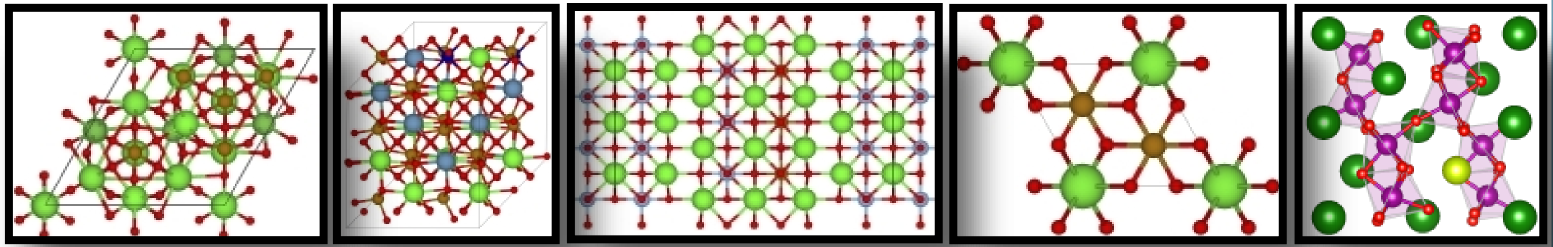
SAND2023-07704C

From data-driven modeling to systems level co-design: progress in materials discovery and optimization for hydrogen storage and generation



Matthew Witman, Anuj Goyal, Stephan Lany, Pinwen Guan, Anthony McDaniel, Kriston Brooks, Claudia Zlotea, Vitalie Stavila, Mark Allendorf, ***et al.***

Senior Member of the Technical Staff

Energy Nanomaterials Department

Sandia National Laboratories, Livermore, CA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Acknowledgments, collaborations, and funding

Sandia National Laboratories
- Mark Allendorf
- Vitalie Stavila
- Tony McDaniel
- Jamie Trindell
- Josh Sugar
- Andrea Ambrosini
- Laura Achola
- Jeffery Chames
- Robert Horton
- Lennie Klebanoff
- Sapan Agarwal
- Justin Wong
- Reese Jones
- Emily Allendorf
- Catalin Spataru
- Norm Bartelt
- Pinwen Guan

NREL – National Renewable Energy Laboratory
- Stephan Lany
- Anuj Goyal
- Nick Wunder
- Max Gallant
- Rachel Hurst
- Tom Gennet
- Noemi Leick

Lawrence Livermore National Laboratory
- Tadashi Ogitsu
- Brandon Wood
- Tae Wook Heo

Pacific Northwest National Laboratory
- Kriston Brooks
- Sam Sprik

UPEC – Université Paris-Est Créteil Val de Marne (Connaissance-Action)
- Claudia Zlotea
- Nayely Pineda-Romero
- Anis Bouzidi

Uppsala Universitet
- Martin Sahlberg
- Gustav Ek
- Rebecca Clulow

The University of Nottingham
- Sanliang Ling
- David Grant
- Gavin Walker
- Matthew Wadge

Brown
- Boyuan Xu
- Yue Qi

Experiments

Machine Learning

First principles/DFT

Data infrastructure

Sandia authors gratefully acknowledge research support from the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office through the Hydrogen Storage Materials Advanced Research Consortium (HyMARC) and HydroGEN. This work was supported by the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories.

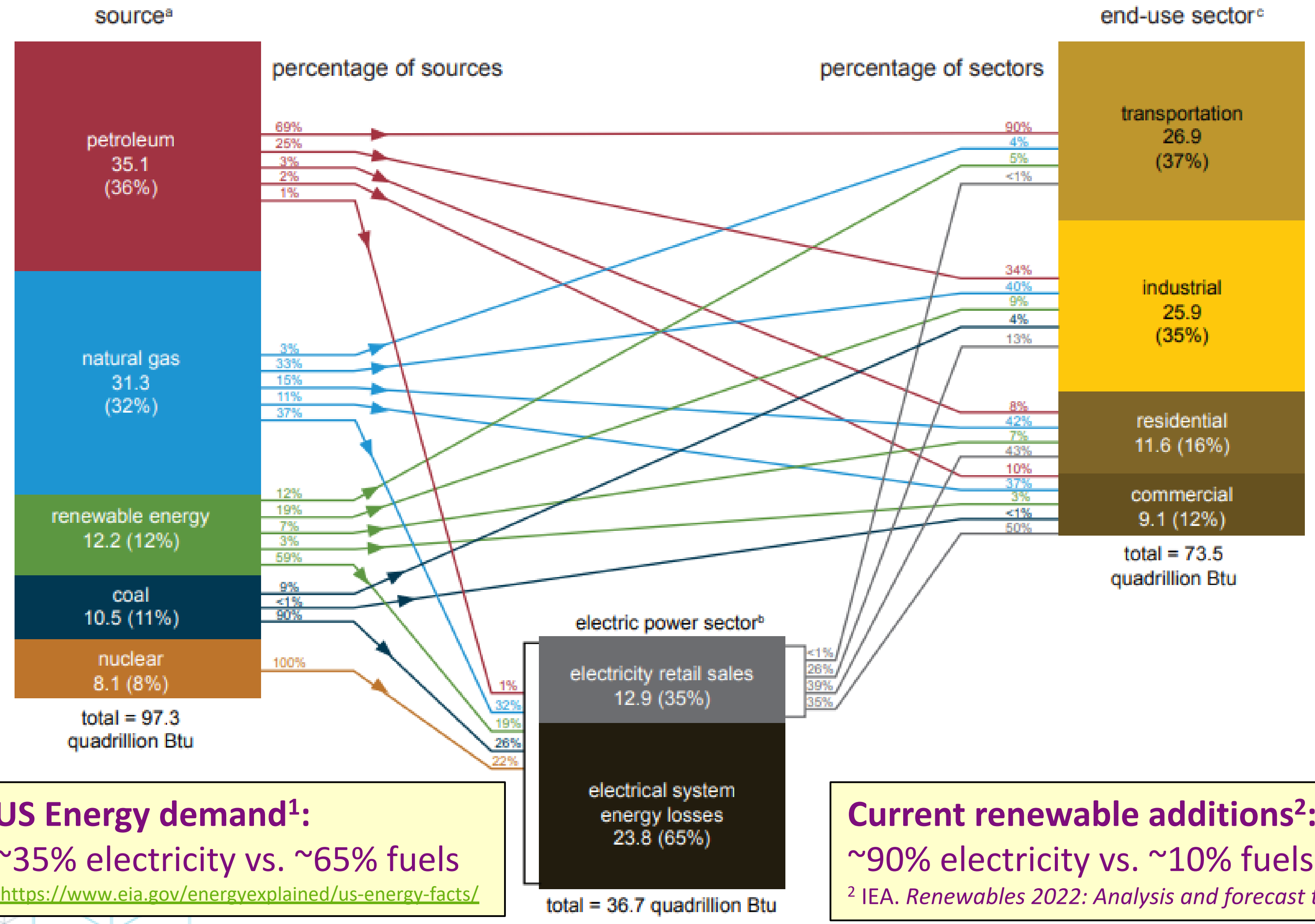
HyMARC – Hydrogen Materials Advanced Research Consortium

HydroGEN – Advanced Water Splitting Materials

LDRD – Laboratory Directed Research & Development

Better hydrogen energy materials to improve energy security and mitigate green house gas emissions *will be critical*

A massive mismatch between energy demand and new renewable capacity



US Energy demand[1]:
~35% electricity vs. ~65% fuels
[1]https://www.eia.gov/energyexplained/us-energy-facts/

Current renewable additions[2]:
~90% electricity vs. ~10% fuels
[2] IEA. *Renewables 2022: Analysis and forecast to 2027*

Reasonable to expect full electrification of …?

Heavy duty vehicles
(~40% of transportation demand)
(~15% of total demand):
Trucks?
Maritime?
Aviation?

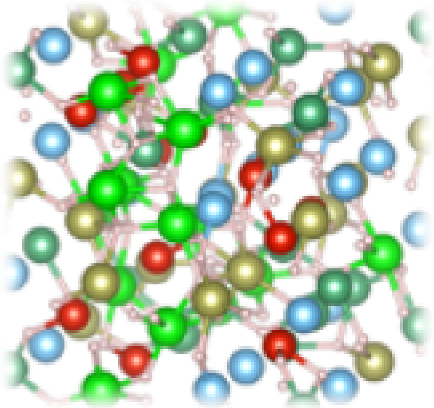
Heat-based industrial applications
(~35% of total demand):
Chemicals?
Steel production?
Cement?
Ammonia synthesis?

