



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

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University of Colorado, Boulder
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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: Tony McDaniel, SNL
EMN Collaborator: Eric Coker, SNL
EMN Collaborator: Andrea Ambrosini, SNL

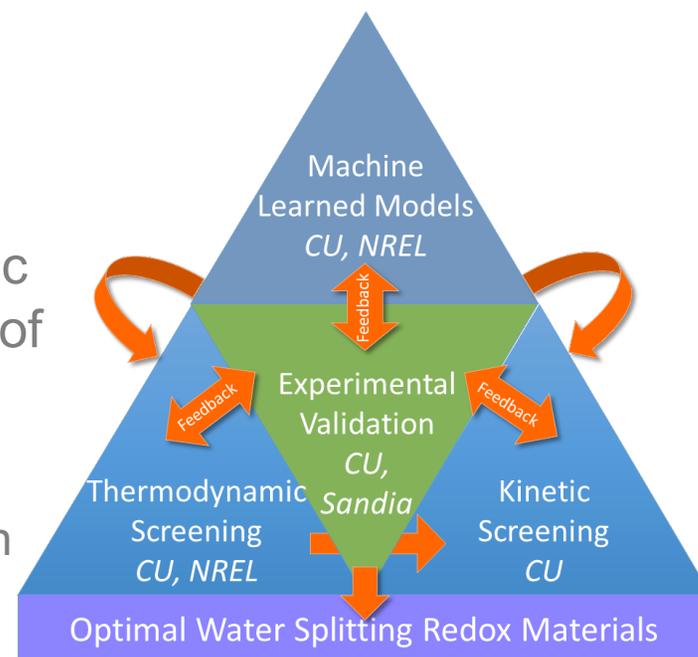
Award #	EE0008088
Start/End Date	10/01/2017 – 6/30/2020
Year 1 Funding*	\$0.28 M
Year 2 Funding*	\$0.41 M

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 II we will validate our optimization approach for designing doped materials with improved thermodynamic and kinetic properties for STCH



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



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 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	<i>Ceria</i> : 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

Sandia National Laboratory (SNL),
Tony McDaniel – Stagnation flow reactor experiments

Eric Coker – High-temperature XRD and TGA
Andrea Ambrosini – Material synthesis



Approach- Innovation and Milestones

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

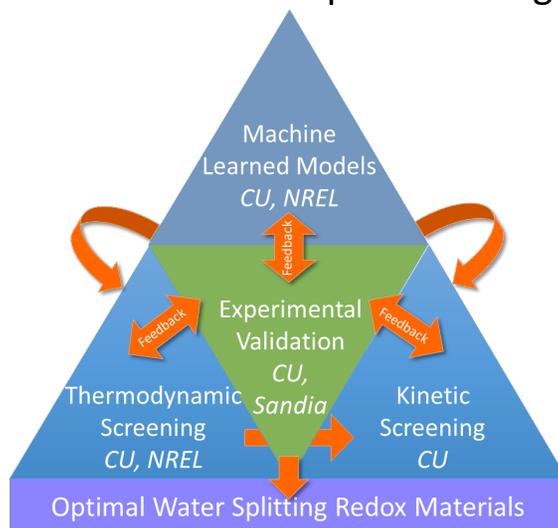
Task 1: Machine learning prediction of material stability

- ✓ M1.3.1 100% Complete: 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
- ✓ M2.1.3 100% Complete: Screen all ternary perovskites based on stability and vacancy energy
- **CU/NREL Node Collaboration**



Task 3: Kinetic screening of active materials

- Identify kinetically active materials through computational screening and ML models
- ✓ M3.3.1 100% Complete: Developed ML model based on new rapid TS bounding method to screen for kinetic viability

Task 4: Experimental demonstration of active materials

- Utilize SFR, TGA, and HT-XRD to evaluate thermodynamic and kinetic properties of new materials
- Provide feedback to computational thermodynamic and kinetic screening
- **CU/SNL node collaboration**
- GNG2: Experimentally demonstrate a doped material with $>250 \mu\text{mol H}_2/\text{g}/\text{cycle}$ at $T_{\text{red}} < 1400^\circ\text{C}$ and $\Delta T < 400^\circ\text{C}$ which loses $< 10\%$ of H_2 production in cycles 50 – 100 and reaches 80% of equilibrium H_2 production in < 10 minutes. $\text{H}_2\text{O}:\text{H}_2$ ratios $< 1000:1$ or a TEA will be conducted.



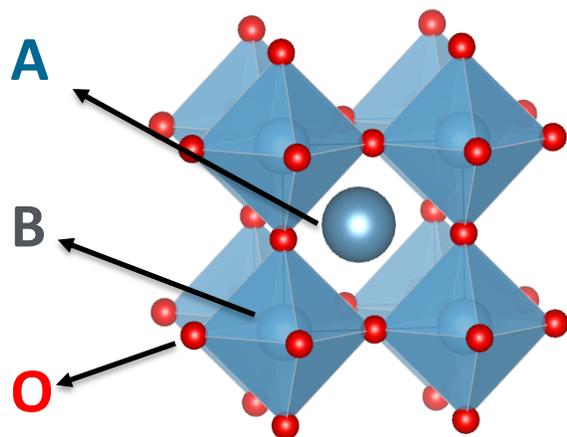
Relevance and Impact

- ▶ Overall Objective: Develop STCH redox materials with improved efficiency and stability utilizing machine-learned models, *ab initio* calculations, and experiments capable of meeting the DOE Hydrogen and Fuel Cells Program goal of $< \$2/\text{kg H}_2$
- ▶ BP2 Objective: Extend the approaches developed in BP1 for ternary materials to design new doped materials with improved thermodynamic and kinetic properties for STCH
- ▶ EMN Node Utilization - provide critical information/feedback to all aspects of the project
 - **Task 2**: Thermodynamic evaluation of charged vs. neutral defects in perovskites in progress with **Stephan Lany at NREL**
 - Allows for the design of materials through both enthalpic and entropic contributions
 - **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, Eric Coker, James Park, and Andrea Ambrosini at SNL**
 - Stagnation flow reactor provides measurement of H_2 produced by new materials (GNG2)
 - Thermal analysis provides direct comparison for thermodynamic screening
- ▶ Our collaboration with Lany (NREL) and McDaniel 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.

