HydroGEN Seedling: Computationally Accelerated Discovery and Experimental Demonstration of High-Performance Materials for Advanced Solar Thermochemical Hydrogen Production

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Overall Objectives

- Utilize materials informatics and machine learning to computationally screen material stability and viability for solar thermochemical hydrogen (STCH) production.

- Validate the effectiveness of our materials-by-design approach by experimentally demonstrating materials with computationally predicted thermodynamic and kinetic properties.

- Apply machine learning techniques to computationally prototype new doped metal oxides rapidly for thermodynamic and kinetic viability and experimentally demonstrate materials with improved hydrogen productivity, reaction kinetics, and durability.

Fiscal Year (FY) 2019 Objectives

- Apply machine learning techniques to evaluate the viability of new doped metal oxides for STCH.

- Validate our material screening approach by demonstrating the performance of a doped material with improved thermodynamic and kinetic properties.

- Develop and utilize an accelerated pseudo transition state approach and machine-learned models to rapidly computationally screen materials for kinetic viability.

- Demonstrate a doped material with hydrogen production above 250 μmol H_2/g at reduction temperatures ≤1,400°C that reaches 80% of equilibrium hydrogen production within 10 minutes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Materials and Catalysts Development

- High-Temperature Robust Materials.

Technical Targets

This project is contributing progress towards meeting the DOE hydrogen production target for the "Annual Reaction Material Cost per TBD H_2" from the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan for solar-driven high-temperature thermochemical hydrogen production. This metric incorporates active material improvements through "decreased material usage, improved cycle time, and increased material lifetime." Specifically, this project is working towards the following goals to meet DOE targets:

- Hydrogen productivity: >00 μmol H_2/g

- Operating Temperature: T_{red} ≤1,400°C and ΔT ≤400°C

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- Cycle Times: <7 minutes for 80% of equilibrium hydrogen production

- Stability: <10% decrease in reactivity between cycles 100 and 200.

FY 2019 Accomplishments

- Demonstrated the use of a bond-valence prediction method for reducing the number and computational expense of density functional theory (DFT) calculations required for thermodynamic screening new perovskite structures.

- Evaluated the stability of over 2500 perovskite structures using DFT calculations and the bond-valence prediction method.

- Developed a machine-learned model to predict the activation barrier of oxygen diffusion which is 1,000 times faster than traditional transition state calculations and significantly accelerates the kinetic screening of new materials.

- Applied the kinetic barrier bounding method developed in Year 1 to determine the range of activation barriers for 270 charged neutral and 60 charged oxygen vacancy diffusion reactions.

- Conducted a deep-dive analysis into the thermodynamic and kinetic properties of hercynite, which demonstrates the role of a complex combination of charged antisite-vacancy defect pairs in enabling the STCH performance of hercynite.

INTRODUCTION

A sustainable hydrogen economy based on the low-cost production of hydrogen from renewable resources has the potential to transform the energy sector drastically. While solar energy is the most abundant renewable energy resource, the capture, storage, and distribution of it remains a challenge. Solar thermochemical hydrogen production (STCH) provides a promising route for efficient utilization of this disperse resource because it utilizes the entire solar spectrum to convert water to an energy-dense fuel, hydrogen. Like other large-scale hydrogen production methods, STCH suffers from significant technical challenges related to both the discovery of efficient water splitting materials and the development of an efficient process that exploits these materials. Despite the significant number of materials that have been examined for STCH, an optimal redox material to drive this process has yet to be developed. This research focuses on developing a powerful new approach for materials discovery that combines quantum mechanical and machine-learned models with experimental feedback to accelerate the development of new, durable redox materials.

During the first year of the project, the team developed a machine-learned descriptor that improves the accuracy of predicting single and double perovskite stability to 92% from 74% for the conventional method. This descriptor can then be used for initial screening of perovskites to eliminate the need to use expensive first-principles DFT quantum mechanical calculations to determine stability, significantly decreases the number of candidate materials, and reduces the computational expense of stability predictions from several hours to milliseconds per material. The team also developed a second machine-learned descriptor that predicts thermodynamic stability at relevant high-temperature conditions (>1,300°C), which further reduces the set of viable materials and thus the computational expense of accurately prototyping new materials and further narrows the pool of candidate materials requiring experimental testing. In Year 2 of the project, the team focused on applying these machine-learned models on the pool of candidate materials and conducting quantum mechanical screening on the thermodynamic properties of the stable materials. In addition, a new machine-learned model was developed for predicting the kinetic diffusion barriers of new materials. Due to the high computational cost of calculations to predict kinetics, high-throughput computational screening of materials usually neglects kinetics and focuses only on the thermodynamic properties of candidate materials. This machine-learned model significantly accelerates the kinetic screening of candidates and will be used as the first step in screening materials for their kinetic viability.

