



Energy Materials Network
U.S. Department of Energy



HydroGEN
Advanced Water Splitting Materials

Computationally Accelerated Discovery and Experimental Demonstration of High- Performance Materials for Advanced STCH Hydrogen Production

P.I. Charles Musgrave
University of Colorado, Boulder
April 30, 2019

Project ID #P166

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Project Overview

Project Partners

PI: Charles Musgrave, University of Colorado
Co-PI: Alan Weimer, University of Colorado
SP: Aaron Holder, University of Colorado, NREL
EMN Collaborator: Stephan Lany, NREL
EMN Collaborator: Senevieve Saur, NREL
EMN Collaborator: Tony McDaniel, SNL
EMN Collaborator: Eric Coker, SNL

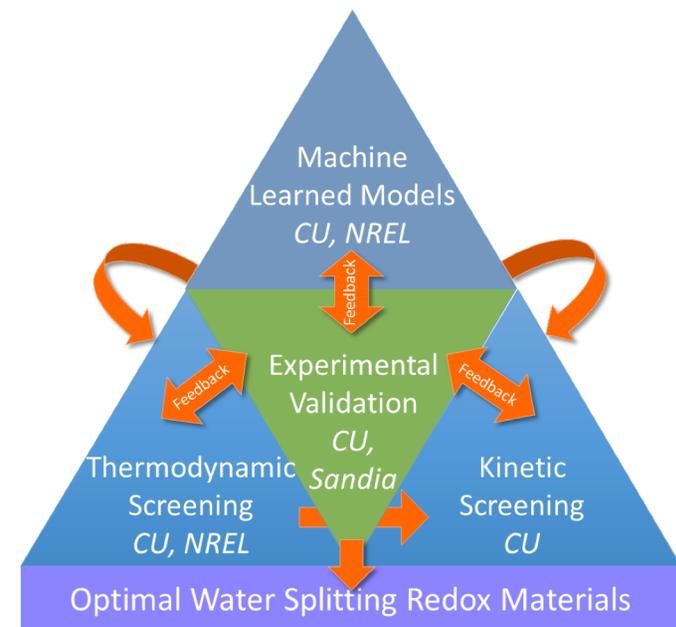
Award #	EE0008088
Start/End Date	10/01/2017 – 6/30/2020
Year 1 Funding*	\$0.28 M
Year 2 Funding*	\$0.41 M

Project Vision

Develop and utilize machine-learned models coupled with *ab initio* thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials

Project Impact

In Phase I we will demonstrate the accuracy of thermodynamic and kinetic models for predicting the properties of STCH materials which will allow for rapid screening and discovery of new materials



* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)
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Approach- Summary

Project Motivation

This project builds on prior collaborative computational and experimental work at CU Boulder which demonstrated the viability of new materials for STCH. It combines efforts at CU, NREL, and SNL involving machine learning, *ab initio* calculations, and experiment to develop new perovskites and spinels for more efficient STCH production.

Barriers

Vast number of possible metal oxides for STCH – utilize machine learning in conjunction with *ab initio* calculations and experiments to rapidly screen huge numbers of new candidate materials.

Key Impact

Metric	State of the Art	Proposed
Computational Validation	N/A	Matching expt and comp. thermo. and kinetic properties
H ₂ productivity	Ceria: 130 $\mu\text{mol/g}$ (1500°C/1000°C)	200 $\mu\text{mol H}_2/\text{g}$
Temperature	$T_{RED} \geq 1500^\circ\text{C}$ $\Delta T \geq 700^\circ\text{C}$	$T_{RED} \leq 1450^\circ\text{C}$ $\Delta T \leq 400^\circ\text{C}$

Partnerships

National Renewable Energy Laboratory (NREL), Golden, CO

Stephan Lany – DFT defect calculations

Genevieve Saur - Technoeconomic analysis

Sandia National Laboratory (SNL),

Tony McDaniel – Stagnation flow reactor experiments

Eric Coker – High-temperature XRD and TGA



Approach- Innovation

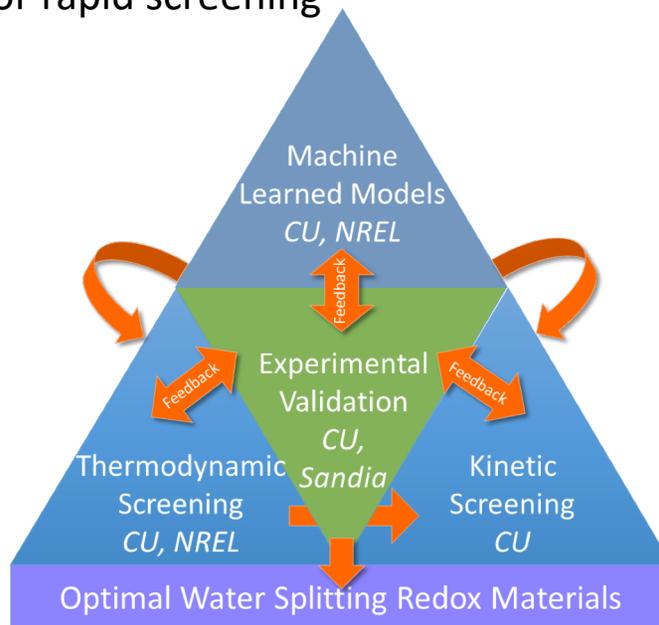
Utilize machine-learned models coupled with *ab initio* thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials

Task 1: Machine learning prediction of material stability

- Develop machine learning models to predict stability of materials at STCH conditions for rapid screening • **CU/NREL node collaboration**

Task 2: Thermodynamic screening of active materials

- Computationally evaluate candidate materials for thermodynamic viability
- Utilize ML models to filter materials; provide candidate materials for computational kinetic screening
- CU/NREL Node Collaboration**



Task 3: Kinetic screening of active materials

- Identify kinetically active materials through computational screening
- Incorporate feedback from experimental testing at **SNL node**

Task 4: Experimental demonstration of active materials

- Utilize SFR and TGA to evaluate thermodynamic and kinetic properties of new materials
- Provide feedback to computational thermodynamic and kinetic screening
- CU/SNL node collaboration**
- GNG1: Experimentally demonstrate 3 materials with $>200\mu\text{mol H}_2/\text{g}/\text{cycle}$ at $T_{\text{red}} < 1450^\circ\text{C}$ and $\Delta T < 400^\circ\text{C}$ whose relative thermodynamic and kinetic performance matches that predicted by computational models