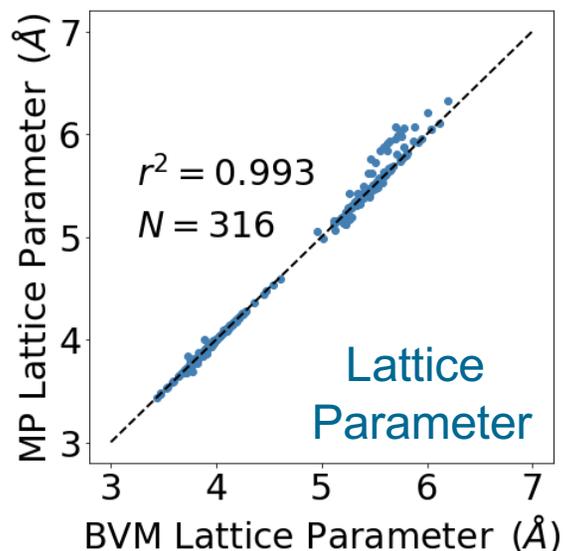


Accomplishments and Progress

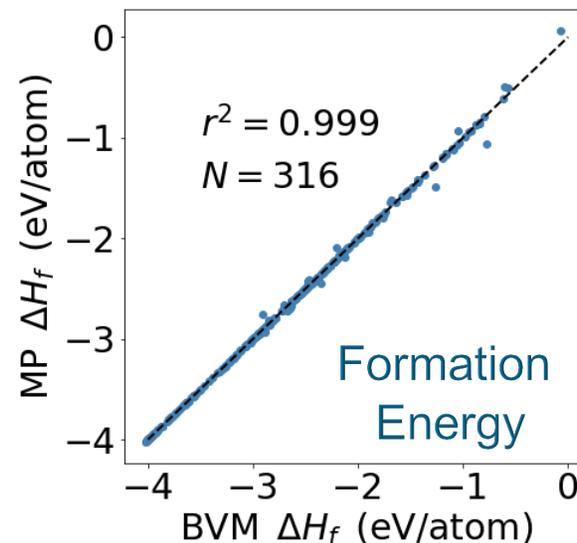
Bond Valence Method High Throughput Generation of Structures for DFT Calculations



$$\min(GII) = \min\left(\frac{\sum_{i=1}^N (d_i^2)}{N}\right)$$



By minimizing GII, accurate cubic perovskite oxide structures can be rapidly generated for high-throughput DFT calculations



Formation energies and lattice constants of 316 cubic ternary perovskites closely agree with Materials Project data

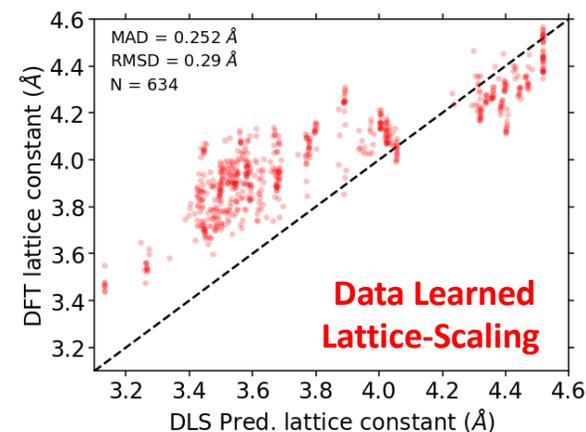
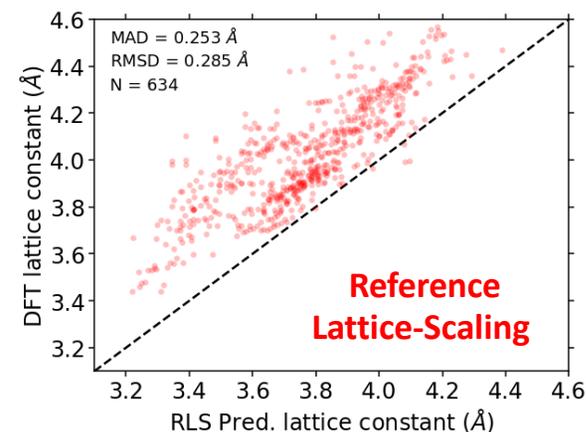
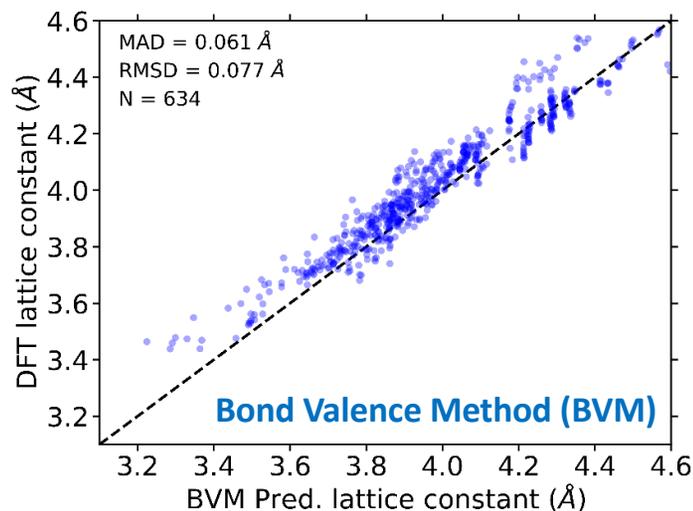
Using the Bond Valence Method (BVM), complex theoretical perovskites ($AA'BB'O_6$) can be accurately modelled and rapidly explored (M2.2.1)



Accomplishments and Progress

BVM structure prediction requires only composition as input and is significantly more accurate than traditional methods.

