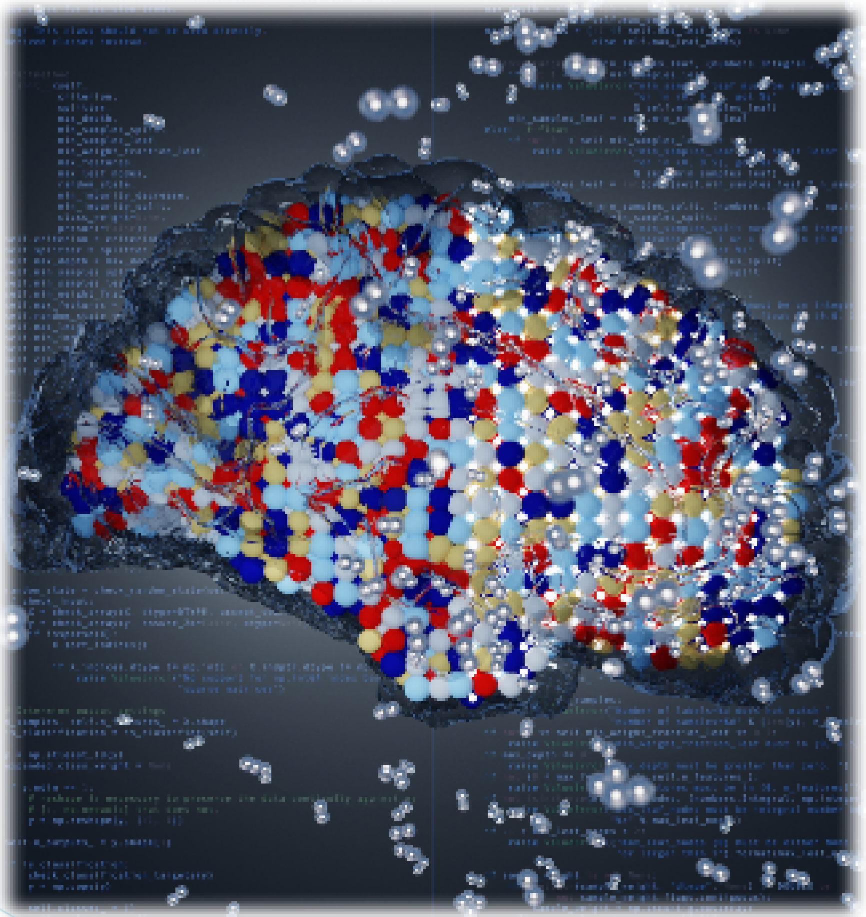
M. Witman, V. Stavila, M. Allendorf, *et al. submitted*

Magnesium-containing high-entropy hydrides

EDS maps show no elemental segregation after cycling under hydrogen



M. Witman, V. Stavila, M. Allendorf, *et al. submitted*



Conclusions:

- Introduced a powerful explainable ML capability for high-throughput screening of high-entropy hydrides
- ML-directed and experimentally validated synthesis of promising high-entropy hydride materials based on both refractory and lightweight metals (*e.g.* Mg, Al)
- Incorporation of magnesium increases the reversible capacity with no phase segregation observed upon cycling under hydrogen
- This approach enables co-design of materials and systems for various hydrogen use cases

Community tools

Zenodo database of hydrogen storage materials properties

zenodo

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November 15, 2022

Dataset Open Access

156 views

133 downloads

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Database for machine learning of hydrogen storage materials properties

Witman, Matthew; Allendorf, Mark; Stavila, Vitalie

Database for machine learning of hydrogen storage materials properties

Matthew Witman[a], Mark Allendorf[a], Vitalie Stavila[a]

[a]Sandia National Laboratories, Livermore, CA

Description

This ML-HydPARK dataset provides a csv file of metal hydride compositions, capacities, and thermodynamic values that can be used as target properties for building, training, and testing machine learning models. It has been parsed and cleaned from the DOE's original publicly available HydPARK database according to the procedure in [1] to make it more suitable for immediate use with data-driven models. Generally, this removed duplicate entries, removed entries missing critical data, and attempted to fix various entries with obvious errors in the data. It is continuously updated under version control as new metal alloy hydrides are published in the open literature. Most entries contain data on the enthalpy and entropy of the hydriding reaction, as well the maximum hydrogen capacity, for which compositional machine learning models can be trained [1,2].

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