APPROACH

This project focuses on the design and demonstration of mixed metal oxides for STCH with a predominant emphasis on perovskites and spinels. The redox stability of these materials at conditions at which they undergo an oxygen vacancy mediated STCH mechanism will be evaluated and their thermodynamic and kinetic

properties will be tuned through compositional (doping) control. We will ensure that properties are evaluated with the correct topology (structure and coordination) at STCH conditions. To achieve DOE targets, materials will be designed with low thermal reduction temperatures (<1,400°C), high hydrogen production capacity (>300 µmol H_2/g/cycle), material stability and reactivity over many cycles (<10% loss in hydrogen production from cycles 100 to 200), and rapid reduction and oxidation kinetics (reaching 80% of equilibrium in <7 minutes). This work will consist of four tasks to develop novel water splitting materials. We will: (1) develop machine-learned models for predicting stability in perovskites, (2) screen active materials for thermodynamic viability, (3) screen active materials for kinetic viability, and (4) experimentally test promising materials for redox cycling durability and thermodynamic and kinetic performance.

The identification and development of optimal materials for STCH using computationally guided approaches requires the ability to rapidly and accurately predict the behavior of new materials. Typical high-throughput calculations rely on an evaluation of stability from 0 K ground-state calculations. In Task 1, we have utilized materials informatics and machine learning to develop two models to predict the stability of perovskites without any quantum mechanical calculations and to predict the thermodynamic stability of materials at high-temperature conditions. In addition to being stable at relevant operating conditions, new materials must also possess high hydrogen productivity at low reduction temperatures in order to meet DOE targets for efficient and economic large scale hydrogen production. In Task 2, metal oxides are screened using a series of thermodynamic screening steps based on stability and neutral and charged vacancy formation. The initial thermodynamic screening has been conducted on ternary materials (ABO_3) with optimization of active materials through compositional control (alloying) conducted later. In order to complete Tasks 1 and 2, the team is working closely with the National Renewable Energy Laboratory (NREL) HydroGEN node for First Principles Materials Theory. Beyond the screening of thermodynamic material properties, STCH materials must reduce and oxidize at practical rates. However, current computational evaluations of new materials either screen-based exclusively on thermodynamic properties or calculate kinetics using computationally demanding techniques that are often as slow as or slower than experimental evaluation of kinetic properties. In Task 3, we are developing high-throughput methods based on pseudo transition state (TS) and machine-learned TS models to screen redox materials that pass the thermodynamic screening. The final aspect of this project is the experimental validation and demonstration of computationally screened materials. In Task 4, we are performing experiments to demonstrate the water splitting ability of candidate materials both at the University of Colorado and the Sandia National Laboratory HydroGEN node for the Laser Heated Stagnation Flow Reactor. Feedback from experiments will validate our models for candidate active materials identified from the rapid thermodynamic and kinetic screenings.

RESULTS

During FY19, the team identified methods to rapidly predict perovskite structure from the composition by combining the machine-learned descriptor for perovskite stability (τ) developed in Year 1 with a bond-valence structure prediction method (SPuDS).