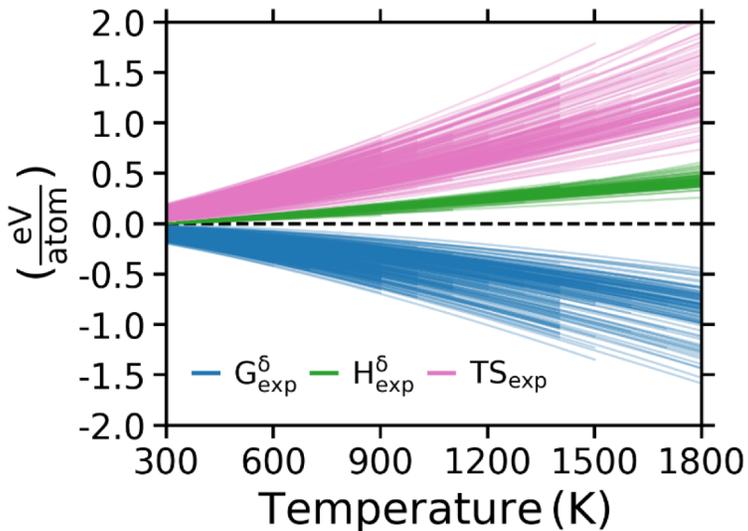


Relevance & Impact

- ▶ DOE Hydrogen and Fuel Cells Program goal of $<\$2/\text{kg H}_2$
 - Improved redox material efficiency and stability is critical to achieving this goal
- ▶ EMN Node Utilization - provide critical information/feedback to all aspects of the project
 - **Task 1:** Machine learning the Gibbs energy of compounds done in conjunction with **Stephan Lany at NREL**
 - Allows for high-throughput screening of material stability at STCH temperatures
 - **Task 2:** Thermodynamic evaluation of charged vs. neutral defects in spinels in progress with **Stephan Lany at NREL**
 - Allows for more accurate thermodynamic assessment of new materials
 - **Task 3:** Kinetic screening will utilize feedback from experiments done in conjunction with **Tony McDaniel at SNL**
 - Kinetics not previously explored in computational STCH work so experimental feedback is critical to developing rapid screening techniques
 - **Task 4:** Experimental testing of materials conducted with **Tony McDaniel at SNL** and **Eric Coker at SNL**
 - Stagnation flow reactor provides measurement of H_2 produced by new materials (GNG1)
 - Thermal analysis provides direct comparison for thermodynamic screening
- ▶ Our interactions with Lany (NREL) and Coker (SNL) will significantly benefit the broader HydroGEN Consortium by providing definitive computational and experimental data to benchmark against and a deeper understanding of what materials properties correlate with better STCH performance.

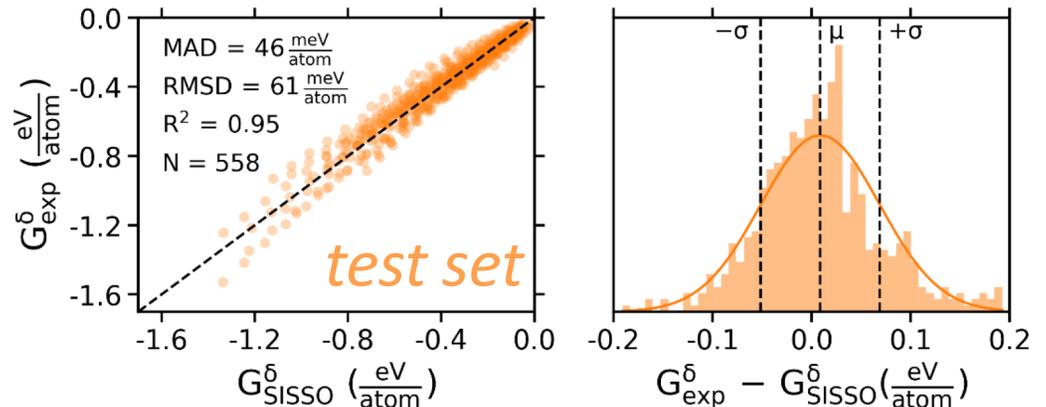


Accomplishments

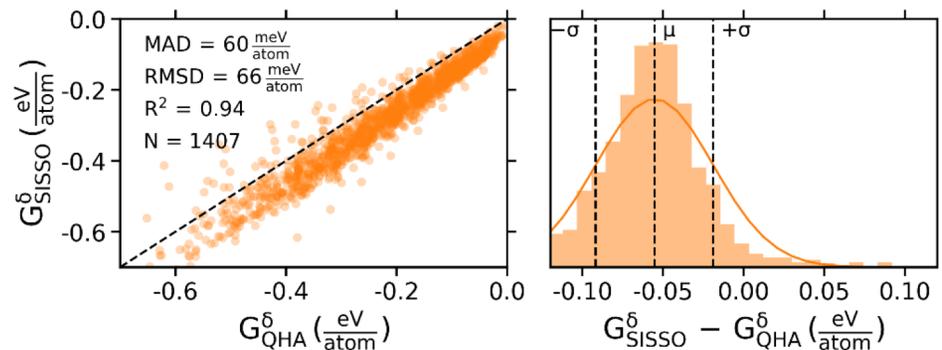


- 312 M_aX_b and $M_aM_bX_c$ solids with exp. measured $G(T)$
- DFT calculations performed at 0K, but stability is T -dependent

Compares well to computationally expensive calculations by quasiharmonic approximation of phonon free energy



- Developed machine-learned model for $G(T)$ using **SISSO** algorithm
- Model depends on composition and 0 K calculated structure (PBE)



**$G(T)$ predicted with MAE = ~ 45 meV/atom (on excluded test set) up to 1800 K
- will enable rapid screening materials based on stability (M1.1.1 – M1.3.1)**

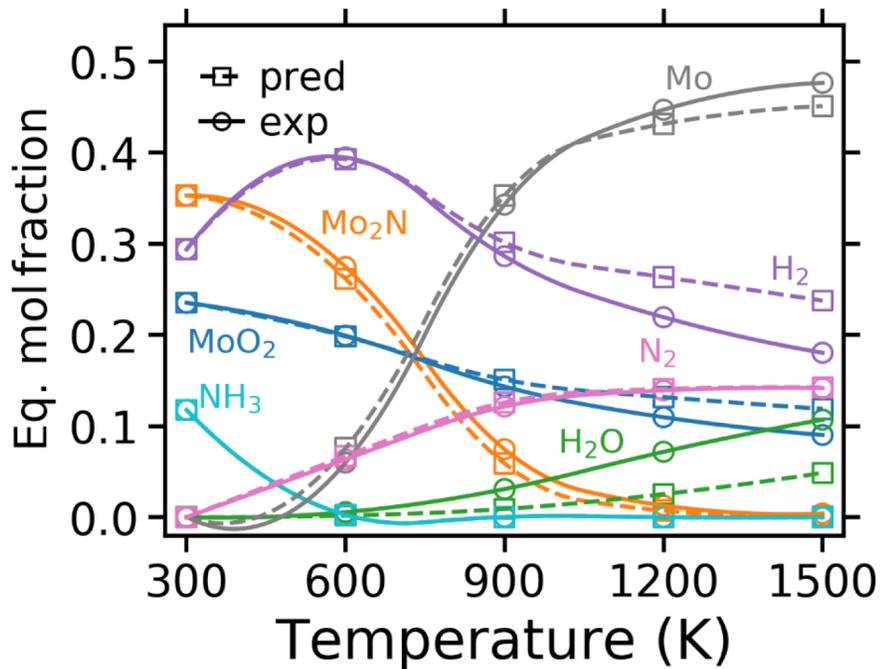
Bartel, Millican, Deml, Rumptz, Tumas, Weimer, Lany, Stevanovic, Musgrave, Holder,

