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

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Project Partners

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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)
### 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

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
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</thead>
<tbody>
<tr>
<td>Computational Validation</td>
<td>N/A</td>
<td>Matching expt and comp. thermo. and kinetic properties</td>
</tr>
<tr>
<td>H₂ productivity</td>
<td>Ceria: 130 μmol/g (1500°C/1000°C)</td>
<td>200 μmol H₂/g</td>
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<tr>
<td>Temperature</td>
<td>$T_{\text{RED}} \geq 1500°C$ $\Delta T \geq 700°C$</td>
<td>$T_{\text{RED}} \leq 1450°C$ $\Delta T \leq 400°C$</td>
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### 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
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.

**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.

**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.

- **GNG1**: Experimentally demonstrate 3 materials with >200µmol H₂/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 H₂**
  - 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 H₂ 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

- 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)

HydroGEN: Advanced Water Splitting Materials

NREL Node Collaboration
Accomplishments

Simulated equilibrium using Gibbs energy minimization in virtual reactor

\[ \text{Mo}_2\text{N} + 4\text{H}_2\text{O} \leftrightarrow 2\text{MoO}_2 + \text{NH}_3 + 2.5\text{H}_2 \]

\[ \text{NH}_3 \leftrightarrow 0.5\text{N}_2 + 1.5\text{H}_2 \]

\[ \text{MoO}_2 + 2\text{H}_2 \leftrightarrow \text{Mo} + 2\text{H}_2\text{O} \]

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

NREL Node Collaboration
HydroGEN: Advanced Water Splitting Materials

Bartel, Rumptz, Weimer, Holder, Musgrave, ACS Appl. Mater. Interfaces, Accepted (2019)
Accomplishments

- 576 $ABX_3$ solids classified experimentally as perovskite vs nonperovskite
- **Descriptor for perovskite stability** $\tau$ 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

V. Goldschmidt 1926

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

Bartel et al. 2019

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

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)


HydroGEN: Advanced Water Splitting Materials

NREL Node Collaboration
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

HydroGEN: Advanced Water Splitting Materials


NREL Node Collaboration
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 $\text{V}_{\text{O}}$ concentration by 3-4X.
- Degree of reduction strongly depends on cation stoichiometry, maximum Fe solubility 0.5 in spinel.

NREL Node Collaboration (Lany)
Study of Charged Vacancies and Defect Pairs in Cobalt Iron Aluminate Alloy

- **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 Spinels (M2.1.1 – M2.1.2)

**HydroGEN: Advanced Water Splitting Materials**
Accomplishments

- Applied TS model developed in BP1 to 23 unique spinels and perovskites
- Identified rate determining step for $\text{H}_2$ evolution reaction
- Kinetics of $\text{O}_2$ 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 $O_{\text{vac}}$ 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)
Utilize Machine Learning (ML) models coupled with ab initio thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials.

**Collaboration: Effectiveness**

**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 with 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 with 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**

- Key partner for experimentally demonstrating hydrogen production and kinetics of new materials (GNG1).

**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.
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 (H₂ production above 250 µmol/g/cycle at reduction temperatures < 1400°C which loses less than 10% of its H₂ production between cycles 50 and 100) and with improved kinetic properties (reaches 80% of equilibrium H₂ production within 10 minutes). Oxidation will either be operated at H₂O:H₂ ratios of less than 1000:1 or a TEA will be conducted to verify that higher H₂O:H₂ 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 \( \mu \)mol \( H_2/g/cycle \) at \( T_{red}=1450°C \) and \( \Delta T<400°C \) (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)
Publications:

Presentations:
Publications & Presentations (continued):