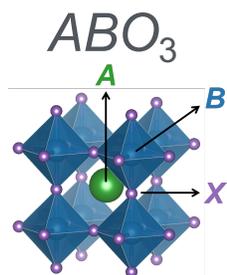
- 634 ternary perovskite oxides optimized using DFT and compared to BVM predicted structures
- Traditional lattice scaling and structural-prototyping predict structures with **RMSD = 0.29 Å**
- The BVM predicts cubic lattice constants much more accurately with **RMSD = 0.08 Å**
- Accurate cubic lattice constants are predicted using BVM however, structural distortions need to be accounted for



BVM shows significant improvement in structure prediction compared to traditionally used lattice scaling methods: RMSD = 0.08 Å vs. 0.29 Å



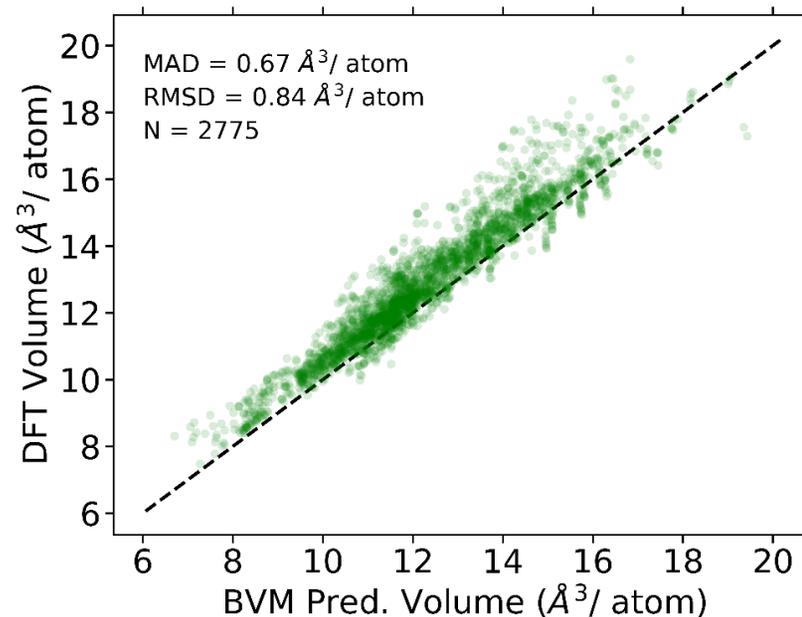
Accomplishments and Progress



Predicting Perovskite Distortions

- 634 materials (τ -stable/metastable)
- 8 common tilting systems
- BVM structure prediction requires only composition

Glazer Tilt System	Space Group	Crystal System	Expt. Frequency
a+a+a+	Im-3	cubic	22
a-b+a-	Pnma	orthorhombic	119
a-a-a-	R-3c	trigonal	24
a+b0c-	Cmcm	orthorhombic	6
a0b-b-	Imma	orthorhombic	6
a0a0c+	P4/mbm	tetragonal	5
a0a0c-	I4/mcm	tetragonal	9
a0a0a0	Pm-3m	cubic	21



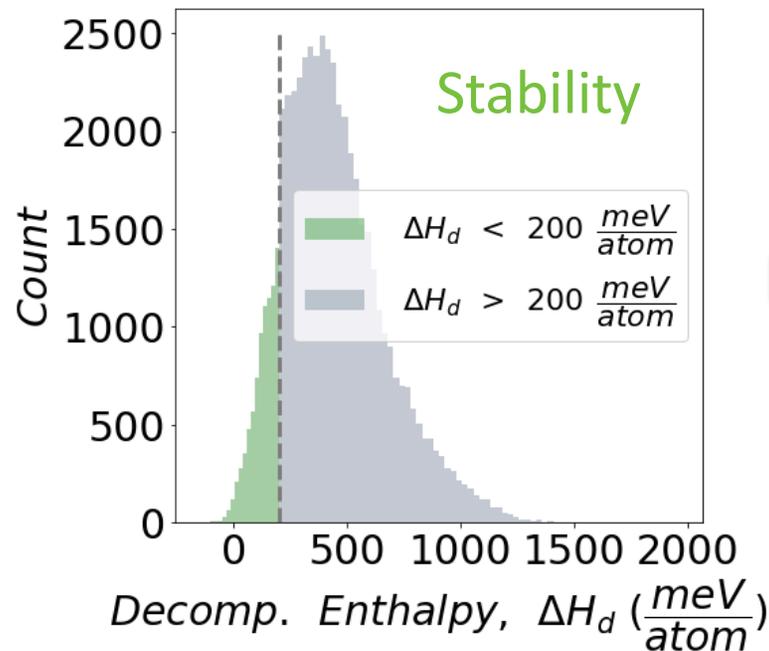
- GII BVM-based minimizations performed on DFT optimized geometries to preserve distorted symmetries
- Volume comparisons provide estimate of structural dissimilarity

BVM accurately predicts distorted ternary perovskite structures with RMSD = 0.84 Å³/atom