Nature Communications, 9 (1), 4168 (2018)

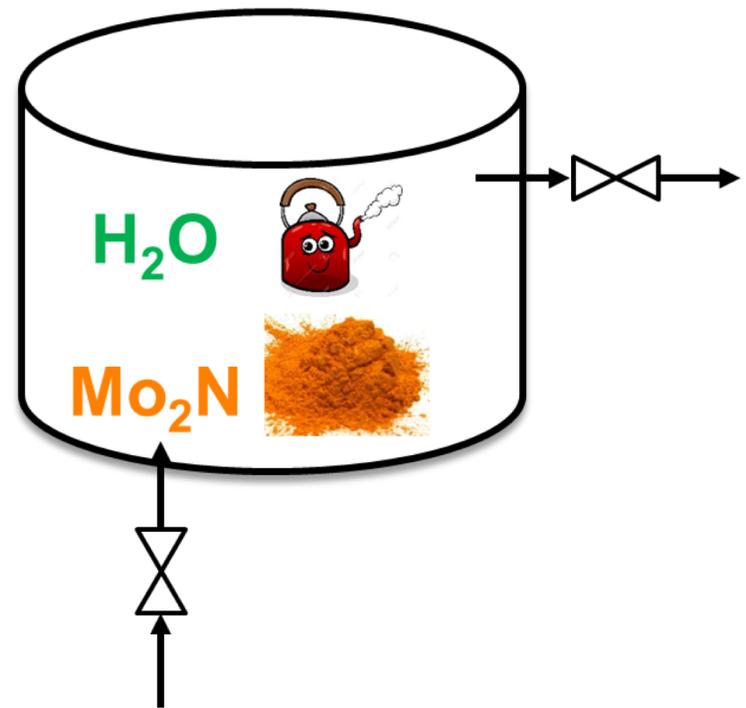
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Accomplishments



Simulated equilibrium using Gibbs energy minimization in virtual reactor



Descriptor enables high-throughput predictions of reaction energetics and thermochemical equilibrium (M1.1.1 – M1.3.1)

NREL Node Collaboration

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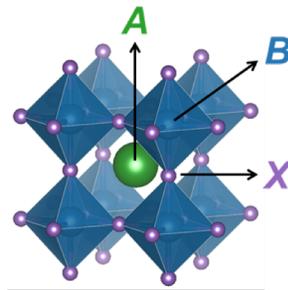
[Bartel](#), [Rumptz](#), [Weimer](#), [Holder](#), [Musgrave](#), *ACS Appl. Mater. Interfaces*, Accepted (2019)

[Bartel](#), [S. Millican](#), [Deml](#), [Rumptz](#), [Tumas](#), [Weimer](#), [Lany](#), [Stevanovic](#), [Musgrave](#), [Holder](#), *Nature Communications*, 9 (1), 4168 (2018)



Accomplishments

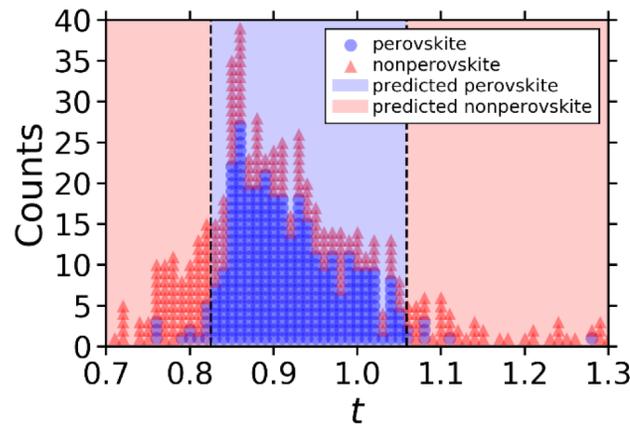
- 576 ABX_3 solids classified experimentally as perovskite vs nonperovskite
- **Descriptor for perovskite stability** τ discovered using state-of-the-art ML built upon **SISSO** algorithm
- Rapid search across 10^9 - 10^{11} potential descriptors
- Targets low-dimensional expressions
- Maximizes interpretability
- Established accuracy and ideal bounds for Goldschmidt factor



H																	He															
Li	Be											B	C	N	O	F	Ne															
Na	Mg											Al	Si	P	S	Cl	Ar															
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr															
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe															
Cs	Ba			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn														
Fr	Ra																															
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																		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

V. Goldschmidt 1926

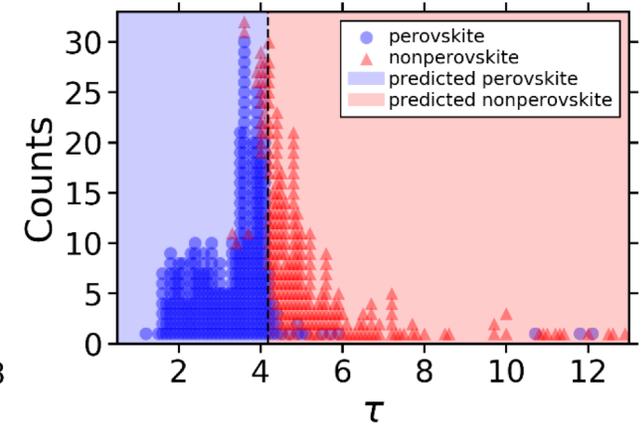
$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$