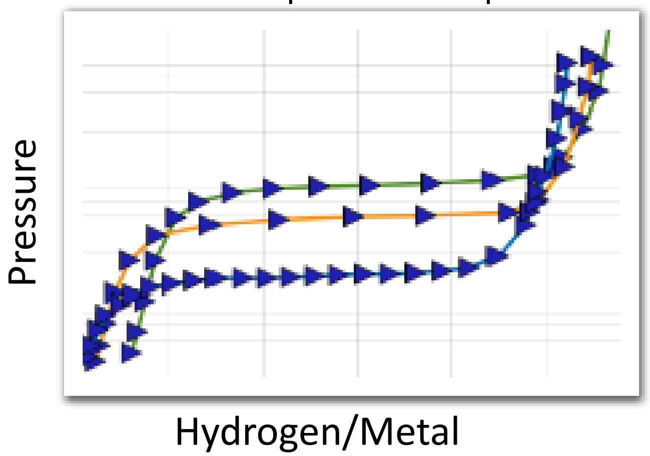
First Energy Earthshot Aims to Slash the Cost of Clean Hydrogen by 80% to $1 per Kilogram in One Decade

More H_2 energy material development needed: but trial-and-error development by **experiments** and/or **1st principles calculation** is too costly

Application #1: High entropy alloy hydrides for H_2 storage

$$\mathbf{M} + \frac{x}{2}\mathbf{H_2} \leftrightarrow \mathbf{MH_x}$$

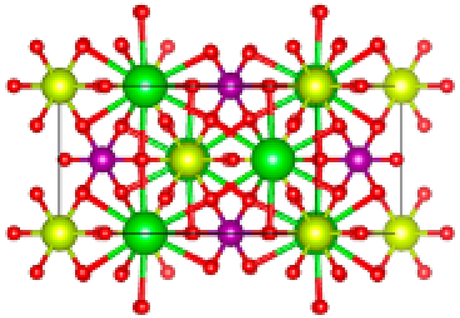


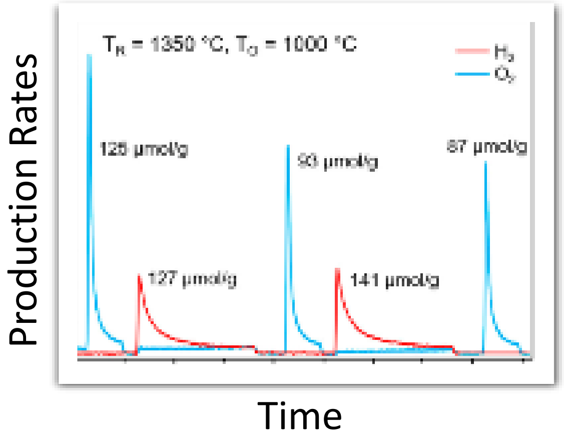


Experiments: Measure PCT curves (ΔH, ΔS, and capacity)
1st principles: Low-sample estimation of ΔH

Application #2: Metal oxides for solar thermochemical (STCH) H_2 generation

$$\mathbf{MO_x} \xrightarrow{\Delta} \mathbf{MO_{x-\delta}} + \frac{\delta}{2}\mathbf{O_2} \text{ (reduction T)}$$
$$\mathbf{MO_{x-\delta}} + \boldsymbol{\delta}\mathbf{H_2O} \rightarrow \mathbf{MO_x} + \boldsymbol{\delta}\mathbf{H_2} \text{ (oxidation T)}$$





Experiments: Measure H_2 / O_2 production rates
1st principles: Compute ΔH of oxygen vacancy formation

Months to synthesize and fully characterize and test a material
Months to predict *even just a proxy* for performance for a small # of materials

Outline: A survey of data-driven materials discovery and systems modeling tasks in hydrogen energy applications at Sandia

Part I:
Accelerated screening of oxides for high-temperature clean-energy applications
- ➢ graph neural networks / defect property predictions / first principles thermodynamics

Part II:
Towards Pareto optimal high entropy alloy hydrides
- ➢ statistical learning models / graph neural networks / metal-hydrogen phase diagrams / experiments

Part III:
The importance of systems level co-design in evaluating hydrogen storage materials
- ➢ Experiments + systems-level modeling

Outline: A survey of data-driven materials discovery and systems modeling tasks in hydrogen energy applications at Sandia

Part I:

Accelerated screening of oxides for high-temperature clean-energy applications

- graph neural networks / defect property predictions / first principles thermodynamics

Part II:

Towards Pareto optimal high entropy alloy hydrides

- statistical learning models / graph neural networks / metal-hydrogen phase diagrams / experiments

Part III:

The importance of systems level co-design in evaluating hydrogen storage materials

- Experiments + systems-level modeling

Outline: A survey of data-driven materials discovery and systems modeling tasks in hydrogen energy applications at Sandia

Part I:
Accelerated screening of oxides for high-temperature clean-energy applications
- ➢ graph neural networks / defect property predictions / first principles thermodynamics

Part II:
Towards Pareto optimal high entropy alloy hydrides
- ➢ statistical learning models / graph neural networks / metal-hydrogen phase diagrams / experiments

Part III:
The importance of systems level co-design in evaluating hydrogen storage materials
- ➢ Experiments + systems-level modeling

Outline: A survey of data-driven materials discovery and systems modeling tasks in hydrogen energy applications at Sandia

Part I:
Accelerated screening of oxides for high-temperature clean-energy applications
- ➢ graph neural networks / defect property predictions / first principles thermodynamics

Part II:
Towards Pareto optimal high entropy alloy hydrides
- ➢ statistical learning models / graph neural networks / metal-hydrogen phase diagrams / experiments

Part III:
The importance of systems level co-design in evaluating hydrogen storage materials
- ➢ Experiments + systems-level modeling

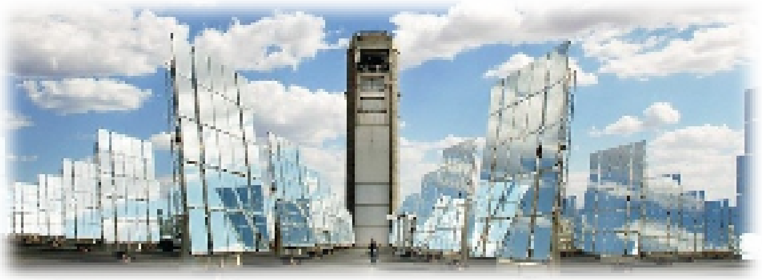
Part I:
Defect GNN accelerated screening of oxides for high-temperature clean-energy applications

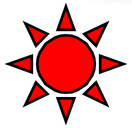
Key concepts:
- Graph neural networks to directly predict *relaxed vacancy properties* from the host structure
- High-throughput screening of vacancy formation enthalpies
- New oxides for water-splitting, fuel cells, CO_2 conversion, and thermochemical energy storage

Witman, Goyal, Ogitsu, McDaniel, Lany. *Nature Computational Science*, **2023**
Witman, et al. *In prep*

Solar thermochemical water splitting (STCH) is one of several prominent pathways to *green* (CO_2 emissions free) H_2

Direct 2 step redox cycle (*nb.* >300 proposed cycles…) [1]





Thermal reduction: T_r ~ 1300 C

O_2

$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2$$

Oxidation: T_o ~ 1000 C

$$MO_{x-\delta} + \delta H_2O \rightarrow MO_x + \delta H_2$$

H_2

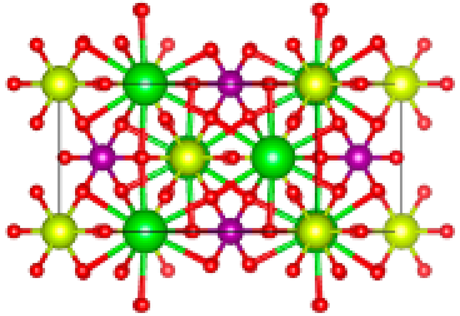
H_2O

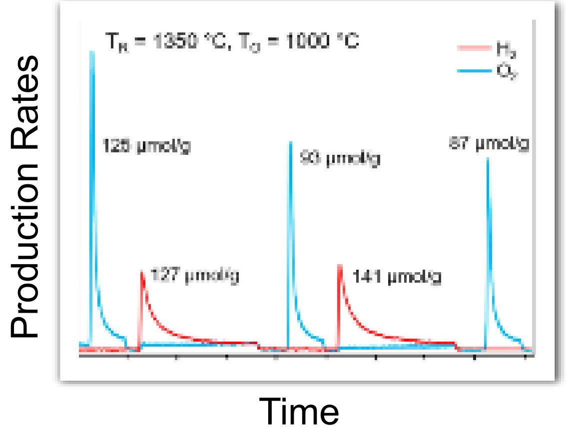
No MO_x yet that meets all requirements for T_r, stability, kinetics, etc.

[1] www.energy.gov/eere/fuelcells/hydrogen-production-thermochemical-water-splitting

Top candidates (BCM-12R) are well-studied & characterized

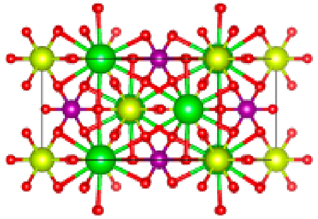
Experiments: Directly measure and evaluate H_2 and O_2 production rates





~Month to synthesize, characterize, test 1 material

1st principles (DFT): Compute oxygen vacancy formation enthalpy (e.g., ΔH_d^O) of all sites



Thermodynamic "sweet-spot":

