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
June 13, 2018

Project ID #PD166

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NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

Project Overview

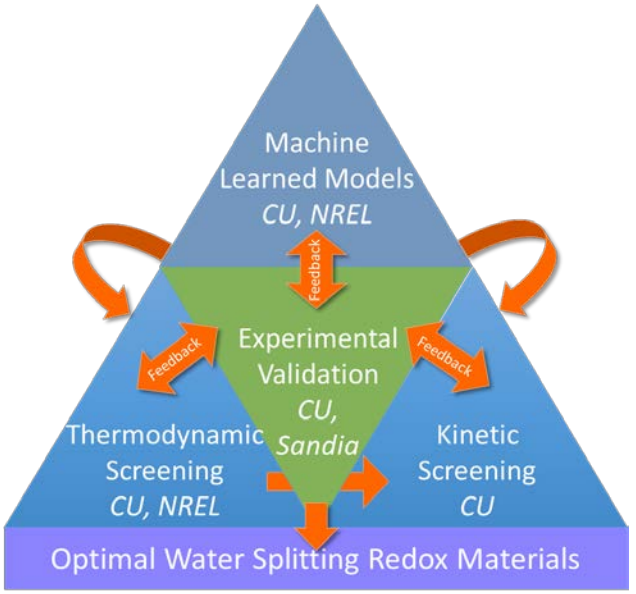
Project Partners

PI: Charles Musgrave, University of Colorado
Co-PI: Alan Weimer, University of Colorado
SP: Aaron Holder, University of Colorado, NREL

Award #	EE0008088
Start Date Yr 1 End Date Project End Date	10/01/2017 9/31/2018 TBD
Total DOE Share Total Cost Share Year 1 DOE Funding*	$999,907 $111,363 $248,818

Project Vision

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)*

Approach- Summary

Project Motivation

This project builds on prior collaborative computational and experimental work at CU Boulder which demonstrated the viability of new spinels for STCH. This project 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 µmol/g (1500°C/1000°C)*	*200 µmol H_2/g*
Temperature	$T_{RED} \geq 1500°C$ $\Delta T \geq 700°C$	$T_{RED} \leq 1450°C$ $\Delta T \leq 400°C$

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

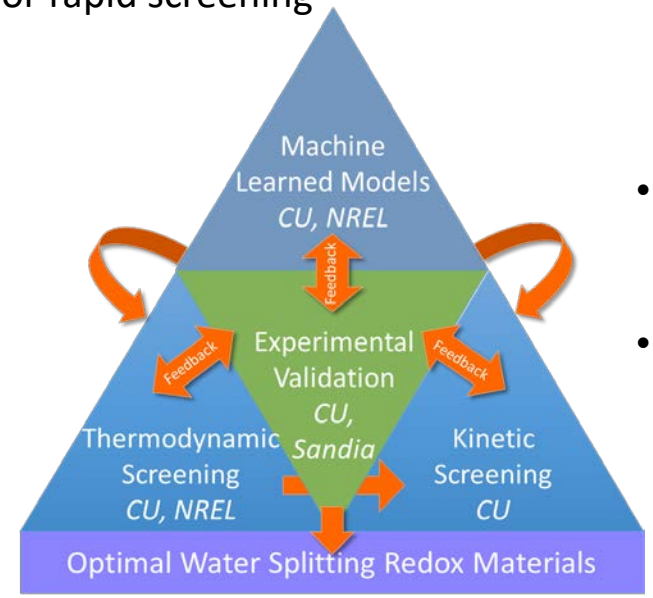
Utilize machine-learned models coupled with *ab initio* thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials

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***

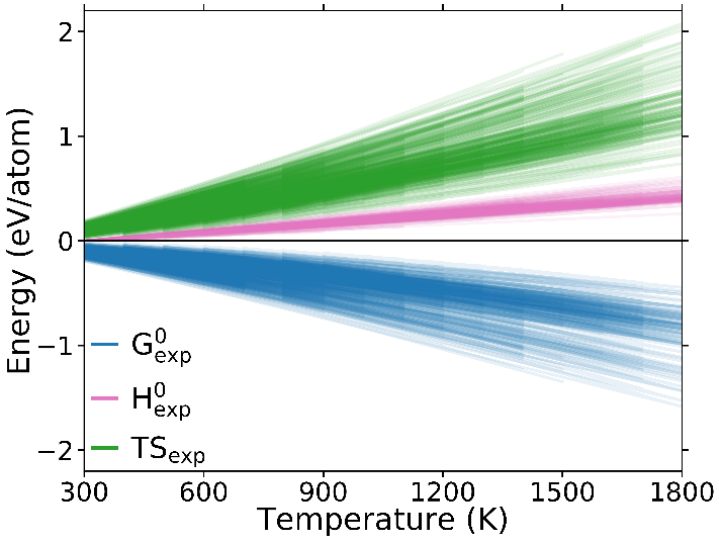
Task 4: Experimental demonstration of active materials

- 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 >200µmol H_2/g/cycle at T_{red}<1450°C and ΔT<400°C whose relative thermodynamic and kinetic performance matches that predicted by computational models