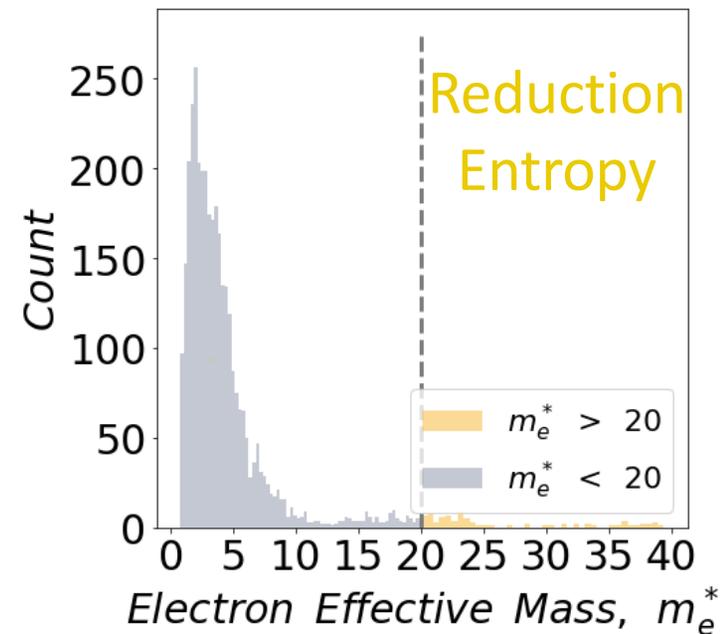


Accomplishments and Progress

High-Throughput Screening: Stability and Reduction Entropy



DFT relaxations on > 50,000 BVM generated structures ~7,700 stable structures ($\Delta H_{\text{decomp}} \leq 200$ meV/atom)



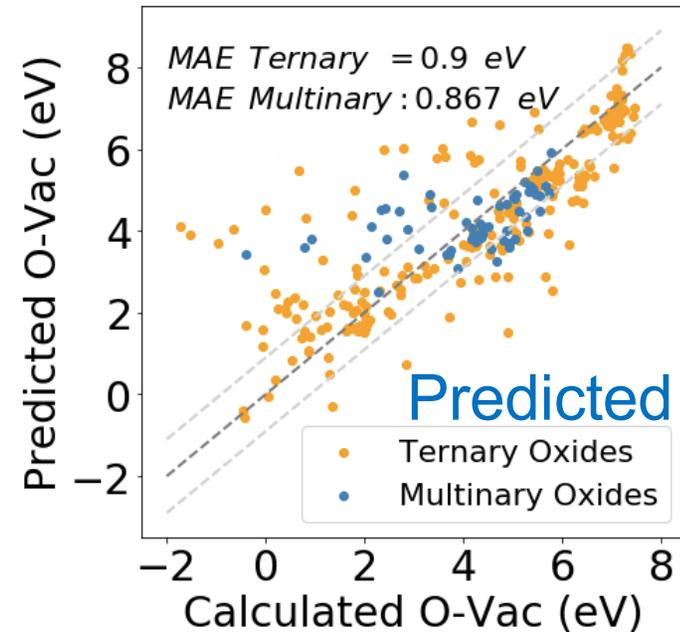
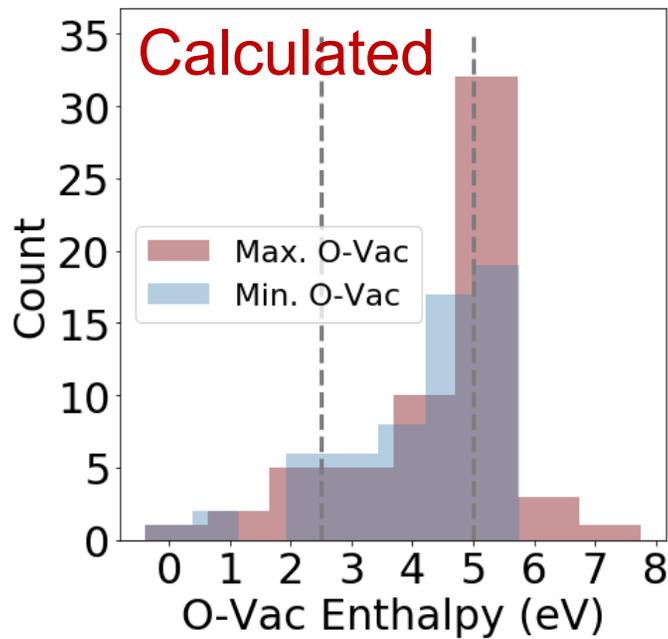
Reduction entropy estimated using effective mass descriptor
76 materials with $m_e^* \geq 20$

~7,700 stable multinary oxides identified from DFT calculations (M2.1.3, M2.2.1)
76 candidates identified with high effective mass/electronic entropies (M2.1.3, M2.2.1)



Accomplishments and Progress

Vacancy Enthalpies: Calculations and Regression Model Predictions



- Oxygen vacancies calculated for all unique O sites in 76 candidates with high m_e^*
- ~40 oxides within STCH active range (2.4 – 5 eV)
- **NREL Node Collaboration**
- Regression model trained on ternary perovskites oxides predicts the vacancy formation enthalpies of multinary perovskites with similar MAE
- Developing ML model for improved accuracy

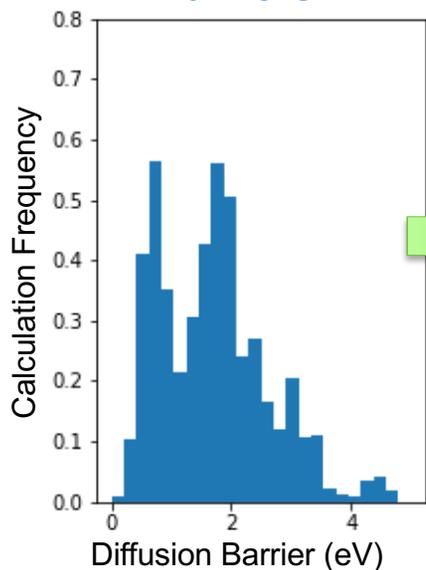
~40 stable oxides with high m_e^* have vacancies within STCH active range (M2.1.3, M2.2.1)