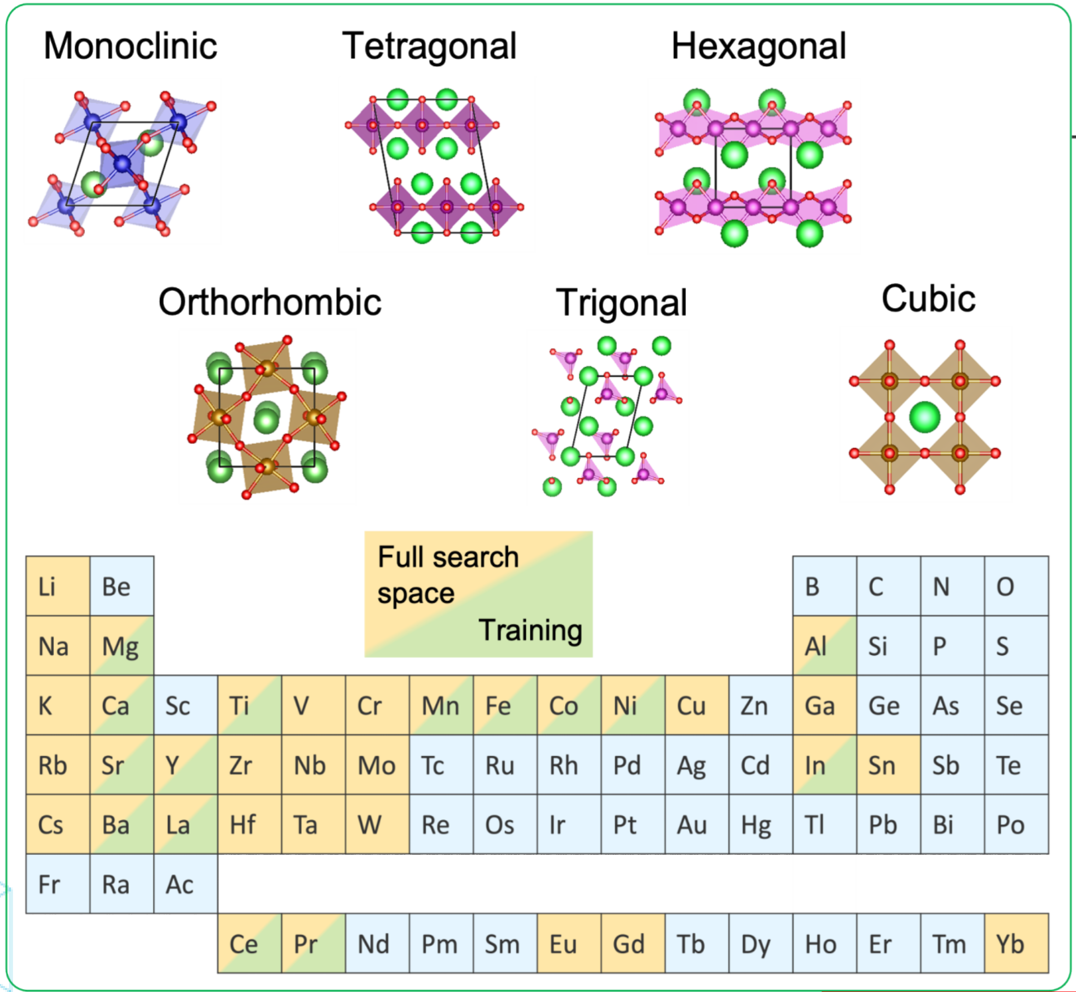
At least one $\Delta H_d^O \in [2.3, 4.0]$ eV

All $\Delta H_d^O > 2.3$ eV

~Month to compute this proxy for handful of materials

Fun aside: Bladerunner 2049 solar farms – failed to solve the STCH problem?

Search for materials with $\Delta H_d^O \in [2.3, 4.0]$ eV rapidly encounters computational barriers (A. Goyal)



DFT workflow

A. Material Space

Diversity in Training:
40 unique crystal structures and
38 unique compositions

B. Host Calculations

Relaxed structure,
Atomic spin and oxidation state,
Enthalpy of formation,
Bandgap, Electron effective mass

C. Defect Calculations

Calculated oxide space:
~200 binary + ternary host structures
~1500 defect relaxations

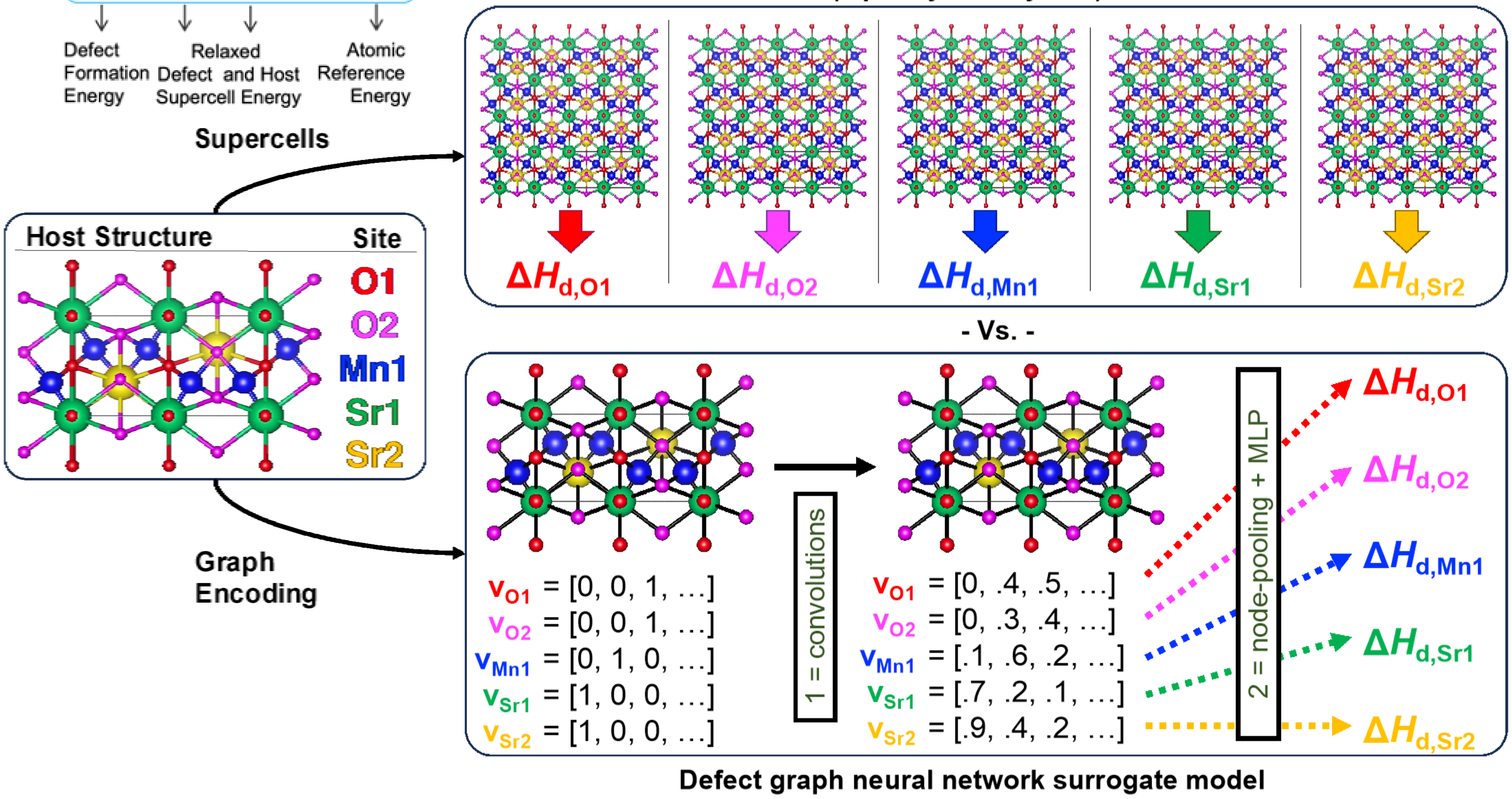
Existing oxide space:
~10,000s (up to senary) host structures
~1Ms defect relaxations

~1 years' work

100s years' work… so more efficient model needed

Defect GNN surrogate models for vacancy formation enthalpy supercell relaxations

$$\Delta H_d = E_d - E_H + \sum_i n_i \mu_i^{ref}$$

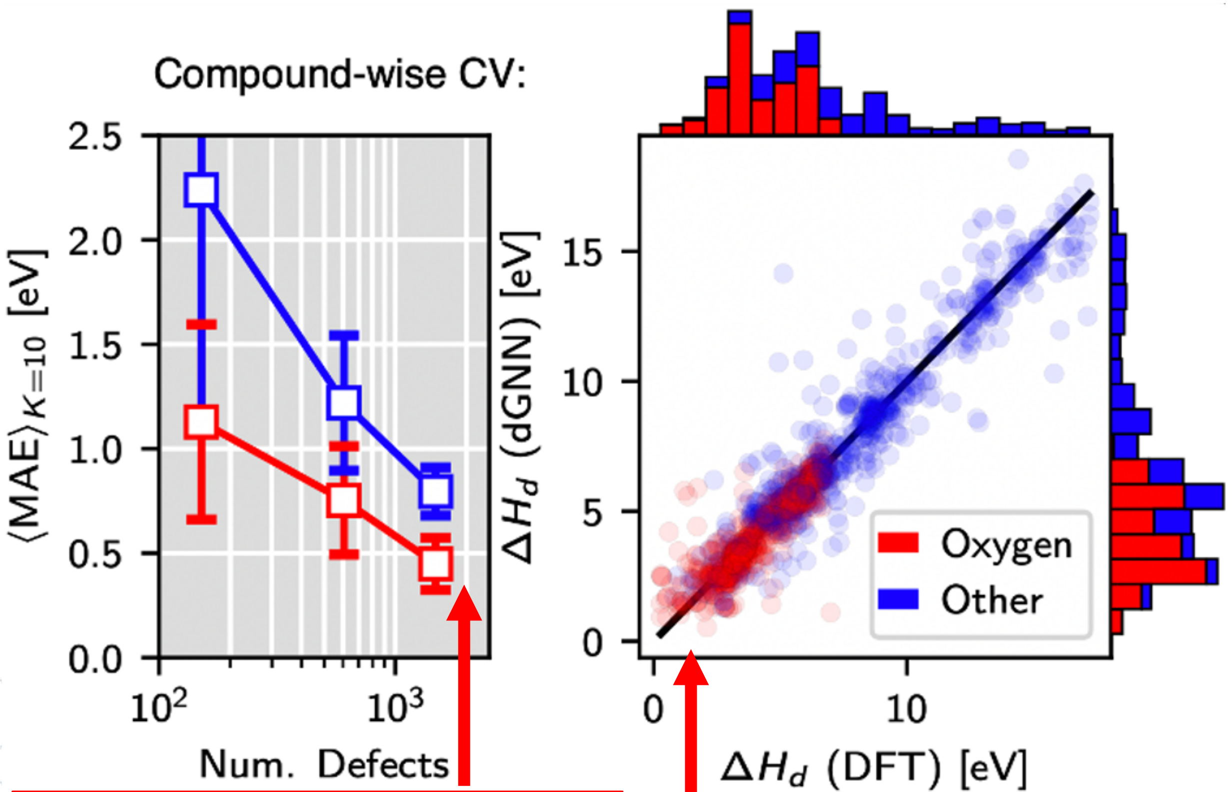


Pros:
- Generalizable (no manual feature engineering)
- Chemistry & structure agnostic
- Improvable w/more data
- Many orders of magnitude faster than DFT