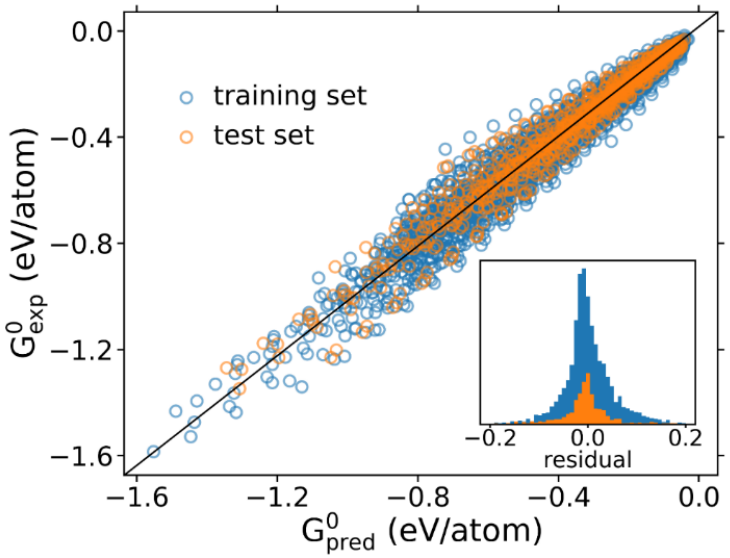
Relevance & Impact

- DOE Hydrogen and Fuel Cells Program goal of <$2/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 datato benchmark against and a deeper understanding of what materials properties correlate with better STCH performance.

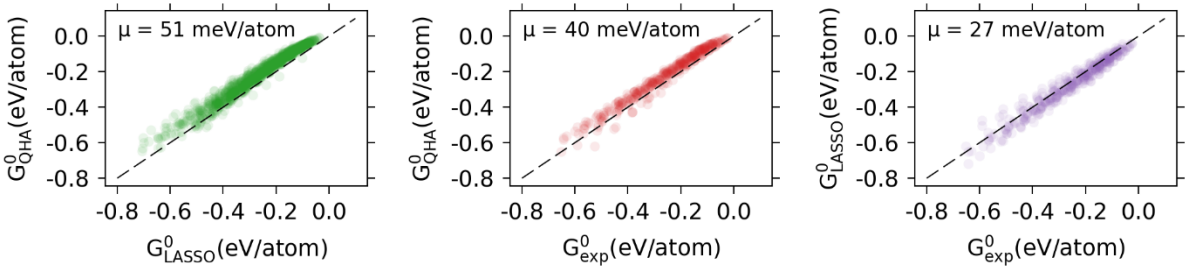
Accomplishments



- 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



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



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

NREL Node Collaboration

$G^0(T)$ predicted with MAE = ~40 meV/atom (on excluded test set) up to 1800 K - will enable rapid screening materials based on stability (M1.1.1 – M1.3.1)