Regression model enables rapid screening of >100,000 multinary compositions without performing DFT defect calculations (although accuracy needs improvement)

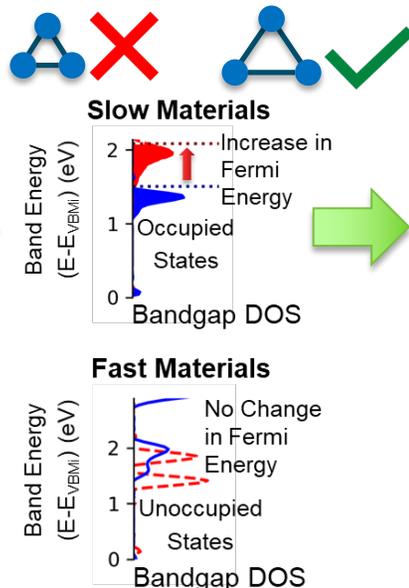


Accomplishments and Progress

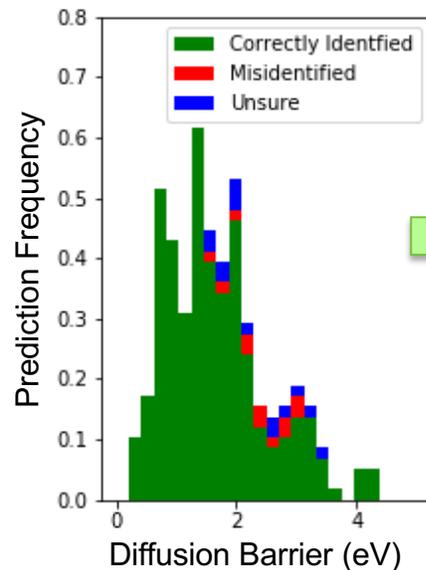
Calculated Diffusion Barriers



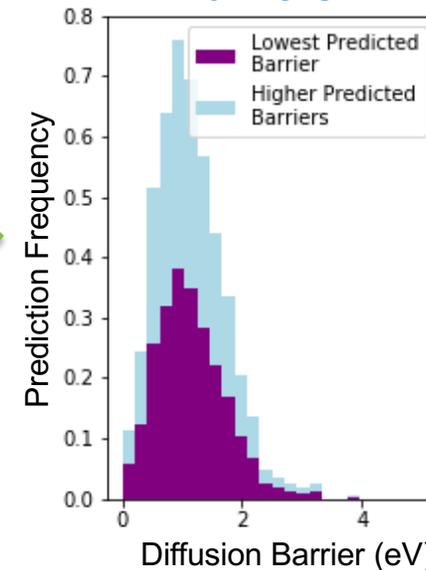
Developed ML Model



Benchmarked Model



Predicted Diffusion Barriers

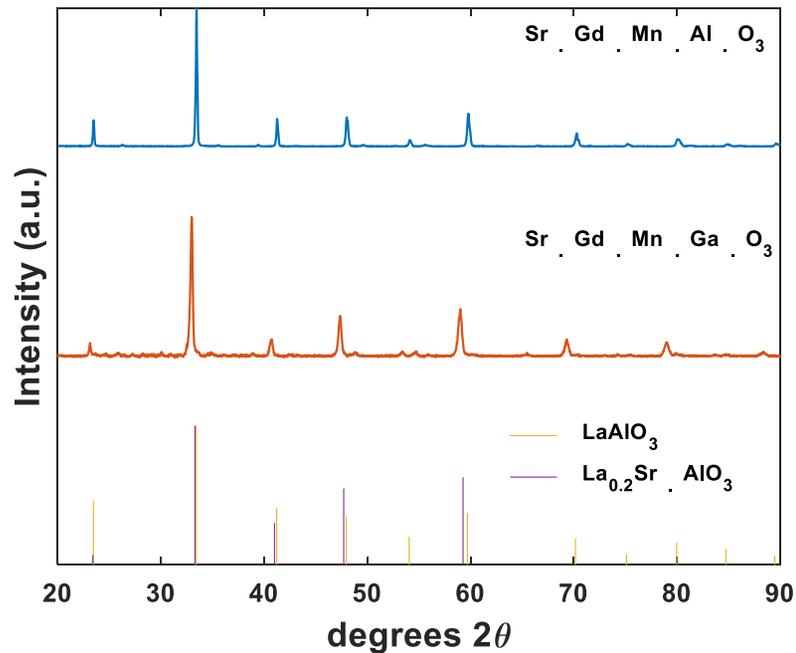


- Studied > 500 diffusion pathways in > 90 unique spinel and perovskite materials
- Developed machine learned model to profile kinetic behavior based on properties from only the bulk unit cell
- Able to distinguish between fast and slow materials with 91% - 96% accuracy
- Enables rapid kinetic screening of STCH materials (~1000 materials shown)