Cons:
- Highly data reliant
- Not really interpretable

Defect GNN approach validated for use in high-throughput screening exercise

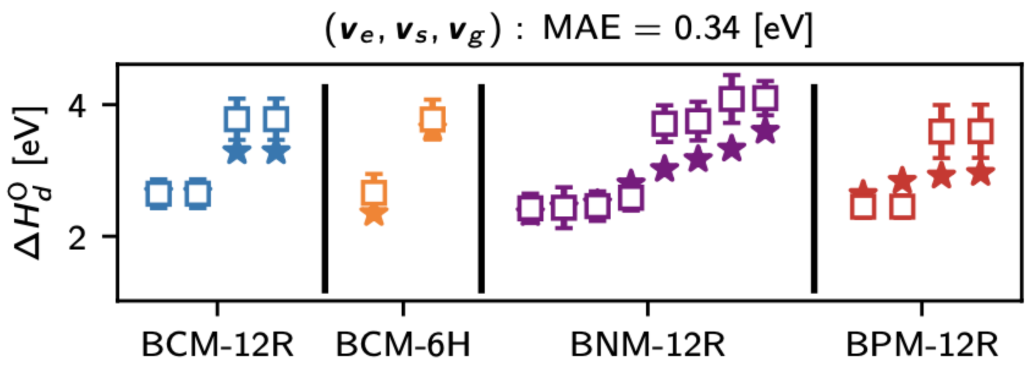
Benchmark accuracy was met for HT screening



- ➢ MAE < 500 meV
- ➢ Still have log-linear decrease w/more data
- ➢ Minutes to train on CPUs

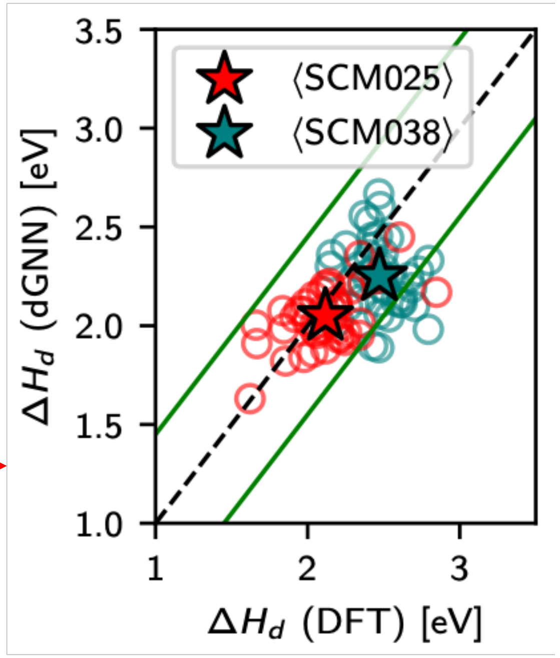
- ➢ Can predict O *and* non-O vacancies

Additional tests on more complicated materials than the training set (quaternaries & solid solutions)



$Ba_4XMn_3O_{12}$
[X = Ce, Nb, Pr]

$Sr_{1-x}Ce_xMnO_3$
x = {0.25, 0.38}



High-throughput screening 2,000 oxides (50,000 unique defects) rediscovers known water-splitting oxides and identifies new ones (~10 top candidates)

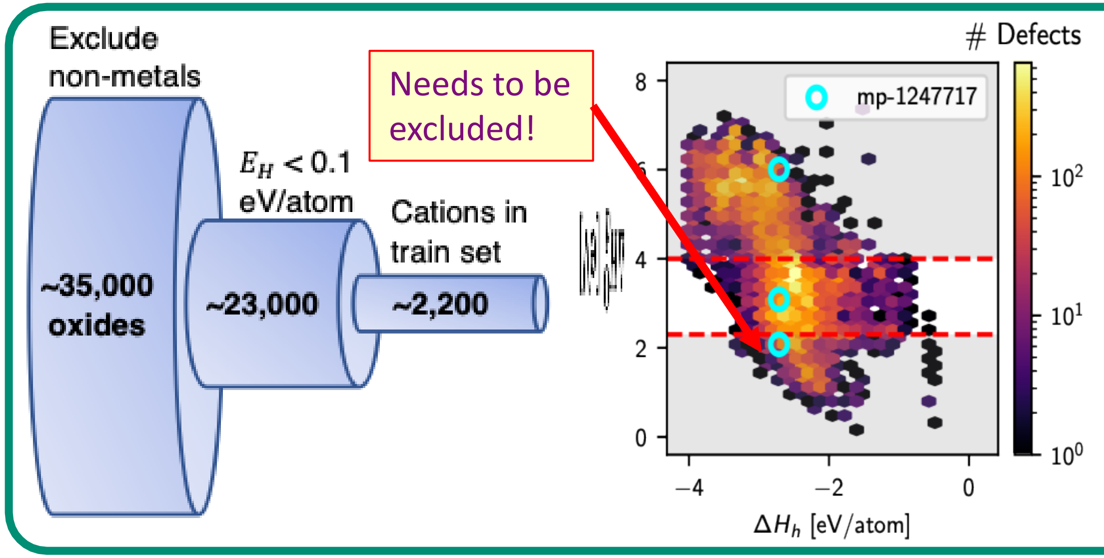
(1) Co-design of host defects and stability for water-splitting

Metric	Requirement
Frac. of defects w/$\Delta H_d^O > 2.3$ eV	$x_{\text{min}} = 1$
Frac. of defects w/$\Delta H_d^O \in [2.3, 4.0]$ eV	$x_{\text{rng}} > 0$
Host stability criteria (ranges intersect)	$\Delta\mu'_{O_2} \cap \Delta\mu_{O_2}^{\phi_H<X} \neq \emptyset$

Operating range for STCH

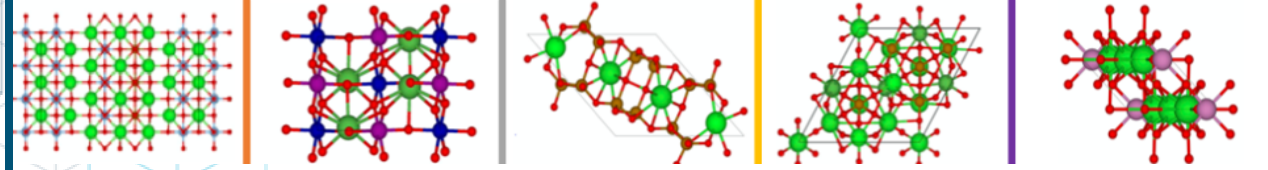
Range where host's grand energy above hull (ϕ_H) is < X