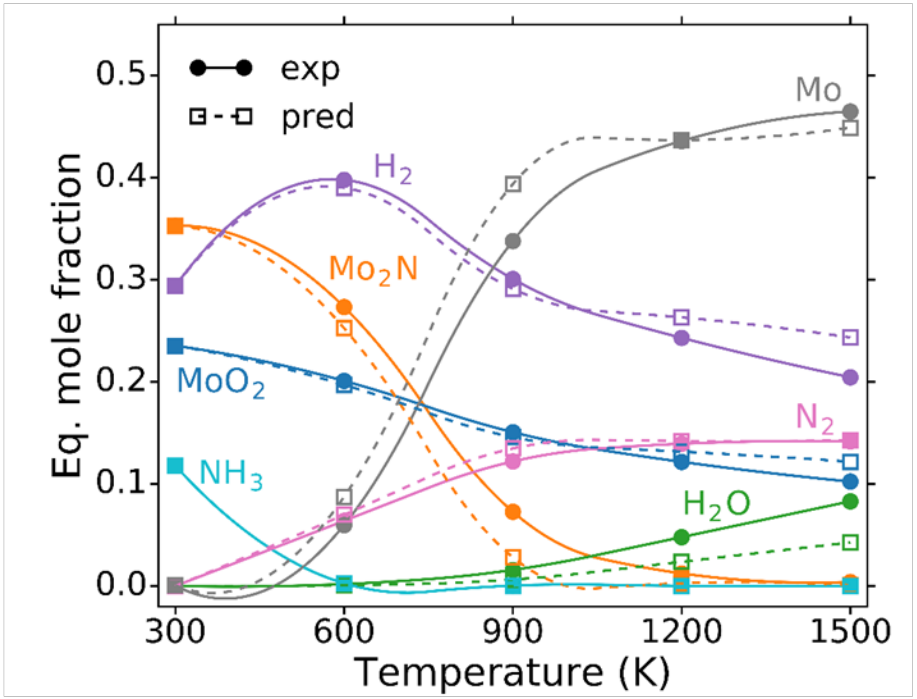
Accomplishments

$$Mo_2N + 4H_2O \leftrightarrow 2MoO_2 + NH_3 + 2.5H_2$$

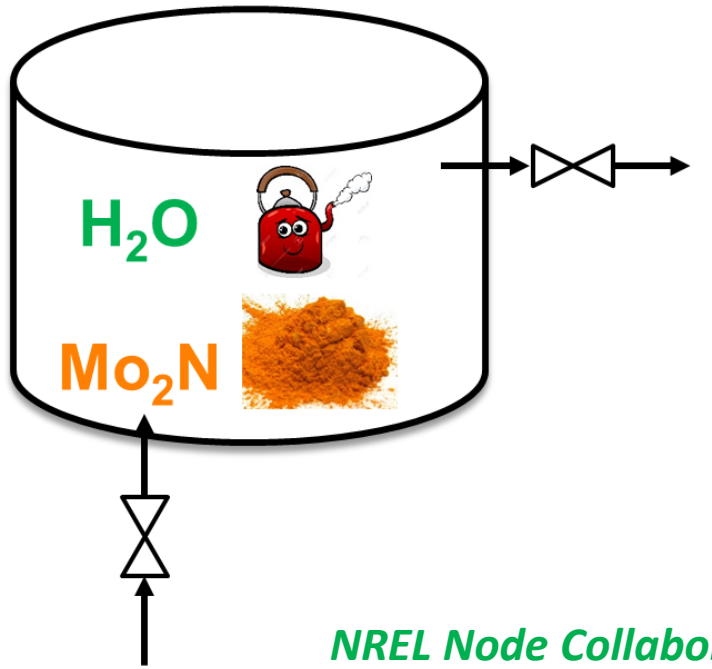
$$2Mo + 0.5N_2 \leftrightarrow Mo_2N$$

$$NH_3 \leftrightarrow 0.5N_2 + 1.5H_2$$

$$MoO_2 + 2H_2 \leftrightarrow Mo + 2H_2O$$



Simulated equilibrium using Gibbs energy minimization in virtual reactor



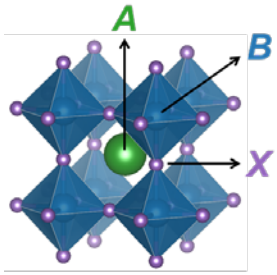
NREL Node Collaboration

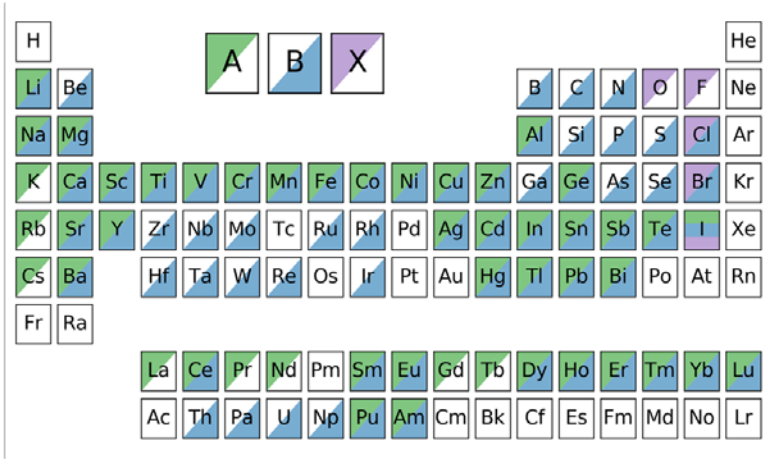
Descriptor enables high-throughput predictions of reaction energetics and thermochemical equilibrium (M1.1.1 – M1.3.1)

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[1]
- Rapid search across 10^9-10^{11} potential descriptors
- Targets low-dimensional expressions
- Maximizes interpretability
- Established accuracy and ideal bounds for Goldschmidt factor

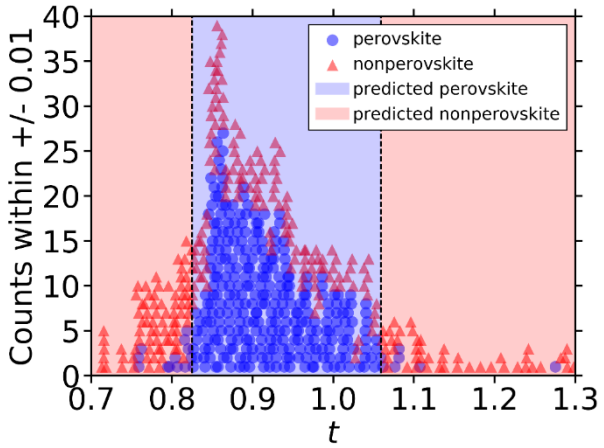
Developed descriptor with 92% accuracy for predicting perovskite stability – New 1st screening step to reduce number of DFT calculations (M1.1.1 – M1.3.1)





V. Goldschmidt 1926

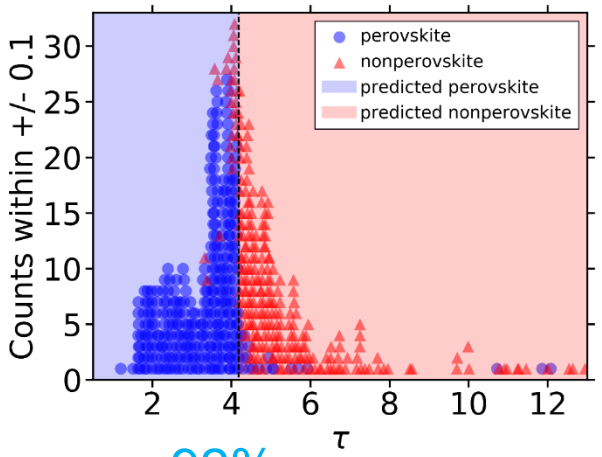
$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$



74% accuracy

Bartel *et al.* 2018[2]