74% accuracy

Bartel et al. 2019

$$\tau = \frac{r_X}{r_B} - n_A \left(n_A - \frac{r_A/r_B}{\ln r_A/r_B} \right)$$

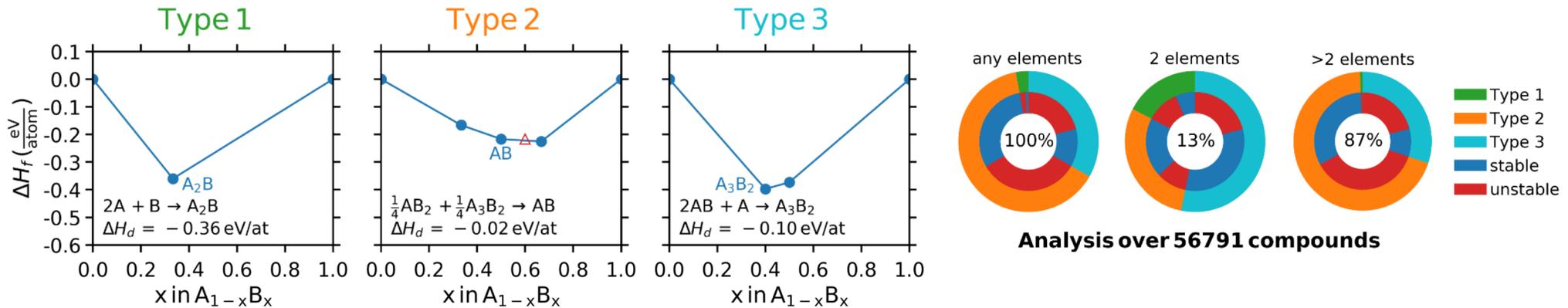


92% accuracy

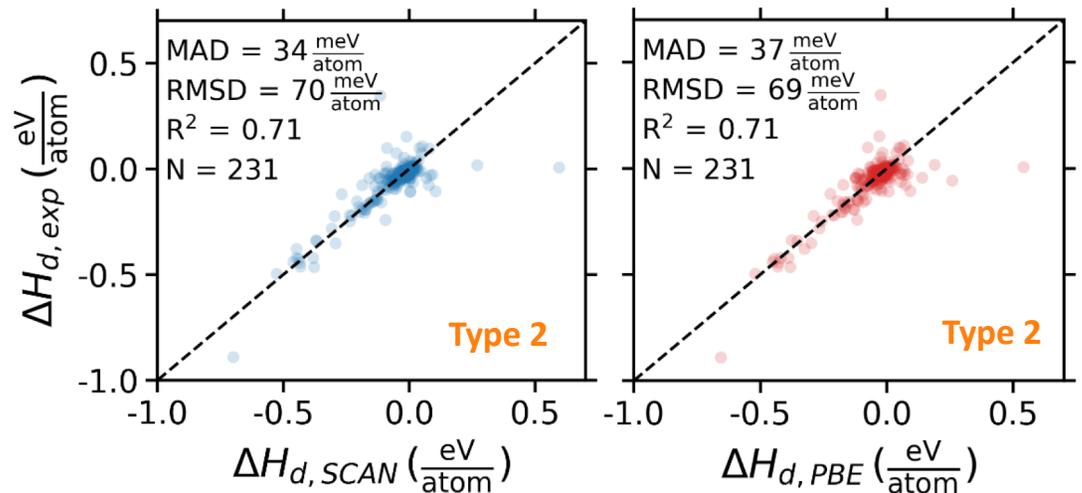
Developed descriptor with 92% accuracy for predicting perovskite stability – New 1st screening step to reduce number of DFT calculations (M1.1.1 – M1.3.1)



Accomplishments



- Classified decomposition (stability) reactions into three types
- Benchmarked SCAN and PBE against experiment for > 1,000 solid-state materials
- Showed that high-throughput DFT approaches experimental accuracy for Type 2 **stability predictions**

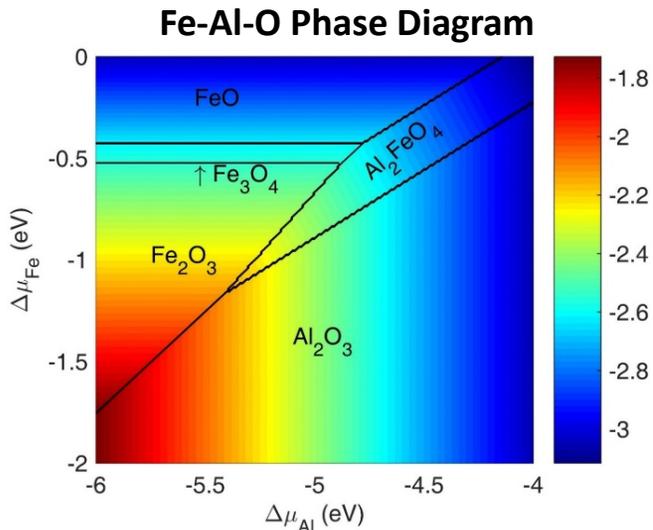


Established basis for benchmarking and understanding first-principles predictions of solid stability (2.1.3)