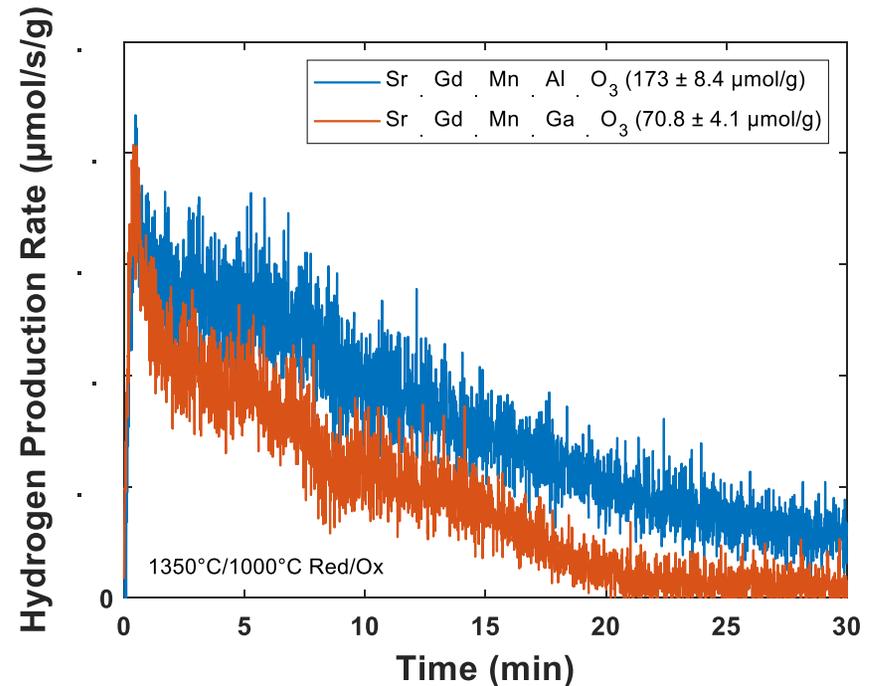
**Machine-learned model for diffusion barriers from simple bulk properties
Distinguishes between fast and slow materials with < 10% failure rate (M3.3.1)**



Accomplishments and Progress



- Synthesized two Gd-based perovskites identified with DFT
- $\text{Sr}_{0.4}\text{Gd}_{0.6}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$ and $\text{Sr}_{0.4}\text{Gd}_{0.6}\text{Mn}_{0.6}\text{Ga}_{0.4}\text{O}_3$ are cubic perovskites [space group Pm-3m (221)]



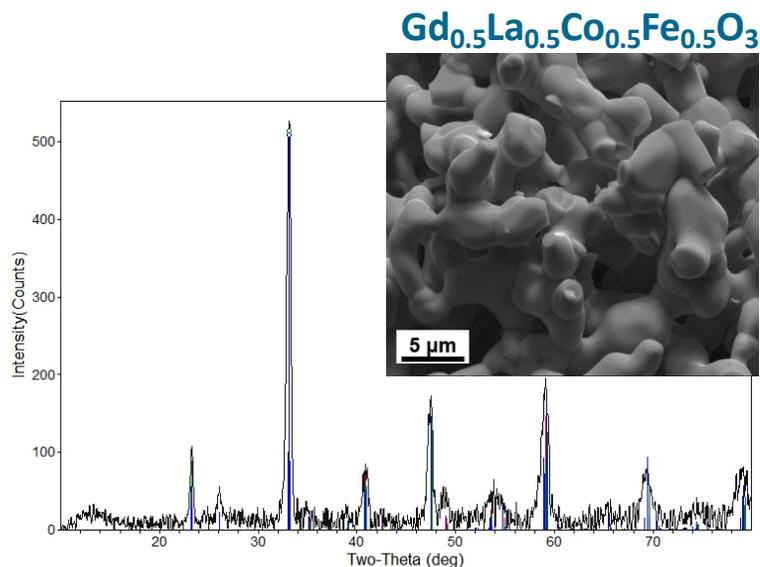
- Both materials shown to split water in CU SFR with 1350°C reduction, 1000°C oxidation
- Materials sent to SNL for further thermodynamic and kinetic evaluation

Materials identified with DFT shown to split water at 1000°C (M4.1.1)



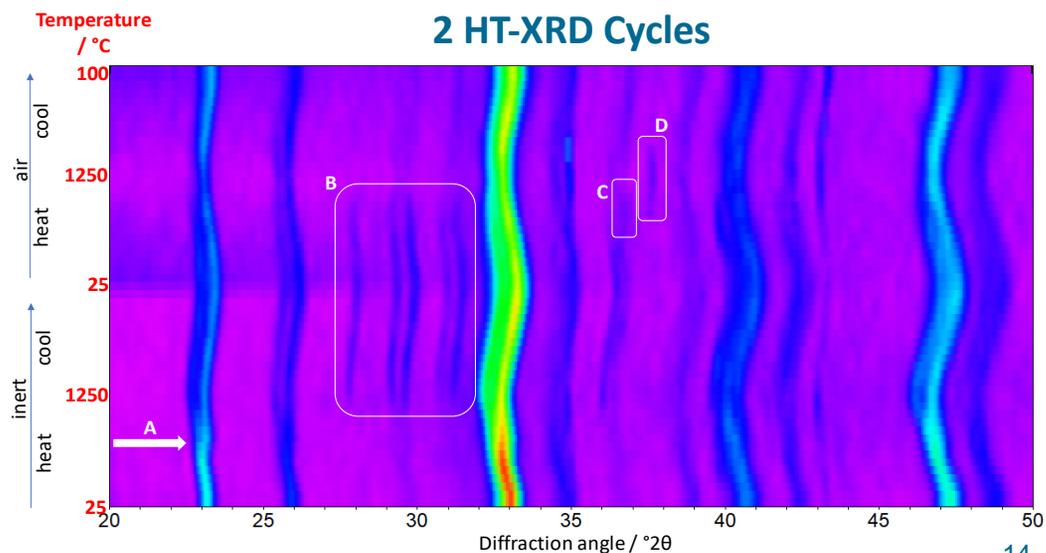
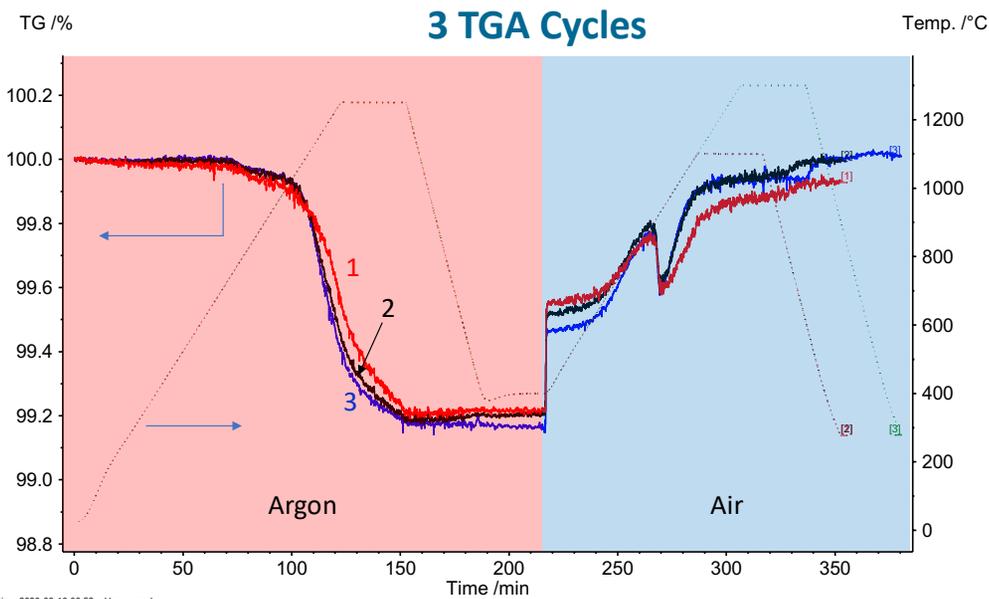
Accomplishments and Progress