(2) Screen the Materials Project for all defects



(3) Identify and filter increasingly promising targets

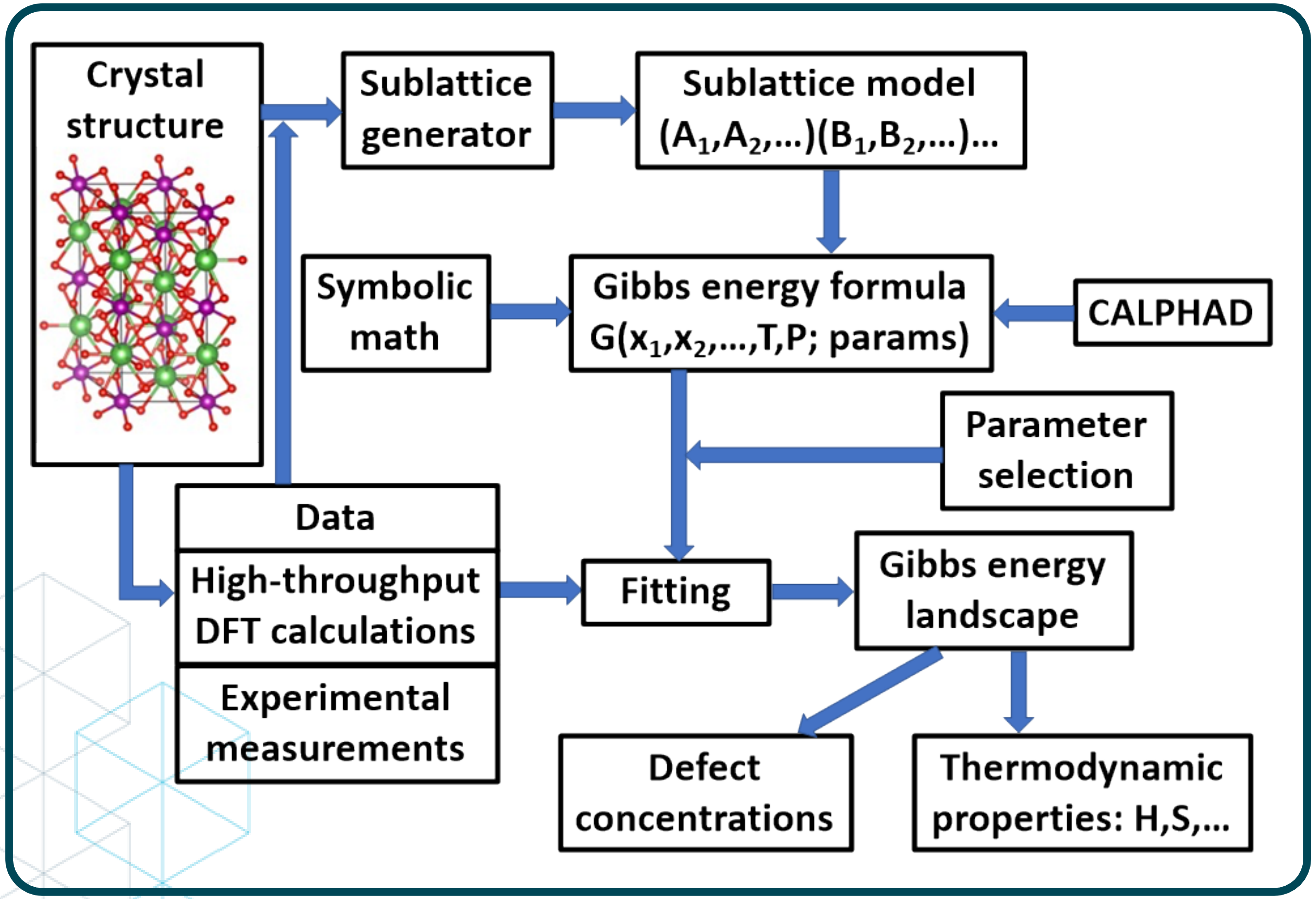
197 formulas (48 training)	114 formulas (33 training)	34 formulas (17 training)	16 formulas (11 training)	9 formulas (9 training)
➢ $x_{\text{min},1} = 1$ ➢ $x_{\text{rng},1} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$	➢ $x_{\text{min},2} = 1$ ➢ $x_{\text{rng},2} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$	➢ $x_{\text{min},3} = 1$ ➢ $x_{\text{rng},3} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H<0.05}$	➢ $x_{\text{min},3} = 1$ ➢ $x_{\text{rng},3} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H=0}$	➢ $x_{\text{min},3} = 1$ ➢ $x_{\text{rng},3} = 1$ ➢ $\Delta\mu_{O_2}^{\phi_H=0}$
$Sr_6Ti_3FeO_{14}$ (mp-1645141)	La_2MnCoO_6 (mp-19208)	$BaSr(FeO_2)_4$ (mp-1228024)	$Ba_5SrLa_2Fe_4O_{15}$ (mp-698793)	$Ba_3In_2O_6$ (mp-20352)



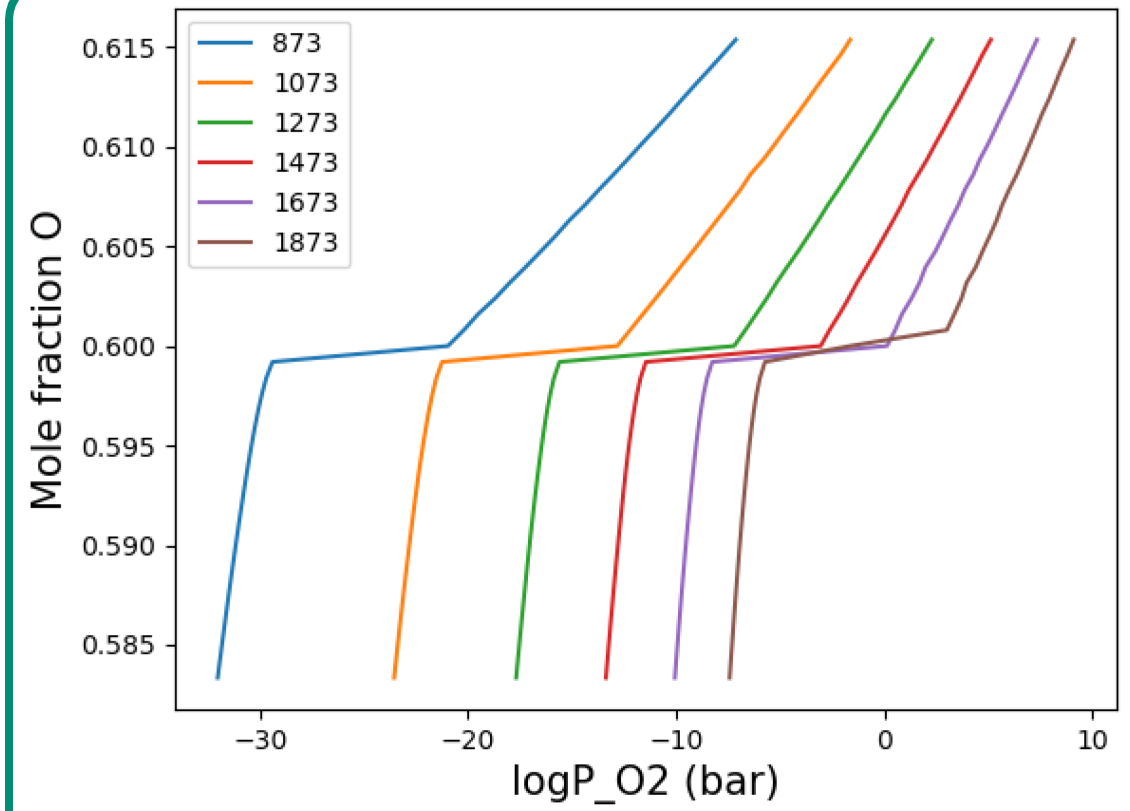
- ➢ Filter candidates with increasingly certain performance
- ➢ Mainly identifies known, synthesizable compounds
- ➢ ~100 are not AXO_3 , $A_{n+1}X_nO_{3n+1}$, $Fe_{3-n}M_nO_4$, CeO_2 , etc.
- ➢ Rediscovers complex, known water-splitting materials (not in training data) like BCM, SCM, and ***new ones***!

If more complex defects (interacting vacancies and substitutions) can be predicted in high-throughput, full phase diagram predictions can be computed in high-throughput

General, automatic workflow development for modeling defect thermodynamics of ionic compounds (P. Guan)



Final result for STCH material $La_{0.8}Sr_{0.2}MnO_3$



- Predicts O off-stoichiometry as a f(T, pO2)
- Currently, only as fast as DFT

Outline: A survey of data-driven materials discovery and systems modeling tasks in hydrogen energy applications at Sandia

Part I:
Accelerated screening of oxides for high-temperature clean-energy applications
- graph neural networks / defect property predictions / first principles thermodynamics

Part II:
Towards Pareto optimal high entropy alloy hydrides
- statistical learning models / graph neural networks / metal-hydrogen phase diagrams / experiments

Part III:
The importance of systems level co-design in evaluating hydrogen storage materials
- Experiments + systems-level modeling

Part II:
Towards Pareto optimal high entropy alloys for H_2 storage[1-7]

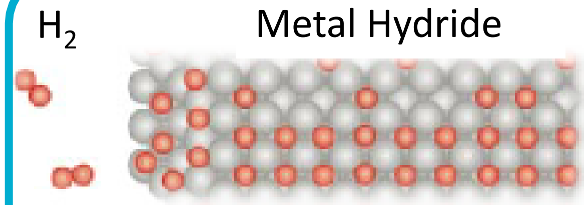
Key concepts:

- Compositional ML models can predict critical hydride properties
- High-throughput screening and synthesis of destabilized high entropy alloy hydrides
- Targeting multi-dimensional Pareto optimal materials for experiments
- First principles PCT modeling

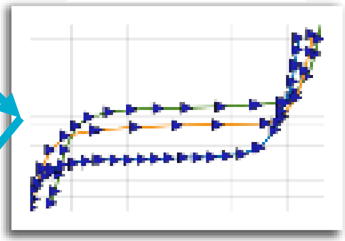
[1]Witman, Ling, Grant, Walker, Agarwal, Stavila, Allendorf. *J. Phys. Chem. Lett.*, 11 (1), **2020**
[2]Witman, Ek, Ling, Chames, Agarwal, Wong, Allendorf, Sahlberg, Stavila. *Chem. Mater.* 30 (11), **2021**
[3]Ek, Nygard, Pavan, Montero, Henry, Sorby, Witman, et al. *Inorg. Chem.*, 60 (2), **2021**
[4]Witman, Stavila. *Submitted Patent*, **2022**
[5]Pineda-Romero, Witman, Stavila, Zlotea, *Intermetallics*, **2022**
[6]Witman, et al. *J. Mater. Chem A*, 11, **2023**
[7]Pineda-Romero, Witman, et al. *In prep.*, **2023**

Explainable machine learning models predict metal hydride thermodynamics

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



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")
- ***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.%