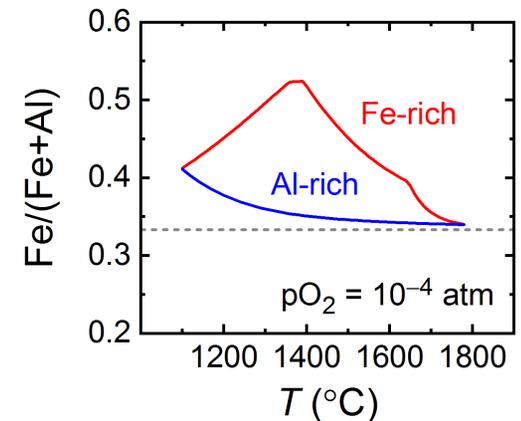
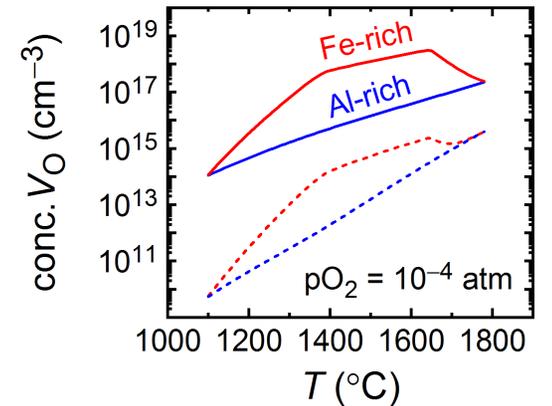
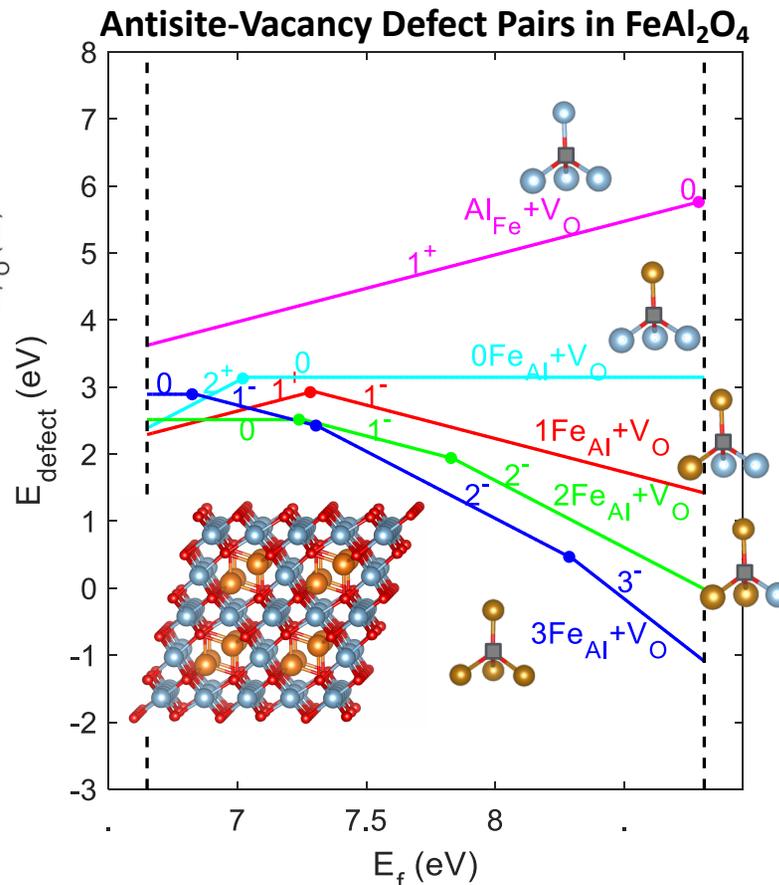


Accomplishments

Study of Charged Vacancies and Defect Pairs in Hercynite



Hercynite stable under STCH conditions: $-3.5 \text{ eV} \leq \Delta\mu_{\text{O}} \leq -2 \text{ eV}$



- Defect energies in normal hercynite ($0\text{Fe}_{\text{Al}}+\text{V}_{\text{O}}$) are high in energy, resulting in low extent of reduction
- Charged antisite-vacancy defect pairs significantly lower in energy, increases V_{O} concentration by 3-4X
- Degree of reduction strongly depends on cation stoichiometry, maximum Fe solubility 0.5 in spinel

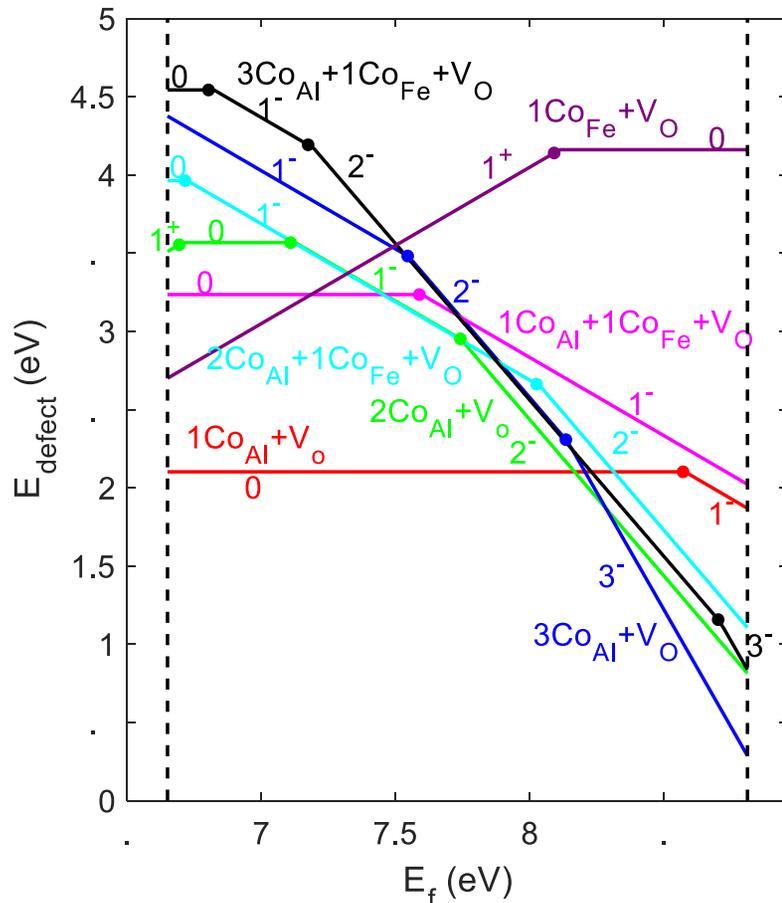
NREL Node Collaboration (Lany)



Accomplishments

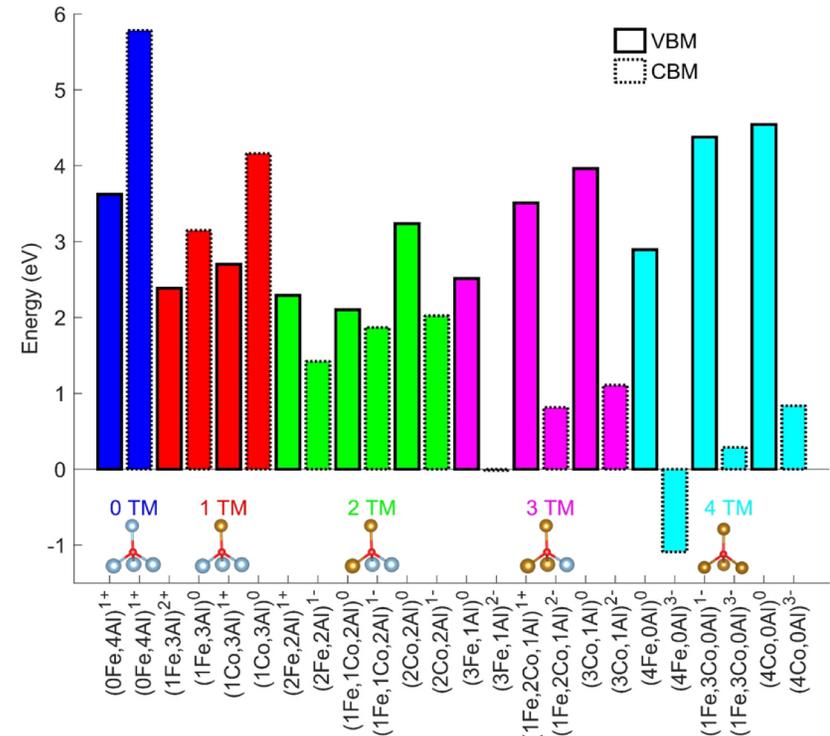
Study of Charged Vacancies and Defect Pairs in Cobalt Iron Aluminate Alloy