SNL Node Collaboration



- 3 additional materials identified with DFT being synthesized/tested at SNL
- $Sr_{0.4}Gd_{0.6}Co_{0.5}Fe_{0.5}O_3$ successfully synthesized and tested with TGA and HT-XRD

Materials successfully cycled in air with repeatable redox behavior. SFR tests ongoing





Response to Reviewers' Comments

- ▶ There is a strong need to vet the computations with experiments as a next step.
 - Agreed and addressing, but with lab closure delays
- ▶ The approach to performing the work is technically sound, but the project needs to do more work around the value of STCH, even if amazing catalysts are found.
 - Project scope can expand when/if superior redox mediators are identified.
- ▶ The reduction in maximum temperature is very modest.
 - As better materials are discovered, we'll push the largest reduction in T that is practical.
- ▶ However, the applied methodology is far away from any application of the described materials, and therefore the impact on the \$2/kg hydrogen goal is very indirect.
 - We disagree. The methods directly target the underlying properties that determine H₂ production costs.
- ▶ STCH is not particularly relevant to the development of the hydrogen economy.
 - This is an open question and multiple H₂ production technologies should be developed in parallel. Discovery of new redox materials key to success of STCH.
- ▶ Conspicuous by its absence is the TEA work that was flagged for the National Renewable Energy Laboratory (NREL); this is mentioned, but no results are reported.
 - This has been delayed to await discovery of promising materials to conduct TEA on.
- ▶ ...it is not clear what the status is of Task 4, the SFR work at SNL.
 - Collaboration continues, but delayed due to lab closures and effort to develop better approaches for predicting promising materials. Plan is to ramp up significantly during BP3.



Response to Reviewers' Comments

- ▶ The project as reported seems a little disconnected from the experimental stages, which will be critical for continued progress. This may be intentional on the part of the project lead, but compressing all of the experimental work may prove challenging.
 - Agreed. Collaboration is increasing significantly towards end of BP2 and into BP3.
- ▶ The final deliverable is purported to be less than 10% loss in hydrogen production capacity between 100 and 200 cycles. While this is certainly an early-technology-readiness-level project, it should have identified the absolute best candidates from the entire class of perovskites. Thus, with 10% capacity loss after only 200 cycles, the material is not adequate, and either a new material needs to be chosen (which should have been chosen in the first place), or a process or engineering design needs to be devised to “save” the material from such a fate. The PI did recognize regeneration as a possibility, although he did admit it is a complex technoeconomic consideration.
 - While we agree with the general comment, the enormity of the challenge of screening materials from a huge number of candidates for very difficult to predict properties makes our goals appropriate for the TRL, scope of the project and challenge of these problems.
- ▶ Validation is not the major topic of the project. A closer link to validating efforts would strengthen the project.
 - Agreed and increased experimental collaboration is planned.
- ▶ The coupling of the computations to the experiments was not convincingly demonstrated. It was unclear what new materials were actually synthesized and tested. The temperature reduction goals are modest.
 - This is increasing but was hampered by lab closures.
- ▶ The commercial context, path forward, and ideas for improved hardware and software are unclear.
 - Agreed, but what is expected for this TRL.
- ▶ The value of STCH is questionable.
 - Yes, this is an open question and expected for this TRL.

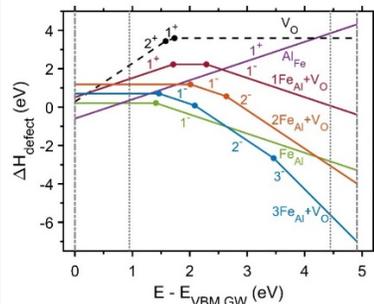


Collaboration: Effectiveness

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

Task 2: Thermodynamic Screening

Collaborator: NREL – Stephan Lany
First Principles Materials Theory

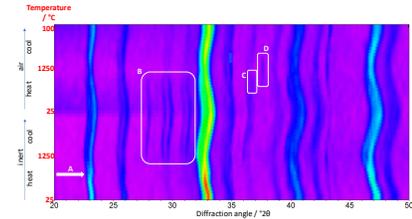


- Key partner in developing an understanding of the role of charged defects
- Critical for incorporating entropy engineering into material design
- Bi-weekly meetings w/ multiple team members