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



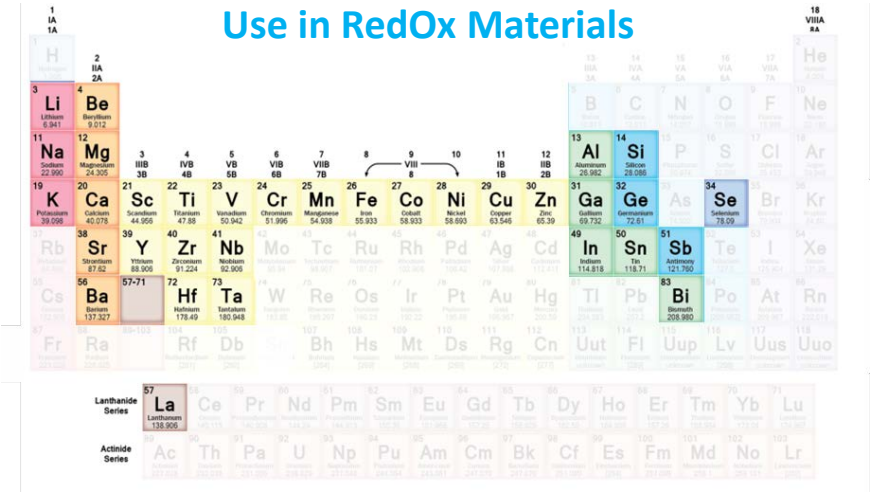
92% accuracy

[1]R. Ouyang, S. Curtarolo, E. Ahmetcik, M. Scheffler, L. Ghiringhelli, arXiv:1710.03319

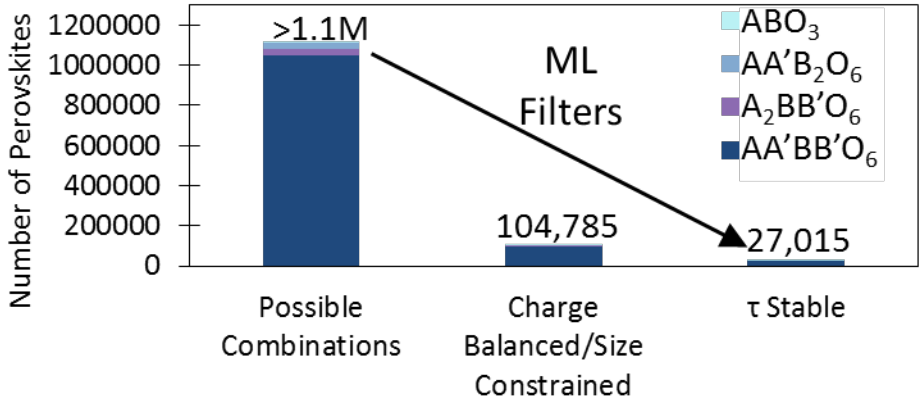
[2]C. Bartel, C. Sutton, B. Goldsmith, R. Ouyang, C. Musgrave, L. Ghiringhelli, M. Scheffler, arXiv:1801.07700

Accomplishments

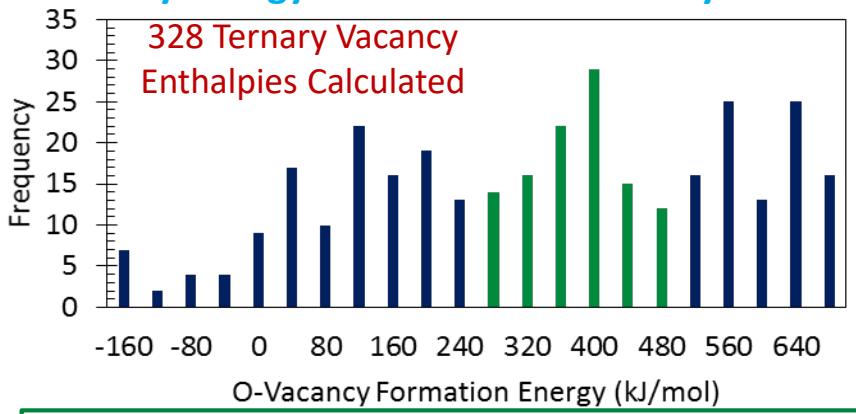
Elements Considered for Use in RedOx Materials



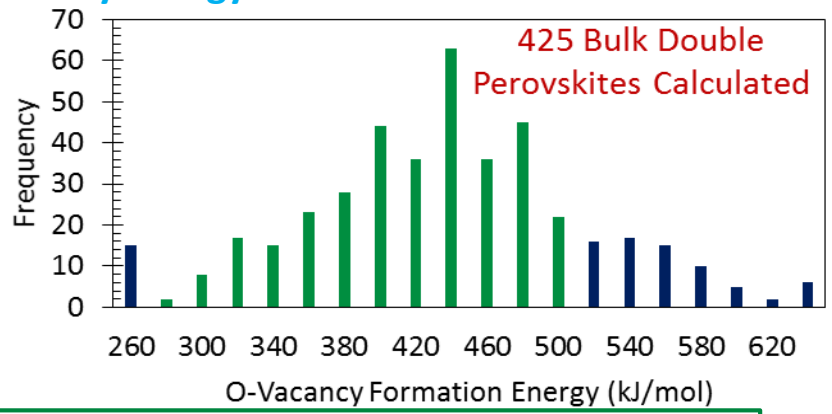
ML filter for perovskite stability significantly reduced number of computationally expensive DFT calculations