Structural relaxations were performed using DFT for 314 ternary oxide perovskites predicted to be stable or slightly meta-stable using the tolerance factor (τ). Each of these materials was evaluated in eight common perovskite tilting systems with the initial structure given by SPuDS. Each structure can be predicted by SPuDS on the order of 1 second, whereas a DFT relaxation using an often poor starting guess may take upwards of 48 hours. As shown in Figure 1, the predicted volume determined using SPuDS matches the DFT relaxed volume remarkably well with a mean absolute deviation of 7.25 $Å^3$. In addition to assessing the accuracy of the volume prediction, the similarity in the crystal structures was also assessed using the structural fingerprinting distance (SFPD) method. As shown in Figure 1, the mean SFPD value between the SPuDS-predicted structure and the DFT ground state structure is 0.42. The typical SFPD values for comparing the structures of cubic and distorted perovskites are 1.5–2. This shows that SPuDS provides an accurate prediction of the structure of perovskites, especially considering its low computational expense, which significantly reduces the cost of each DFT relaxation with only the negligible additional cost of a SPuDS calculation. Beyond providing an improved starting structure for the DFT calculations and determining the stable polymorph, SPuDS also enables the use of structural descriptors in a machine-learned model, as opposed to only compositional

descriptors, to identify promising material properties. We are actively working to develop machine-learned models for important STCH properties based on the structural descriptors provided by SPuDS, but validated using DFT.
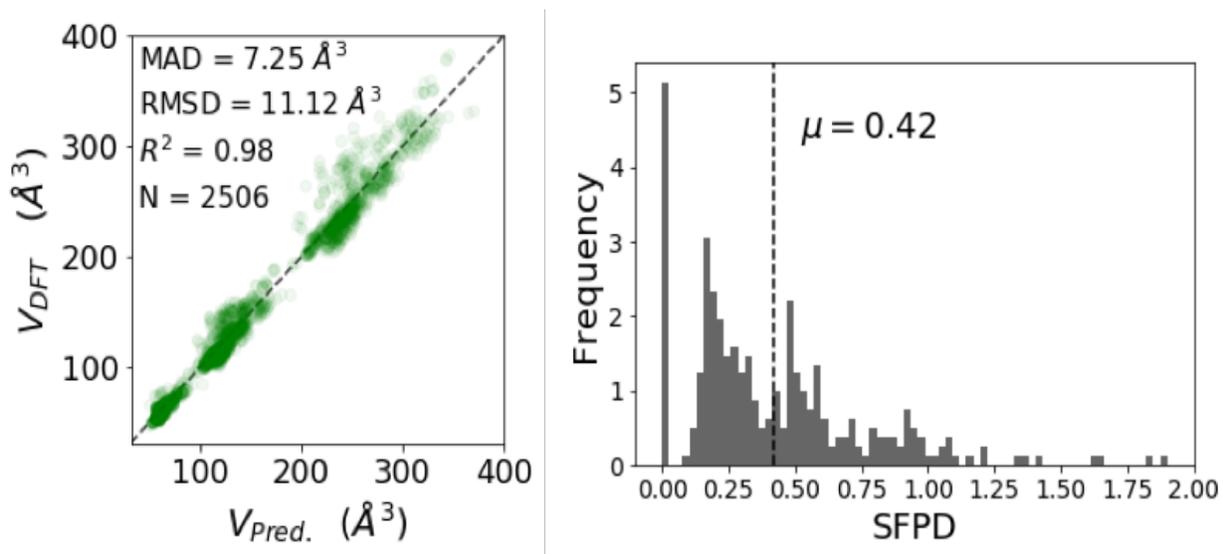

Figure 1. (Left) Comparison of the computed volume from DFT and the predicted volume from a bond-valence structure prediction method (SPuDS) for 2506 different perovskite structures and 314 perovskite compositions. (Right) Calculated structural fingerprinting distance (SFPD) between the DFT ground state polymorph structure and the structure predicted by SPuDS for 314 perovskite compositions.

Additionally, for each of the eight tilting systems given by SPuDS, a Global Instability Index (GII) can be computed, which provides an indication of the relative stability of the predicted polymorph structures. As shown in Figure 2, by utilizing the GII to rank-order the possible perovskite tilting systems, the number of calculations required for each composition to capture 98% of the DFT ground-state structures is reduced from eight to three. Furthermore, 100% of the correct ground state structures are identified with five DFT optimizations, thus reducing the number of DFT optimizations from eight to five to have 100% certainty of identifying the DFT predicted ground state polymorph. This combined approach of applying the machine-learned descriptor τ to initially screen for perovskite stability, utilizing SPuDS to generate initial starting structures, and evaluating the GII to determine the most stable tilting systems not only reduces the computational expense of each DFT relaxation by providing a better starting guess geometry but it also significantly reduces the number of DFT calculations needed to identify the most stable distorted structure.
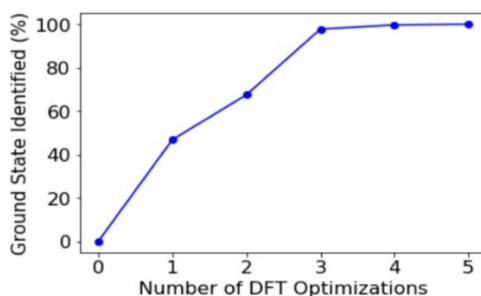