Antisite-Vacancy Defect Pairs in $\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4$



- Similar trends observed in $\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4$ and FeAl_2O_4
- Charged antisite-vacancy defect pairs lower in energy

Defect Pair Summary in FeAl_2O_4 and $\text{Co}_x\text{Fe}_{1-x}\text{Al}_2\text{O}_4$

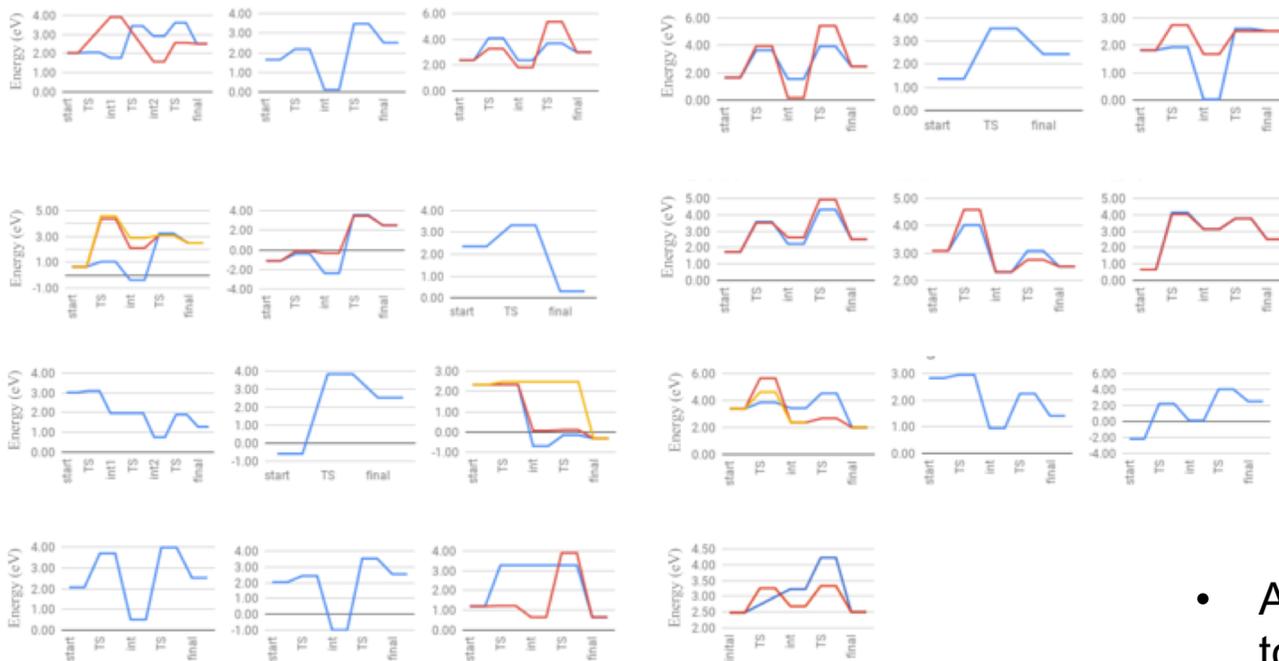


- Decrease in $E(V_O)$ with increasing Co or Fe nearest neighbors at CBM
- V_O near Co are higher in energy than those near Fe; lower extent of reduction in Co-alloy
- Consistent with experimental findings

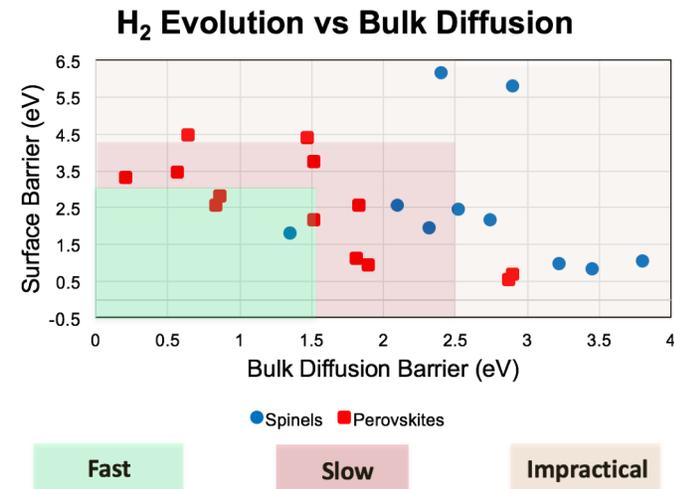
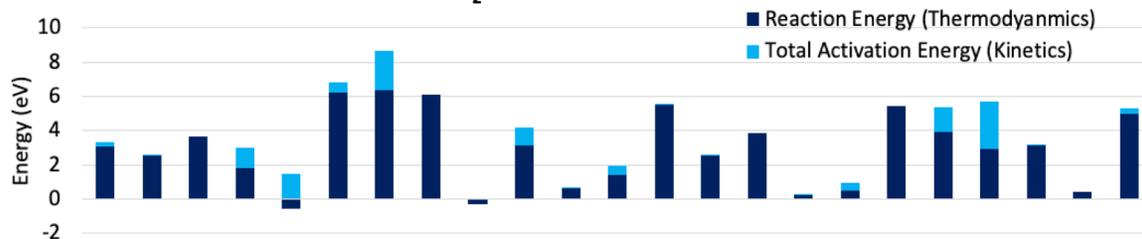
Computational Screening of Ternary Spinel (M2.1.1 – M2.1.2)