Vacancy Energy Distribution in Ternary Perovskites

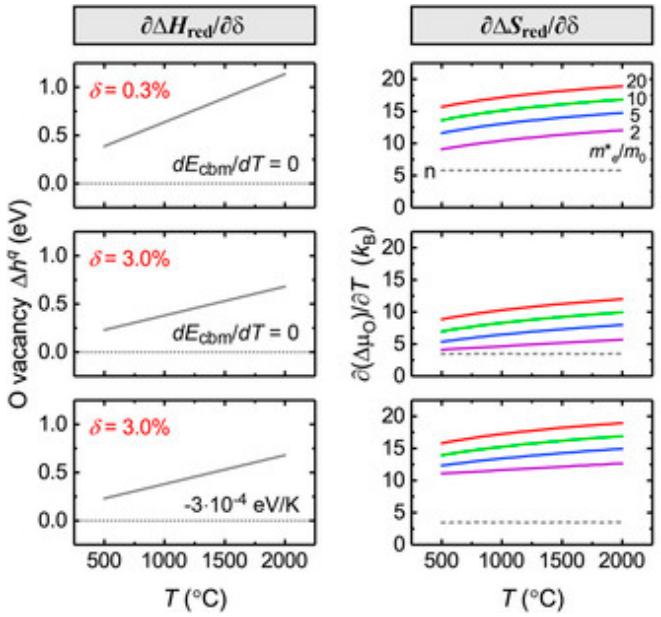


Vacancy Energy Distribution in Double Perovskites



>1.1 M perovskites filtered to 27,015 materials to be screened (M2.1.2)
ML predicted 116 ternary perovskites are stable with E_v that may drive STCH (M2.1.4)
425 double perovskites ($A_2BB'O_6$) screened for STCH using E_v model (M2.2.1)

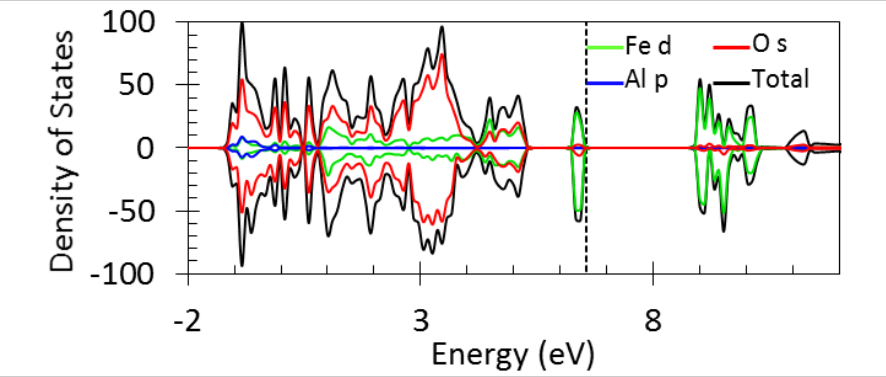
Accomplishments

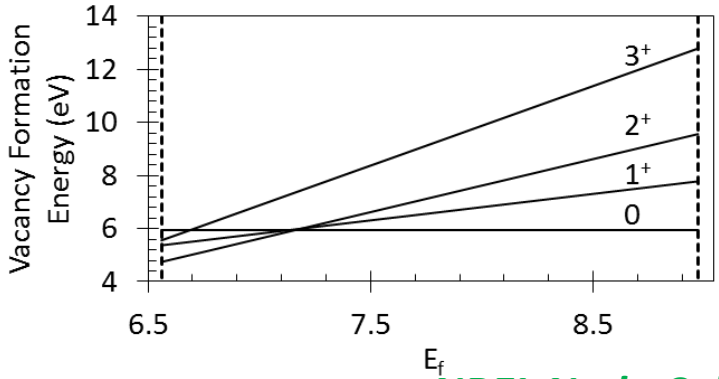


S. Lany. *J Chem Phys.* **148,** 071101 (2018)

Study of Charged O Vacancies

- Electronic entropy of charged defect formation has been demonstrated by S. Lany to **significantly impact predicted STCH behavior**
- Evaluated charged defect formation in hercynite
- Identified isolated band near Fermi level in hercynite – not found in other transition metal aluminates
- Large electronic entropy from charged defects and isolated Fermi band may play a role in improving hercynite performance over other spinel aluminates – to be tested through **SNL Node Collaboration**