Figure 2. Number of DFT calculations required to correctly identify the ground state structure when the GII is used to rank-order the stability of crystal structures for the 8 possible perovskite tilting systems given by SPuDS.

For the kinetic screening of new materials during FY 2019, the team applied the rapid activation barrier bounding approach we developed in FY 2018, which enables the rapid evaluation of the mobility of oxygen vacancies in new materials. The kinetics study was expanded to include 330 bulk diffusion reactions, including

270 for charge-neutral oxygen vacancies and 60 for positively charged oxygen vacancies. The inclusion of investigating charged vacancy diffusion in this past fiscal year was added because, over the course of studying the energies of the formation of oxygen vacancies, we discovered the importance of the vacancy charge state in its overall thermodynamic stability. Of the 60 materials calculated, the diffusion barrier is significantly lower for the charged vacancies ~50% of the time, while the diffusion barriers are relatively similar ~30% of the time. This indicates that charged oxygen vacancies tend to have lower diffusion barriers than neutral vacancies; however, this trend is too weak to be relied upon for screening, and additional calculations need to be performed to predict STCH kinetics.

From the activation barriers calculated using the bounding approach, the team developed a preliminary machine-learned model that is able to predict activation barriers using properties calculated from only the unit cell. While this means that DFT calculations are still necessary, a unit cell calculation is orders of magnitude less computationally demanding than traditional transition state calculations, which require a supercell model and the bounding method developed in FY 2018. This machine-learned model, developed using the SISSO statistical learning algorithm, predicts diffusion barriers with a root mean squared error of 0.38 eV, as illustrated in Figure 3. This level of error is sufficiently low to distinguish between fast and slow diffusion reactions, which we determined to be an approximately 1 eV difference in energy between fast and slow STCH materials, and can, therefore, be used as the approach for the initial kinetic screening of STCH candidates. The calculation of the unit cell properties used as input into this machine-learned model requires approximately 1,000 times less computational time than traditional transition state calculations using a supercell and enables the rapid initial kinetic screening of new materials. Materials that pass this initial screening can then be screened using the bounding approach developed in FY 2018. In the future, this transition state model will be modified to include charged diffusion.
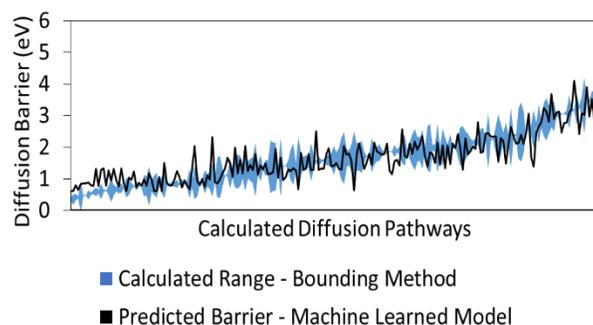

Figure 3. Comparison of the activation barrier bounds calculated using the bounding approach developed in Year 1 (blue) and predicted barrier using the machine learned model developed in Year 2 (black) for O vacancy diffusion. Data is ordered by increasing average calculated activation barrier