Task 4: Experimental Testing

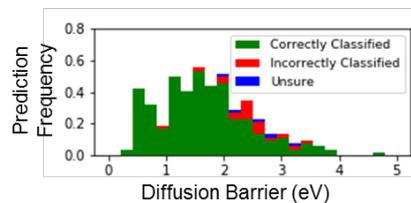
Collaborator: SNL – Eric Coker
HT-XRD and Thermal Analysis

- Analysis will allow for direct comparison between experiments and computation
- Provides feedback for NREL node for understanding entropic contributions and charged defects
- First Gd-based perovskite characterized with HT-XRD and TGA



Task 3: Kinetic Screening

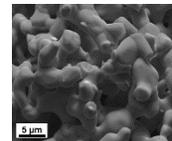
Collaborator: SNL – Tony McDaniel
Laser Heated Stagnation Flow Reactor



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

Collaborator: SNL – Andrea Ambrosini, James Park
Material Synthesis

- Assisting in the development of synthesis routes for complex perovskites
- One perovskite synthesized, two others in process



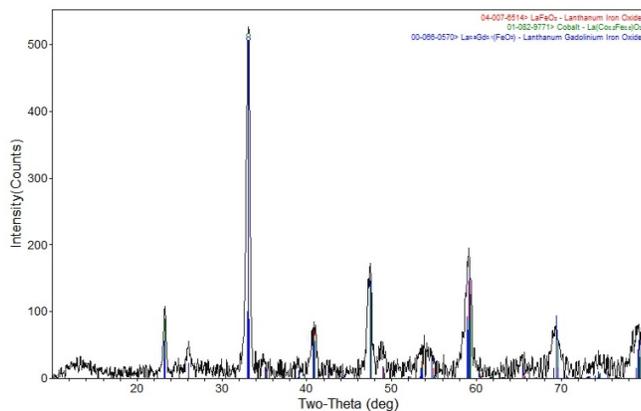
Collaborator: SNL – Tony McDaniel
Laser Heated Stagnation Flow Reactor

- Key partner for experimentally demonstrating H₂ production and kinetics of new materials (GNG2)
- Materials have been sent to SNL for testing



Remaining Challenges and Barriers

- ▶ Experimental testing delayed due to COVID-19
 - Computational screening has continued as planned and list of candidate materials has been further refined to make experimental testing more efficient/productive.
 - Experimental effort was ramping up during most of BP2, but delayed by 2.5 months due to lab closures. Experiments resume ~May 26/June 1.
- ▶ Synthesizing phase-pure compounds can be challenging
 - Kinetic factors and unknown competing phases may be present
 - Utilizing SNL node to assist in the synthesis of difficult compound





Proposed Future Work

Remainder of FY 2020

- ▶ Add calculated multinary perovskite database to Materials Project – enables open-source access to DFT calculations
- ▶ Continue high-throughput DFT calculations from BVM predicted structure to screen for thermodynamic viability
- ▶ **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 $< 1400 \text{ C}$ which loses less than 10% of its H_2 production between $\text{cycles } 50 \text{ and } 100$) and with improved kinetic properties (reaches 80% of equilibrium H_2 production within 10 minutes). Oxidation will either be operated at $H_2O:H_2$ ratios of less than 1000:1 or a TEA will be conducted to verify that higher $H_2O:H_2$ ratios are economically practical with the new material.

FY 2021

- ▶ Computationally screen doped perovskites to tune materials for thermodynamic viability (M2.2.1)
- ▶ Develop perovskite-specific application in conjunction with Materials Project – enables open-source development of perovskite-specific machine-learning models
- ▶ Continue development of descriptors for predicting electronic entropy
- ▶ Utilize ML model for diffusion to identify promising dopants for improving STCH kinetics (M3.4.1)
- ▶ **Final Deliverable:** Demonstrate the performance of a doped material with improved thermodynamic and stability properties (H_2 production above $300 \mu\text{mol/g/cycle}$ at reduction temperatures $< 1400^\circ \text{ C}$ which loses less than 10% of its H_2 production between $\text{cycles } 100 \text{ and } 200$) and a material with improved kinetic properties (reaches 80% of equilibrium H_2 production within 7 minutes). Oxidation will either be operated at $H_2O:H_2$ ratios of less than 1000:1 or a TEA will be conducted to verify that higher $H_2O:H_2$ ratios are economically practical with the new material.

Any proposed future work is subject to change based on funding levels.



Project Summary

Approach: Utilize machine learning models coupled with *ab initio* screening and experiments to accelerate the RD&D of new STCH materials

Accomplishments:

▶ Task 1: Machine Learning

- A linearly regressed model was able to predict the oxygen vacancy enthalpies of multinary oxides, as well as those of ternary oxides, within similar error ranges – **will enable rapid screening of oxygen vacancy enthalpies in complex perovskites**

▶ Task 2: Thermodynamic Screening

- Rapidly generated > 830,000 structures (> 120,000 compounds) using bond valence method (BVM) and performed computed DFT energies of > 50,000 compounds – **BVM enable the rapid relaxation of candidate materials using DFT**
- Identified ~7,700 stable multinary perovskite oxides and selected ~70 STCH candidates based upon their effective mass. ~40 candidates have vacancies within the STCH active range, suggesting these materials could exhibit STCH activity

▶ Task 3: Kinetic Screening

- Developed machine-learned model to calculate diffusion barriers from unit cell properties – **will enable screening based on kinetics**

▶ Task 4: Material Testing

- New doped Gd-based perovskites shown to split water at $T_{\text{red}} = 1350^{\circ}\text{C}$ and $\Delta T = 350^{\circ}\text{C}$ (GNG2)

Collaborations: Collaborating with NREL on computational screening of materials with high reduction entropy and SNL on experimental synthesis, characterization, and STCH testing of new materials