Accomplishments



O₂ Evolution Reaction

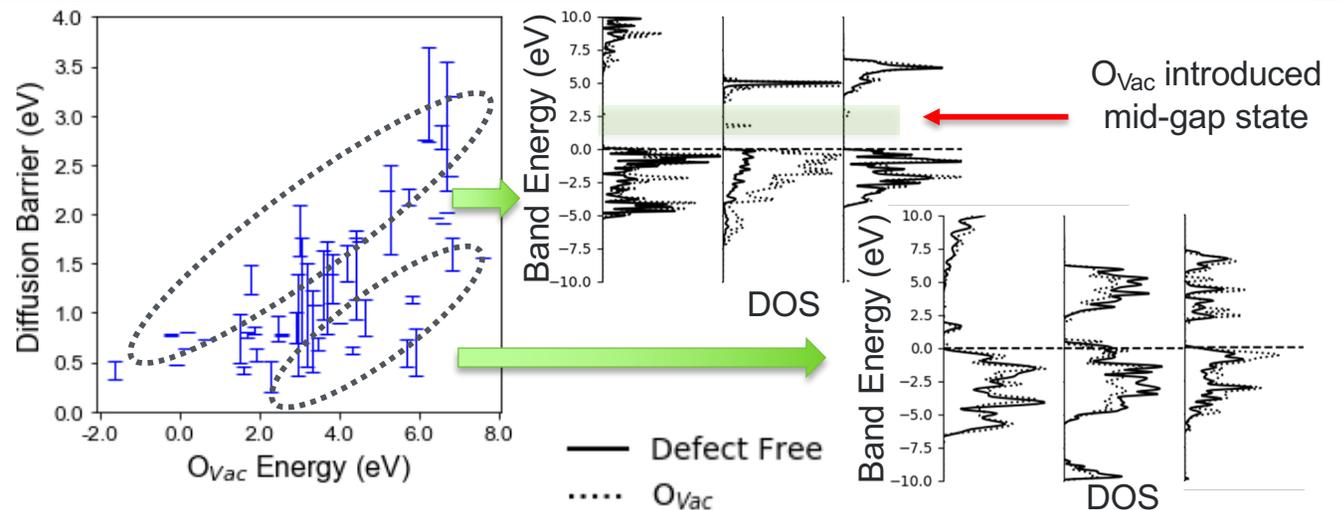
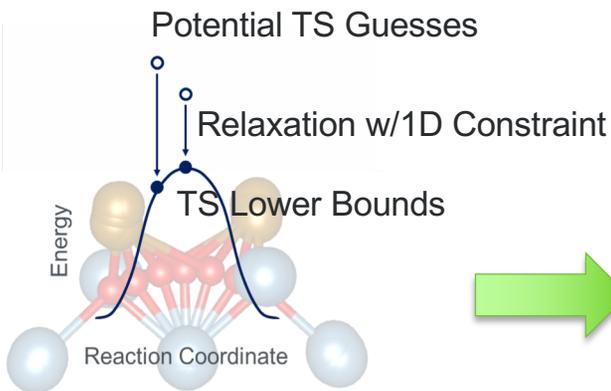


- Applied TS model developed in BP1 to 23 unique spinels and perovskites
- Identified rate determining step for H₂ evolution reaction
- Kinetics of O₂ evolution reaction identified as important for ~50% of studied materials

Identified RLS for oxidation and reduction reactions in the bulk and surface for 20 different materials. (M3.3.1)



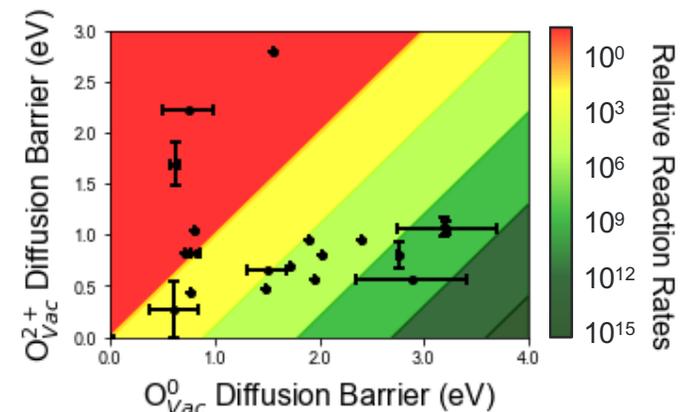
Accomplishments



- Applied TS model developed in BP1 to 60 unique spinel and perovskite type materials
- Identified weak correlation between O_{vac} energy and diffusion barrier
- For insulators and semiconductors identified mid-gap states as predictor of slower rxns

- Compared diffusion barriers of neutral and charged O vacancies
- Once formed, charged vacancies generally have lower diffusion barrier, and consequently faster rates

**Determined diffusion barrier for 60 new materials.
Identified properties of most kinetically viable materials (M3.3.1 – M3.3.2)**



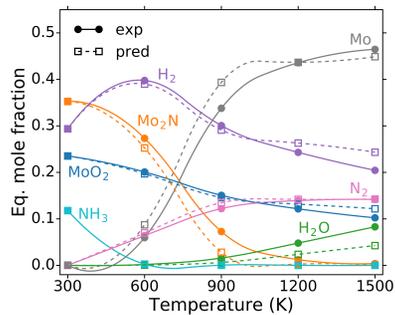


Collaboration: Effectiveness

Utilize Machine Learning (ML) models coupled with *ab initio* thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials

Task 1: Machine Learning

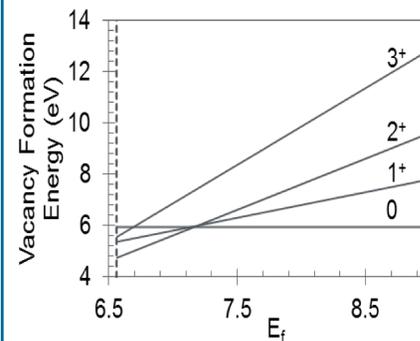
Collaborator: NREL – Stephan Lany – First Principles Materials Theory



- Machine learned model for predicting the Gibbs energy, $G(T)$, developed in collaboration NREL
- Critical for high-throughput equilibrium predictions at relevant conditions

Task 2: Thermodynamic Screening

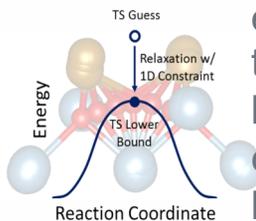
Collaborator: NREL – Stephan Lany – First Principles Materials Theory



- Key partner in developing an understanding of the role of charged defects in spinels
- Possibly critical for accurate screening of new materials
- Bi-weekly in-person mtgs w/multiple team members

Task 3: Kinetic Screening

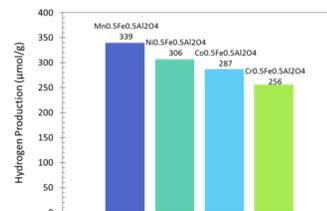
Collaborator: SNL – Tony McDaniel – Laser Heated SFR



- Feedback from experimental testing at SNL will be integrated into computational kinetic models for improved accuracy

Task 4: Experimental Testing

Collaborator: SNL – Tony McDaniel – Laser Heated Stagnation Flow Reactor



Collaborator: SNL – Eric Coker – HT-XRD and Thermal Analysis

- Analysis will allow for direct comparison between experiments and computation
- Feedback for NREL node for understanding entropic contributions and charged defects
- Graduate student trained for 2 weeks for remote operation of equipment
- Testing parameters identified and materials sent to SNL for evaluation