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

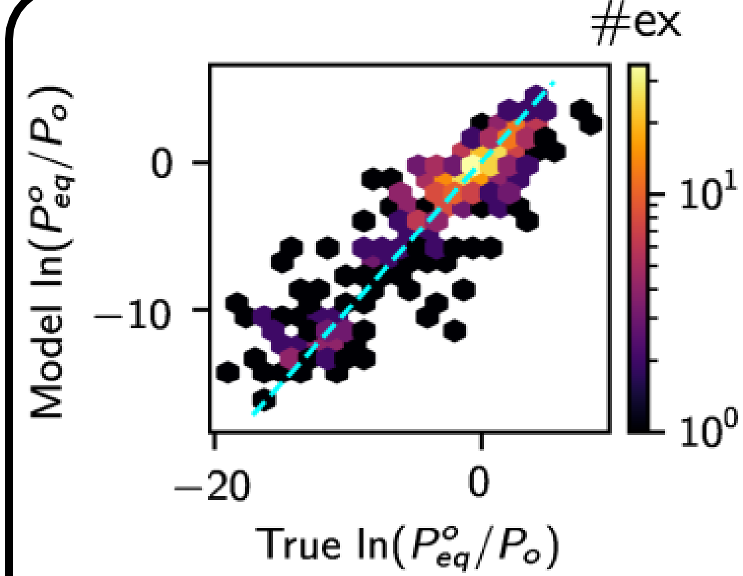
$$\boldsymbol{x} = \{\bar{v}_{pa}, \bar{r}_{cov}, \bar{\chi}, \ldots\} \in \mathbb{R}^{145}$$

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

$v_i \equiv$ ground state vol. per atom

$f_i \equiv$ composition frac. of element i

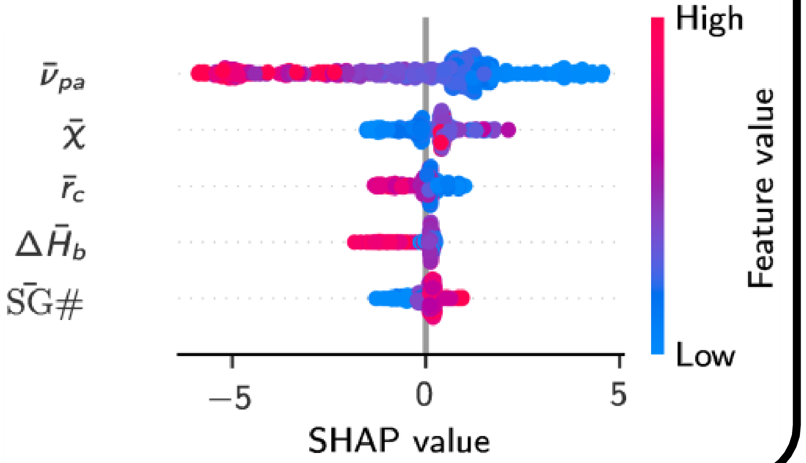
(3) Gradient boosting regression (GBR) model validation and explainability



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

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

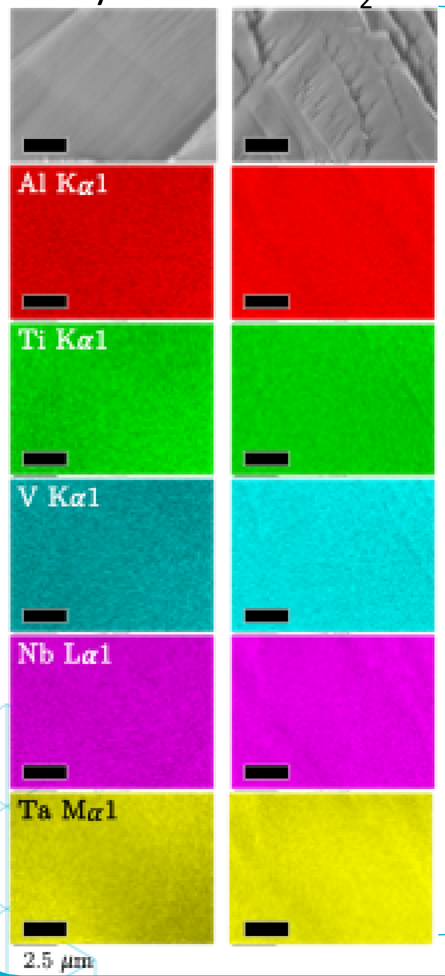
$$\ln\left(\frac{P^o_{eq}}{P_o}\right) \approx -m\,\bar{v}_{pa} + b$$



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

Arc melting synthesis + XRD + EDS confirms phase purity and PCT curves validate destabilization of HEA hydrides

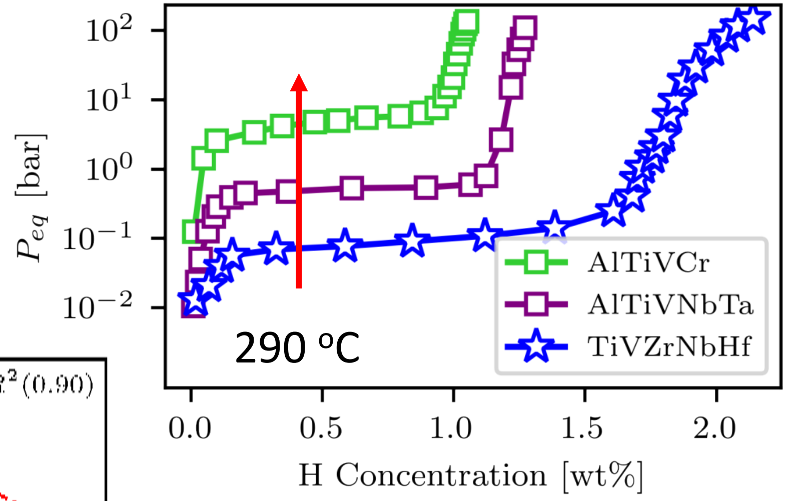
AlTiVNbTa & AlTiVCr synthesis

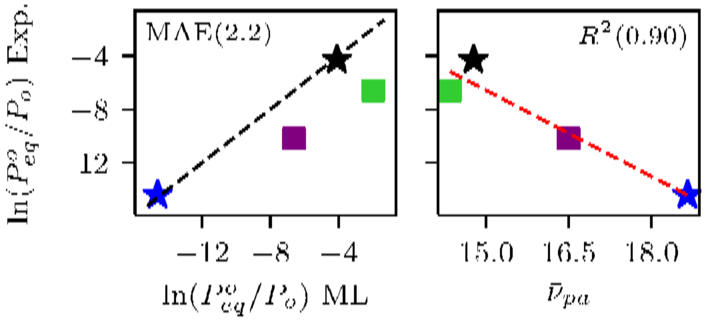


No elemental segregation

ML model & design rule confirmed by PCT experiments

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



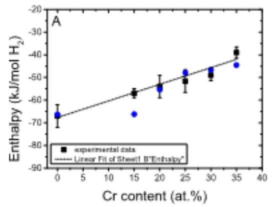


Validated ML model & design rule

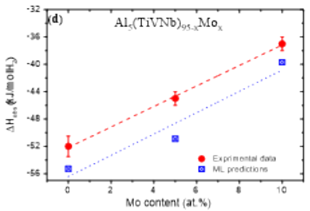
ML-predicted destabilization validated in a variety of studies

Composition	ΔH_{abs} (kJ/mol H_2)
$Ti_{0.33}V_{0.33}Nb_{0.33}$	−67 (5) (exp.)
	−58 (ML)
$Al_{0.10}Ti_{0.30}V_{0.30}Nb_{0.30}$	−48.6 (1.0) (exp.)
	−51 (ML)

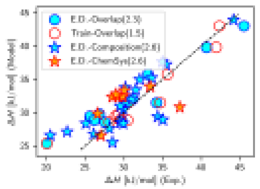
$(TiVNb)_{100-x}Al_x$



$(TiVNb)_{100-x}Cr_x$



$Al_5(TiVNb)_{95-x}Mo_x$



TiFe-X

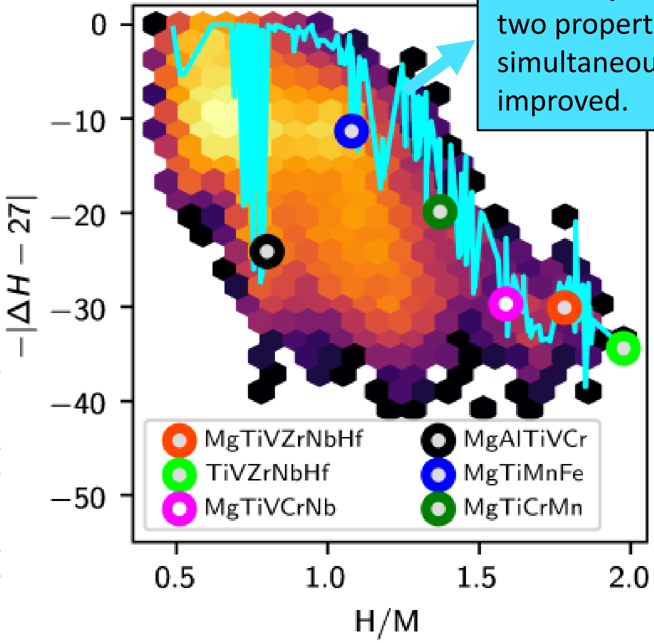
Synthesis + XRD + EDS confirms phase pure synthesis and PCT measurements of Mg-HEA Pareto optimal candidates[1]

Use improved ML models to identify Pareto optimal HEAs

Define objectives / quantities to maximize:

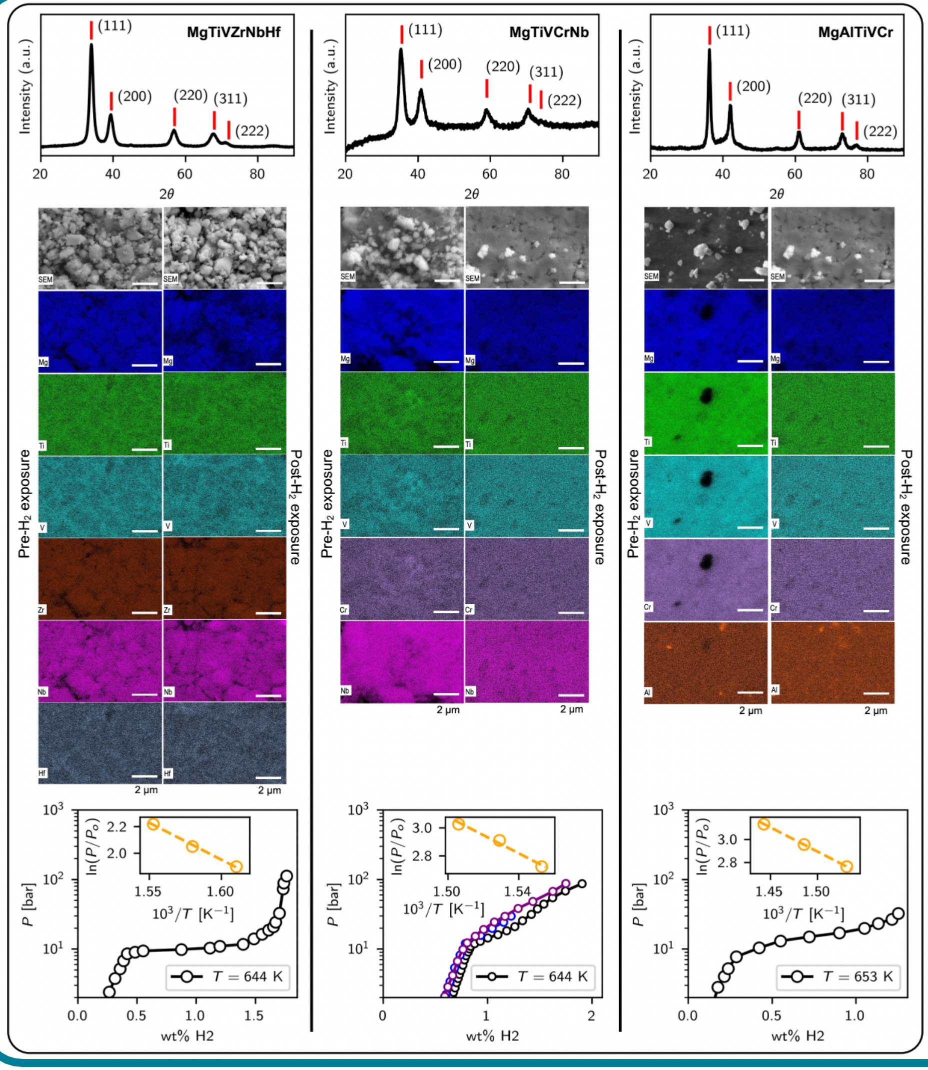
- Optimal thermodynamics -> $-|\Delta H - 27|$
- High volumetric capacity -> H/M
- High gravimetric capacity -> Hwt%
- \- Raw material cost

Pareto optimal = no two properties can be simultaneously improved.



Pareto optimal front reduces screening compositions (~20,000) by 2-3 orders of magnitude to reveal top candidates (~100)

Successful synthesis, characterization, and PCT testing of selected Mg-HEA candidates



- Promising high-capacity candidates
- Relatively large uncertainty in some experimental thermodynamics due to sloped plateau
- Correct ΔH and H/M trend between Mg-HEAs
- Correct ΔH and H/M trend between Mg-HEA and their non-Mg counterparts

[1] Witman, et al. *J. Mater. Chem A,* 11, **2023**.

Automated, first-principles modeling of metal-hydrogen equilibria in high-throughput is needed for a “step change” improvement of metal hydride discovery

- Compositional ML models in the previous approach are hampered by limited experimental data
- Reasonable accuracy is unlikely on *significantly* out-of-training distribution materials
- Lacks key properties contained in a phase diagram (estimated reversible capacity, multiple phase transitions, etc.)

Previous section:

Suggest a new composition → Limited, unbalanced experimental dataset → Compositional ML model

- ~70% accurate phase classifier of {“SS”, “SS+IM” or “IM”}
- $\Delta H, \Delta S$, H/M, or ΔG (dependent on exp training data)

New/ultimate goal:

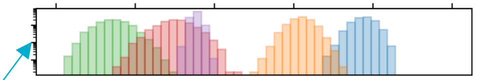
Suggest a new composition

- O(100s) DFT calcs of random alloy cfgs (FCC, BCC, HCP, etc)
- O(100s) DFT calcs of random hydride cfgs

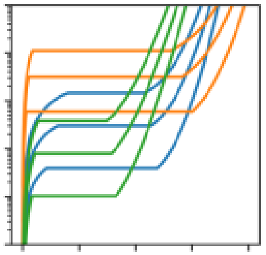
Train GNN model to predict energy from idealized lattice structure

High-throughput sampling and first-principles thermodynamics calcs/sims

Alloy stability predictions



H_2 phase diagrams (PCT)



Calculation of PCT curves (metal-hydrogen phase diagram from first principles calculations)

Mean field theory and Boltzmann weighted PCT calculation

Thermodynamic formalism/assumptions:

$S(x) = k[(1-x)\ln(1-x) + x\ln(x)]$

$G(x) = E(x) - TS(x)$

Energy calculation:

MFT: $E(x) = \bar{E}(x)$

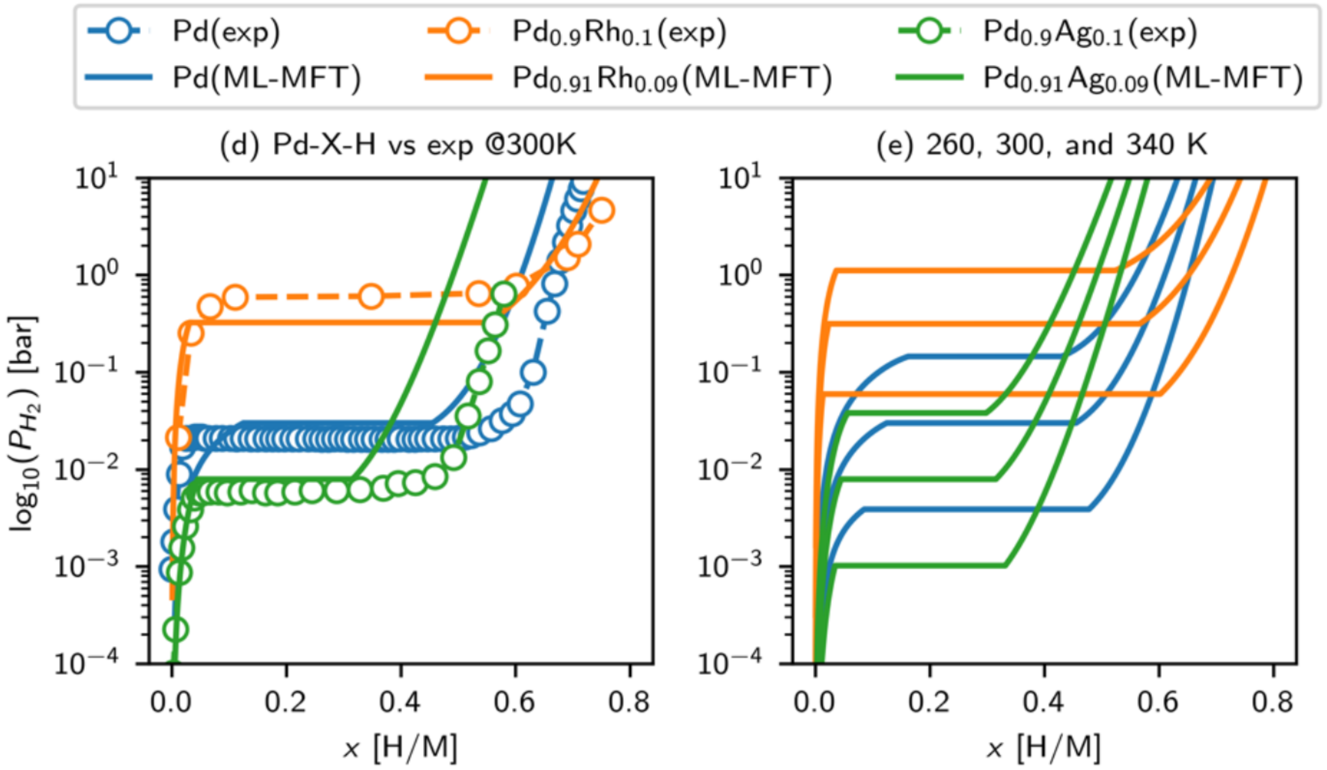
Boltzmann: $E(x) = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

PCT:

- fit $G(x)$ to polynomial
- Differentiate w.r.t x → μ
- $p = p_0 e^{\mu/kT}$

- GNN surrogate models for formation energies

Comparison of computed vs experimental PCT



- Correctly rank plateau pressure, plateau widths, & H/M saturation between alloy systems
- Compute phase envelope

- Additional work needed for thermodynamic approach in more complex hydride and super-hydride material classes

Outline: A survey of data-driven materials discovery and systems modeling tasks in hydrogen energy applications at Sandia

Part I:
Accelerated screening of oxides for high-temperature clean-energy applications
- graph neural networks / defect property predictions / first principles thermodynamics

Part II:
Towards Pareto optimal high entropy alloy hydrides
- statistical learning models / graph neural networks / metal-hydrogen phase diagrams / experiments

Part III:
The importance of systems level co-design in evaluating hydrogen storage materials
- Experiments + systems-level modeling

Part III:
Material *and system* co-design for optimizing nanoscale metal hydride-based hydrogen storage[1]

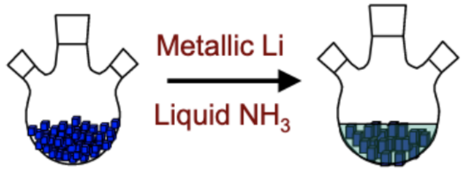
Key concepts:
- Comprehensive experimental characterization of pelletized, nano-scale, complex metal hydrides
- Systems design tools for wholistic design performance