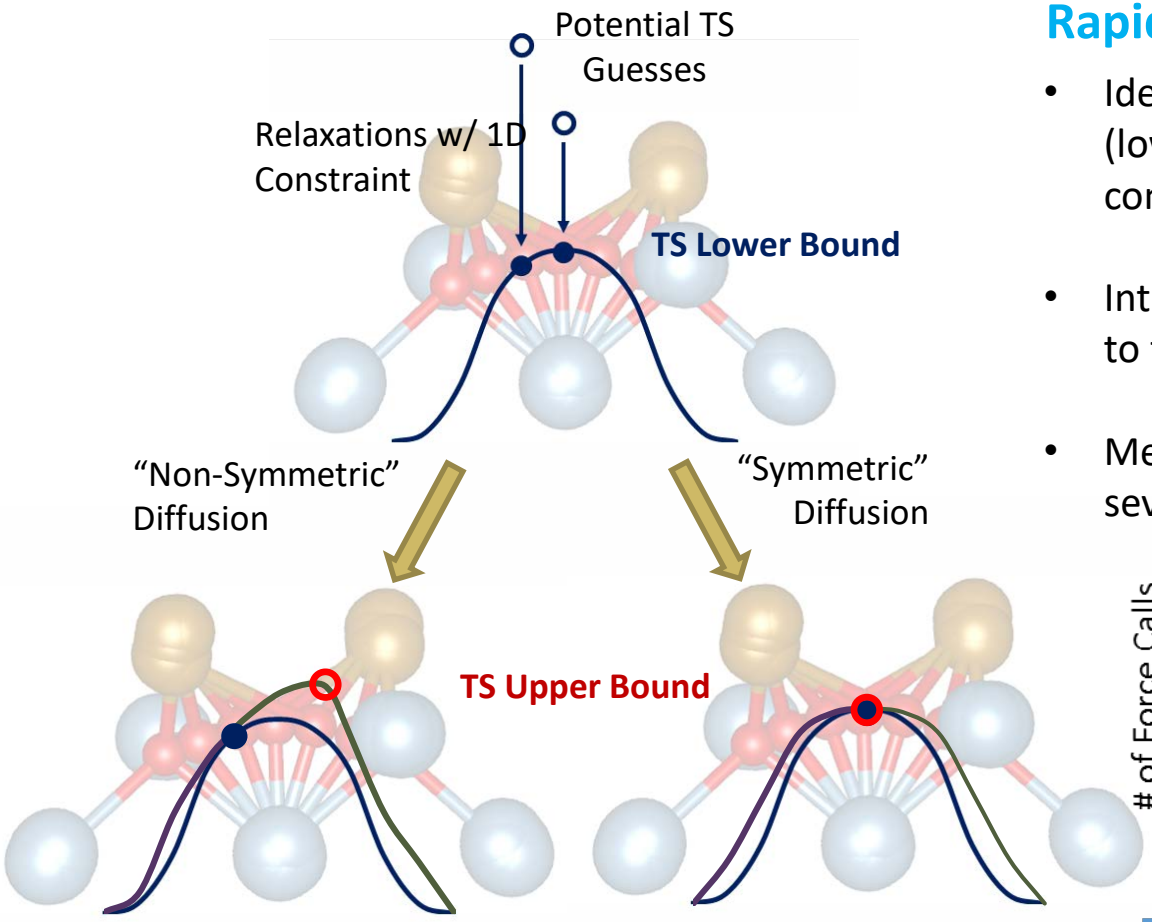




NREL Node Collaboration

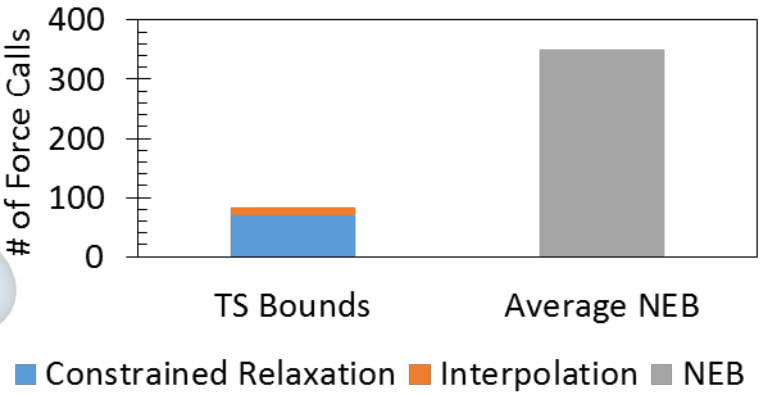
Enhanced understanding of defect formation in spinels shows that more advanced descriptors are required for accurate thermodynamic screening (M2.1.3)

Accomplishments



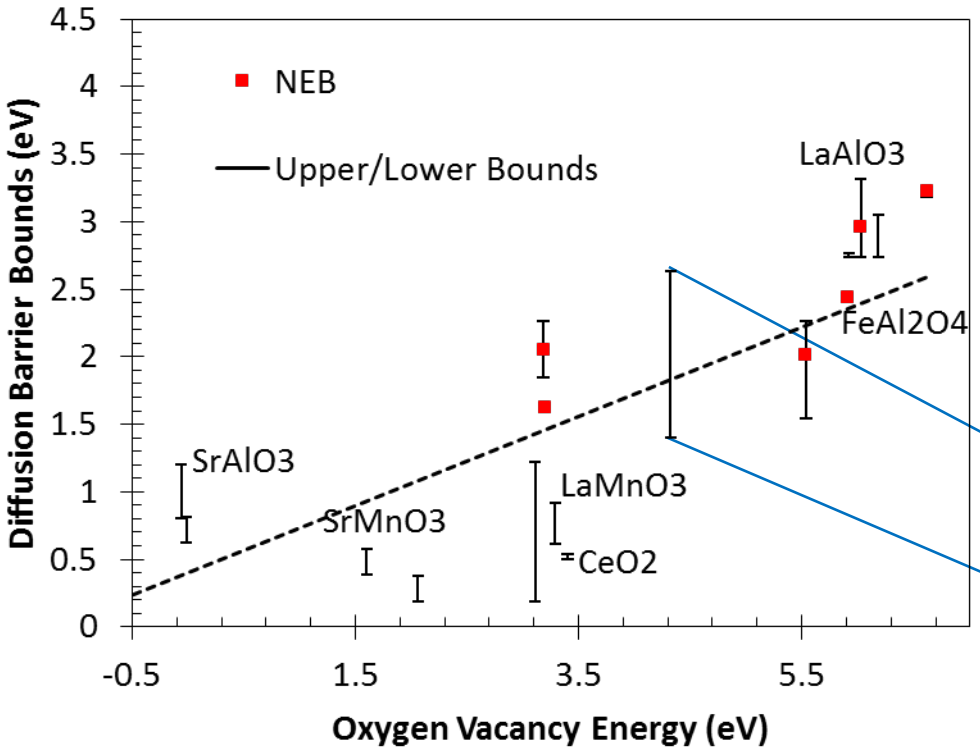
Rapid TS Search for Kinetic Screening

- Identify point on minimum energy pathway (lower bound for transition state) through constrained geometry optimization near TS
- Interpolate to/from this point on the MEP to find an upper bound for the TS
- Method is approximately 5x faster than a seven image NEB TS calculation