Planned Future Work: BP2

Remainder of FY 2019

- ▶ Apply new accelerated thermodynamic stability analysis to access candidate pool for defect calculations.
- ▶ Continue to examine the role of charged defects and associated electronic entropy in spinel aluminate STCH reactions ([NREL node collaboration](#))
- ▶ Continue to apply rapid bulk kinetic screening methods to surface reactions and charged defects
- ▶ Quantify kinetic parameters for feedback to computation ([SNL node collaboration](#))
- ▶ Quantify enthalpy and entropy of spinel aluminates for direct comparison to computation ([SNL node collaboration](#))

Objective: Utilized approaches developed in BP1 to rapidly computationally prototype new STCH materials and demonstrate materials with improved performance

GNG2: Demonstrate the performance of a doped material with improved thermodynamic and stability properties (H_2 production above $250 \mu\text{mol/g/cycle}$ at reduction temperatures $< 1400^\circ \text{C}$ which loses less than 10% of its H_2 production between cycles 50 and 100) and with improved kinetic properties (reaches 80% of equilibrium H_2 production within 10 minutes). Oxidation will either be operated at $\text{H}_2\text{O}:\text{H}_2$ ratios of less than 1000:1 or a TEA will be conducted to verify that higher $\text{H}_2\text{O}:\text{H}_2$ ratios are economically practical with the new material.



Proposed Future Work: BP3

FY 2020

Objective: Computationally prototype doped metal oxides for thermodynamic and kinetic viability and experimentally demonstrate materials with improved H₂ productivity, reaction kinetics, and durability

Final Deliverable:

Demonstrate the performance of a doped material with **improved thermodynamic and stability properties** (H₂ production above 300 μmol/g/cycle at T_{red} < 1400° C which loses less than 10% of its H₂ production between cycles 100 and 200) and a material with **improved kinetic properties** (reaches 80% of equilibrium H₂ production within 7 mins). Oxidation will either be operated at H₂O:H₂ ratios of less than 1000:0 or a TEA will be conducted to verify that higher H₂O:H₂ ratios are economically practical with the new material.



Project Summary

Approach: Utilize Machine Learning (ML) models coupled with *ab initio* thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials

▶ Task 1: Machine Learning

- Descriptor for perovskites stability improves significantly upon Goldschmidt's (M1.1.1 – M1.3.1)
 - 92% of 576 ABX_3 solids correctly classified as perovskite/nonperovskite using only composition (i.e., instantaneous prediction) – **will enable rapid screening for perovskite formation**
- Descriptor for $G(T)$ shown to be comparable to QHA (161 cmpds) and experiment (312 cmpds) (M1.1.1 – M1.3.1) – **will enable rapid screening of materials for stability.**

▶ Task 2: Thermodynamic Screening

- Screened >1.1 M perovskites for stability using ML models; 27,015 predicted to be stable (M2.1.2)
- 1,380 ternary and double perovskites screened based on O-vacancy formation energy (M2.1.4,2.2.1)
- Assessed the inclusion of descriptors beyond enthalpic effects for more accurate thermodynamic screening of spinels (M2.1.1) – **may enable new criteria screening of materials for STWS.**

▶ Task 3: Kinetic Screening

- Developed method to rapidly screen bulk kinetics of new materials (M3.2.1)
- Successfully applied rapid screening method to 60 new and existing materials (M3.2.1)
- Began quantifying kinetics of surface reaction (M3.1.1) – **will enable screening based on kinetics.**

▶ Task 4: Material Testing

- 4 alloys demonstrated with >200 $\mu\text{mol H}_2/\text{g}/\text{cycle}$ at $T_{\text{red}}=1450^\circ\text{C}$ and $\Delta T < 400^\circ\text{C}$ (M4.1.1, GNG1)
- $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4$ shows improved peak rate over undoped hercynite and highest H_2 production of alloyed materials (M3.1.1)



Publications & Presentations

Publications:

C. Bartel, A. Weimer, S. Lany, C. Musgrave, A. Holder, “The role of decomposition reactions in assessing first-principles predictions of solid stability,” *npj Computational Materials* 5 (1), 4 (2019).

C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” *Science Advances* 5 (2), eaav0693 (2019).

C. Bartel, S. Millican, A. Deml, J. Rumptz, W. Tumas, A. Weimer, S. Lany, V. Stevanovic, C. Musgrave, A. Holder, “Physical descriptor for the Gibbs energy of inorganic crystalline solids and temperature-dependent materials chemistry,” *Nature Communications*, 9 (1), 4168 (2018).

Presentations:

C. Musgrave, C. Bartel, A. Holder, C. Sutton, B. Goldsmith, R. Ouyang, L. Ghiringhelli, M. Scheffler, “Ab Initio and Machine Learned Modeling for the Design and Discovery of New Materials for Energy Applications,” *Air Force Research Laboratories*, Dayton, OH, January 2019.

S. Millican, I. Androschuk, A. Weimer, C. Musgrave, “Computational discovery of materials for solar thermochemical hydrogen production” *American Institute of Chemical Engineers*. October 2018.

C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” *American Institute of Chemical Engineers*. October 2018.

C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” *European Materials Research Society*. September 2018.

S. Millican, I. Androschuk, A. Weimer, C. Musgrave. “Rapid Kinetic Profiling of Bulk Diffusion Barriers for Solar Thermal Water Splitting Materials” *21st International Conference on Ternary and Multinary Compounds*. September 2018.



Publications & Presentations

Presentations (continued):

C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” *21st International Conference on Ternary and Multinary Compounds*. September 2018.

C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” *Application of Machine Learning and Data Analytics for Energy Materials Network Consortia 2018*. May 2018.

Millican, S.L., I. Androshchuk, A.W. Weimer, and C.B. Musgrave, “Ab-initio Modeling and Experimental Demonstration of Metal Oxides for Solar Thermochemical Water Splitting,” *American Chemical Society Spring Meeting*, March 2018.

C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, “Improved tolerance factor for classifying the formability of perovskite oxides and halides,” *American Physical Society Annual Meeting*, March 2018.

C. Bartel, S. Millican, A. Deml, J. Rumptz, W. Tumas, A. Weimer, S. Lany, V. Stevanovic, C. Musgrave, A. Holder, “Machine learning the Gibbs energies of inorganic crystalline solids,” *American Physical Society Annual Meeting*, March 2018.

Millican, S.L., I. Androshchuk, A.W. Weimer, and C.B. Musgrave, “Design and Discovery of Mixed Metal Oxides for Solar Thermochemical Water Splitting,” *International Conference and Exposition on Advanced Ceramics and Composites*, January 2018.