[1] Witman, Brooks, Sprik, Gross, Wood, Heo, Klebanoff, Acosta, Reyes Leick, Gennett, Stavila, Allendorf. et al. *In prep.*, 2023

Nano-scaling via host confinement is a powerful technique for destabilizing metal hydrides

Nanoscaling Li_3N in a carbon host enhances a variety of hydrogen storage properties… (V.Stavila et al)

Li_3N nanoconfinement



Bulk

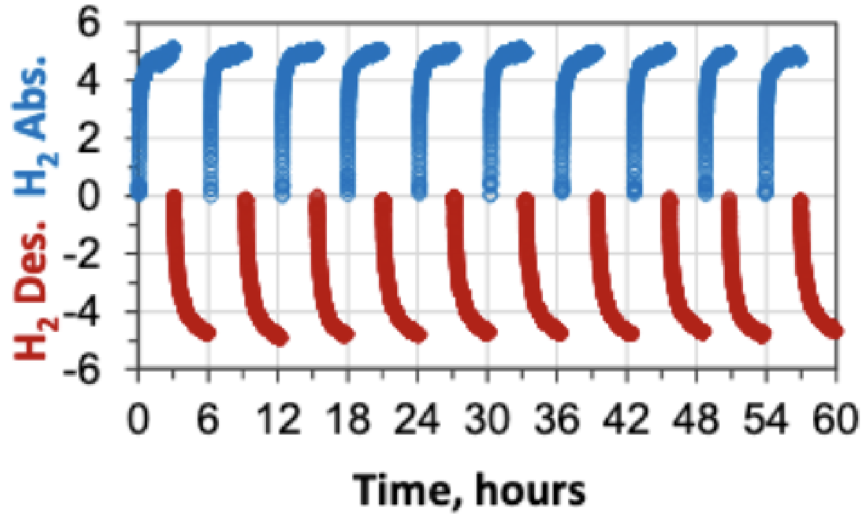
$Li_3N + H_2 \rightleftharpoons Li_2NH + LiH$

$Li_2NH + LiH + H_2 \rightleftharpoons LiNH_2 + 2LiH$

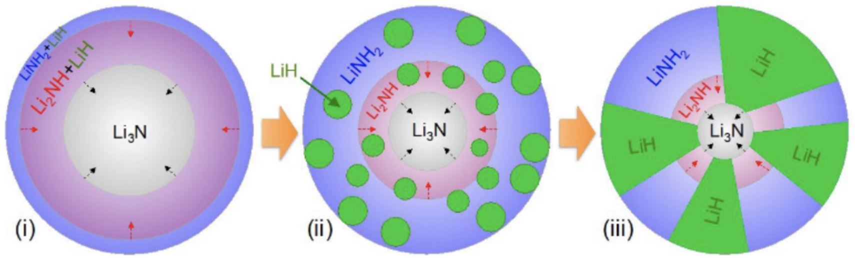
Nano (Li_3N in 3-10 nm nanoporous C):

$Li_3N + 2H_2 \rightleftharpoons LiNH_2 + 2LiH$

- Significant destabilization



- Great cyclability



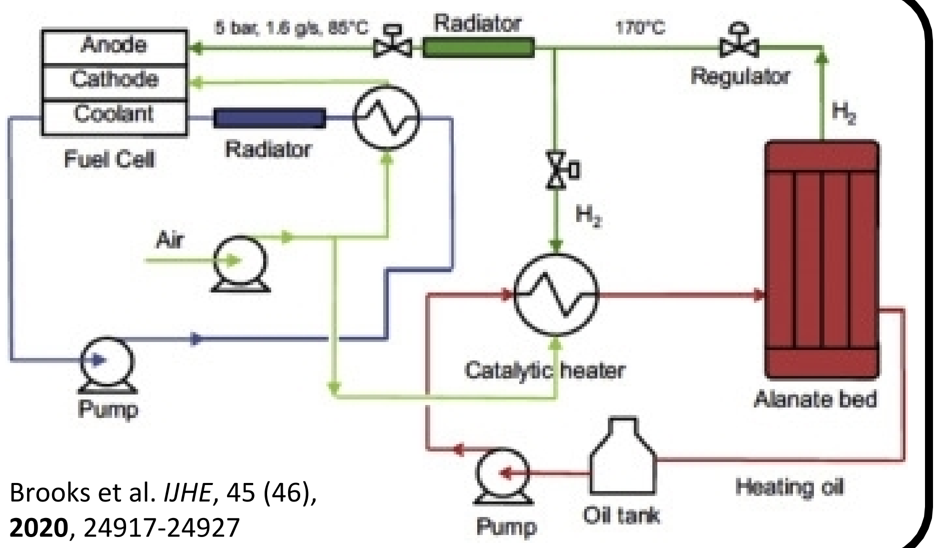
- Favorable nano-interfaces & core-shell structure

But sacrifices other properties… So which one is better for storage?

Material	f_{H2} [wt%]	k [W m^{-1} K^{-1}]	ρ [kg m^{-3}]	ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
Bulk Li_3N	7.1	0.6	821	67.3	126
6nm-Li_3N@C	5.4	3.1	742	46.7	109
% change	-24%	420%	-9.6%	-31%	-15%
	Bad	Good	Bad	Good	Bad

PNNL-developed metal hydride design tool can calculate the *systems-level* gravimetric and volumetric capacity based on material properties

Determine system requirements to store *X* kg of H_2



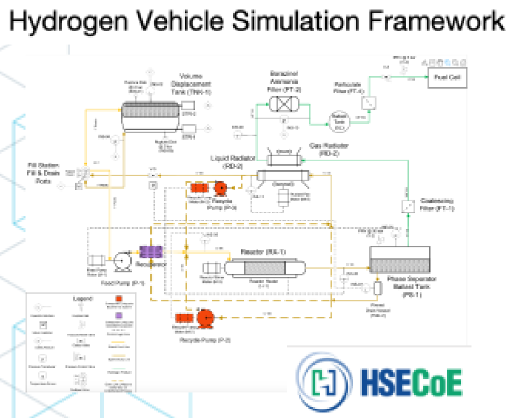
Brooks et al. *IJHE*, 45 (46), **2020**, 24917-24927

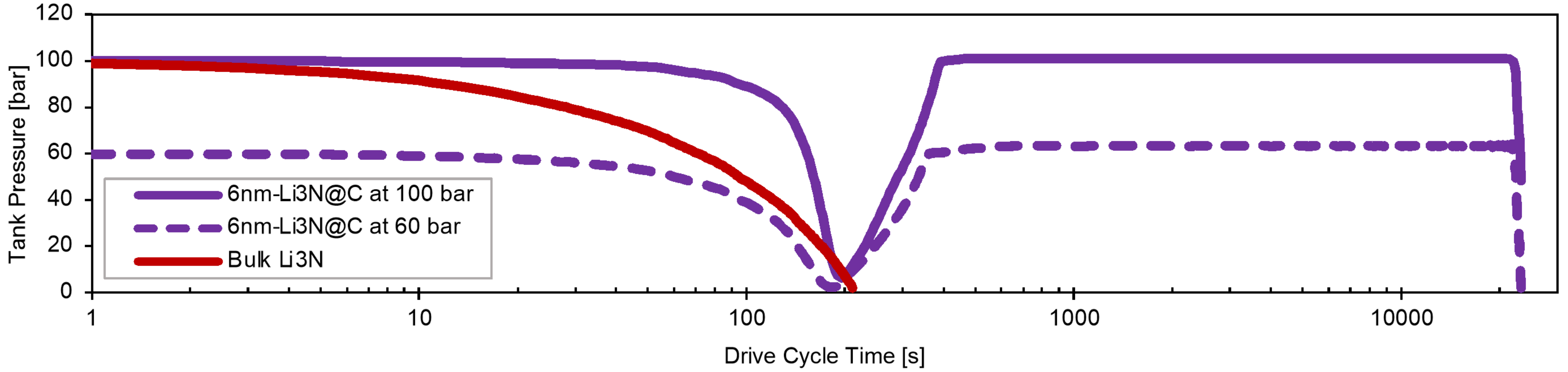
Volumetric systems capacity (VSC) for bulk, nano, and 350 bar

	Li_3N (A286)	6nm-Li_3N@C (A286)	350 bar (A286)
Total mass (kg)	407	325	307
Total volume (m^3)	0.371	0.333	0.274
H_2 burned (kg)	2.94	1.77	N/A
Max Temp. (°C)	494	387	N/A
HEx tubes	811	236	N/A
VSC (g_{H2}/L)	15.1	16.8	20.5

- Nano's VSC is better than that of bulk
- Nano's VSC is approaching that of 350 bar compressed gas
- Group is working on a material to compete or better 700 bar

Most importantly, only nano-Li_3N can *even complete* a simulated drive cycle (K. Brooks)





Concluding remarks

Key takeaways

- Data-driven materials discovery efforts take on many different forms depending on data availability, problem constraints, computational vs. experimental data, etc.

- New/improved materials for hydrogen storage and generation are ripe for discovery across various applications and will help accelerate hydrogen deployment

- Understanding the efficacy of high entropy materials (massive increase in chemical/structural search space) will only exacerbate the need for data-driven insights to drive efficient experimental progress

- *Ultimate* prediction of material performance requires systems-level modeling (often depends on properties beyond current modeling capabilities, at least in high-throughput)

Thank you for your attention!

Always open to questions/comments/collaborations.

Please email:
mwitman@sandia.gov