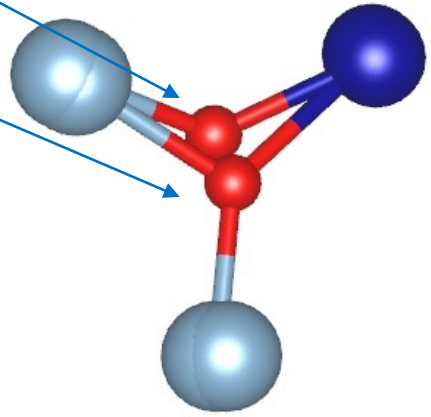
Developed a 5x faster method to rapidly screen the kinetics of new STCH materials – will greatly accelerate materials screening based on kinetics (M3.2.1)

Accomplishments



Rapid TS Search for Kinetic Screening

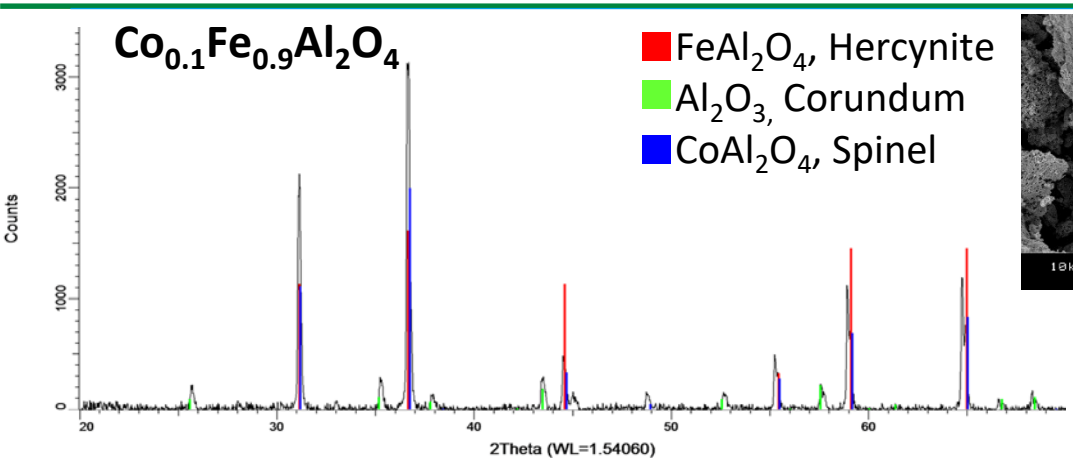
- Results of computationally expensive NEB calculations always within calculated bounds of rapid TS identification
- Diffusion barrier is correlated to oxygen vacancy energy
- Full NEB TS search can be initialized from rapid TS geometries when bounds are not tight

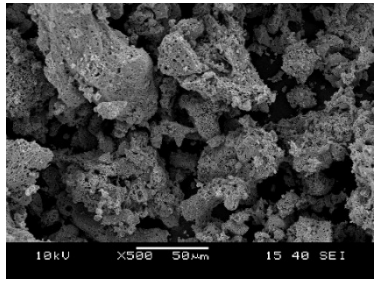


Composite Image of Reaction Geometries

Rapid approach for identifying bounds on the kinetic barriers matches computationally expensive calculations. New approach enables high-throughput kinetic screening (M3.2.1)

Accomplishments

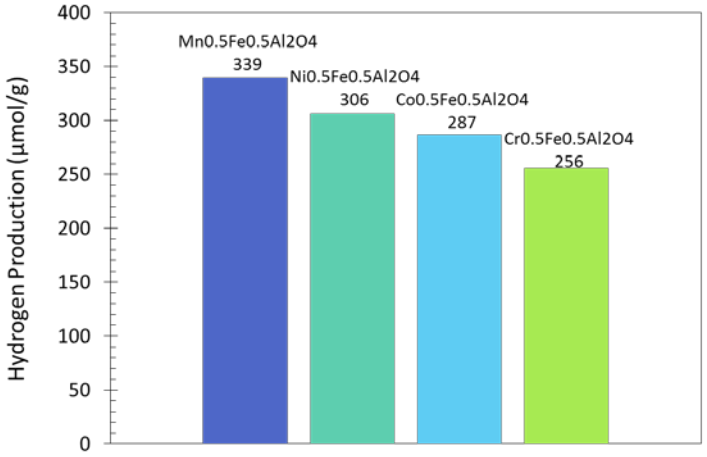


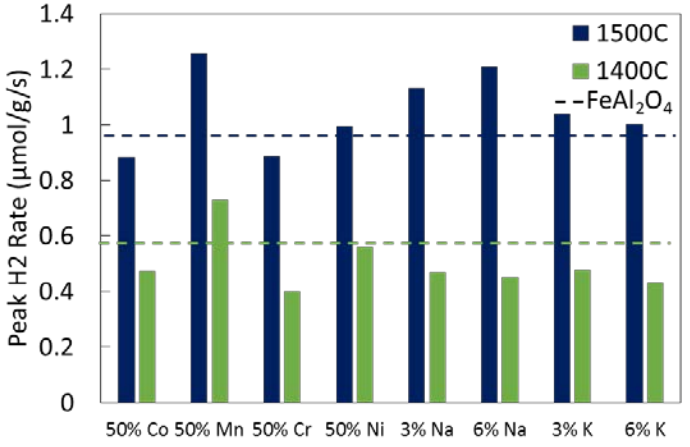


	ICP Molar Ratio	Target Ratio
Co	0.11	0.11
Fe	1	1
Al	1.78	2.22

Materials synthesized with citrate gel method and characterized with XRD, ICP, and SEM

- Water splitting experiments conducted in SFR with 5 Cycles at 1450°C reduction, 1200°C oxidation





Four materials produced > 200 µmol/g at T_{red}=1450°C (M4.1.1, GNG1)
$Mn_{0.5}Fe_{0.5}Al_2O_4$ shows the highest H_2 production of TM hercynite alloys and improved peak rate over undoped hercynite

Accomplishments

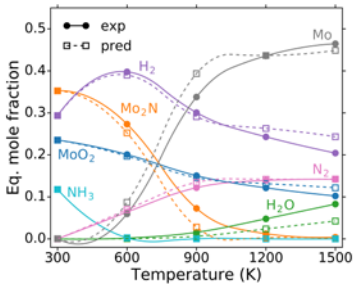
- Go/No-Go
  - Experimentally demonstrate 3 materials with >200µmol H_2/g/cycle at T_{red}<1450°C and ΔT<400°C whose relative thermodynamic and kinetic performance matches that predicted by computational models
  - Three materials demonstrated with >200µmol H_2/g/cycle at T_{red}<1450°C and ΔT<400°C
  - Neutral defects computed; comparison of charged defects underway
  - Bulk kinetics of compounds computed; full surface reaction pathway calculations in progress
  - On track to meet go/no-go
- Significance
  - Demonstrated agreement between computationally predicted and experimentally measured H_2 production for both thermodynamic and kinetic properties
  - Allow for rapid, accurate screening of thermodynamic and kinetics of new materials

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

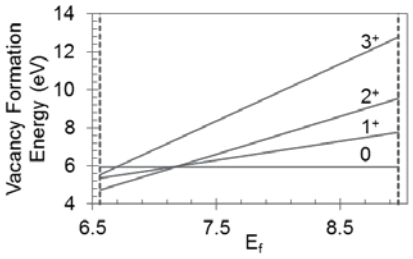
Collaborator: NREL – Stephan Lany – First Principles Materials Theory



- 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

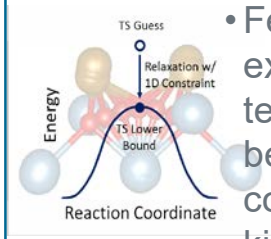
Collaborator: NREL – Stephan Lany – First Principles Materials Theory



- 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 meetings

Task 3: Kinetic Screening

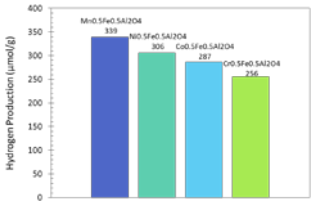
Collaborator: SNL – Tony McDaniel – Laser Heated Stagnation Flow Reactor



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

Task 4: Experimental Testing

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



- Key partner for experimentally demonstrating hydrogen production and kinetics of new materials (GNG1)
- Graduate student trained for 2 weeks for remote operation of equipment

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
- Testing parameters identified and materials sent to SNL for evaluation

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

Additional Collaborations Beyond EMN Nodes

Task 1: Machine Learning

Collaborators: Fritz-Haber-Institute Berlin

Matthias Scheffler – ML model τ for perovskite vs non-perovskite stability

Chris Sutton – ML model for predicting stability of different perovskite phases

Runhai Ouyang – Development of advanced ML methods for descriptor discovery

Luca Ghiringhelli – Application of SISSO ML method for descriptor discovery

Collaborators: Michigan

Brian Goldsmith – Machine learning for material properties prediction

Task 2: Thermodynamic Screening

Collaborators: NREL

Ann Deml – Thermodynamic descriptors for STCH

Bill Tumas – Descriptors for STCH thermodynamics

Vladan Stevanovic – Electronic structure calculations for thermodynamic STCH descriptors

Proposed Future Work

Remainder of FY 2018

- Identify the role of charged defects and associated electronic entropy in spinel aluminate STCH reactions (NREL node collaboration)
- Apply rapid bulk kinetic screening methods to surface reactions
- 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)

FY 2019

- 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 properties (H_2 production above 300 µmol/g/cycle) and a material with improved kinetic properties (reaches 80% of equilibrium H_2 production in 7 minutes)

FY 2020

- Objective: Computationally prototype doped metal oxides for thermodynamic and kinetic viability and experimentally demonstrate materials with improved H_2 productivity, reaction kinetics, and durability
- GNG3: Demonstrate a material with H_2 production above 400 µmol/g/cycle, which reaches 80% of equilibrium H_2 production in less than 5 minutes, and which loses less than 10% of its reactivity between cycles 100 and 200 at reduction temperatures at or below 1400° C

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

Project Summary

Mandatory Slide(s): 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 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 >200µmol H_2/g/cycle at T_{red}=1450°C and ΔT<400°C (M4.1.1, GNG1)
  - $Mn_{0.5}Fe_{0.5}Al_2O_4$ shows improved peak rate over undoped hercynite and highest H_2 production of alloyed materials (M3.1.1)

Technical Back-Up Slides