In addition to the high-throughput calculations conducted for the thermodynamic and kinetic screening of new materials, during FY 2019, the team also performed a deep-dive analysis into the known water splitting material hercynite ($FeAl_2O_4$) in order to understand its performance further. Experimentally, hercynite has been demonstrated to produce a substantial amount of hydrogen; however, its kinetics are slow. From a thermodynamic perspective, it was found that the stability region of hercynite on the Fe-Al-O phase diagram overlaps well with the ideal STCH operating conditions. In normal hercynite, where oxygen is surrounded by one Fe atom and three Al atoms, the neutral oxygen vacancy formation energy is too high to produce a substantial equilibrium vacancy concentration to promote water splitting. Therefore, other defects and defect pairs must be considered. In the spinel structure of hercynite antisite defects (e.g., Fe on an Al site: Fe_{Al}, or Al on a Fe site: Al_{Fe}) result in cation disorder and lead to different local cation environments surrounding each oxygen in the lattice. As shown in Figure 4, when charged antisite-vacancy defect pairs are present, the defect energy in hercynite is substantially reduced. A thermodynamic analysis of these defect pairs indicates that the largest degree of reduction occurs under Fe-rich conditions with a maximum computed Fe solubility in the spinel phase of $Fe/(Fe+Al) \approx 0.5$. These charged defect pairs enable the high degree of reduction that is observed experimentally in hercynite. The team also studied the kinetic behavior of hercynite and found

similar beneficial effects of antisite and charged defects on oxygen vacancy diffusion. While the activation barrier in normal hercynite is very high (2.46 eV), the diffusion barrier is reduced by 0.6 eV for each additional nearest-neighbor Fe atom. Furthermore, Fe-rich conditions are found to provide redox flexibility and increase the rate of vacancy diffusion in the material. This deep-dive study into hercynite demonstrates that the STCH mechanism may not simply be mediated by neutral oxygen vacancies as had been previously assumed, but that charged defects and defect pairs play a critical role in enabling the reduction of some STCH materials. We plan to explore these suggestions to examine whether Fe-rich hercynite might lead to STCH with similarly high hydrogen production, but at significantly faster rates than near stoichiometric hercynite.
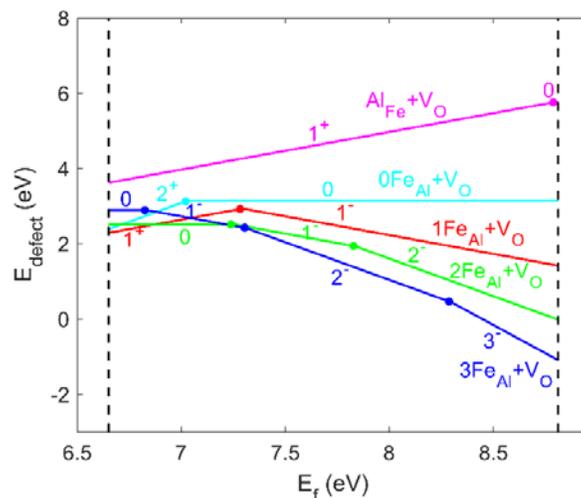

Figure 4. Charged and neutral antisite-oxygen vacancy defect pairs in $FeAl_2O_4$. The energy of one, two, and three Fe_{Al} antisite-oxygen vacancy pairs are shown in red, green, and blue, respectively. In all cases, these defects are most favorable in a negatively charged defect state and are lower in energy than the oxygen vacancy in normal hercynite (teal).

CONCLUSIONS AND UPCOMING ACTIVITIES

The materials-by-design approach has been developed to (1) significantly narrow the candidate materials space, (2) rapidly predict stability at high-temperature conditions, (3) increase the capabilities of state-of-the-art high-throughput kinetic screening, and (4) identify relevant thermodynamic screening parameters. This year, the team has utilized machine learning models to reduce the materials space from millions of candidates to thousands based on stability. This space has been further reduced through the use of a bond-valence prediction method and the stability of over 2,500 perovskite structures has been evaluated using DFT. In the future, the team will screen stable materials based on their defect properties and potential to split water at relevant operating conditions and experimentally validate these materials at CU and Sandia. We will also develop models to rapidly predict the electronic contributions to the entropy, which could be a key factor in determining the thermodynamics of oxidation and reduction of the redox material. In FY19, a new machine-learned model was developed to predict activation barriers for oxygen diffusion rapidly. In the future, this model will be applied to new candidate materials to screen materials for their kinetic properties rapidly. The thermodynamic and kinetic properties of hercynite have been studied in detail, and the role of a complex combination of charged antisite-vacancy defect pairs has been identified. In the future, the performance of Fe-rich hercynite, which has been computationally predicted to outperform stoichiometric hercynite, will be evaluated experimentally. In order to enable effective collaboration, the team at the University of Colorado and the NREL HydroGEN node for First Principles Materials Theory meet biweekly meetings and have collaborated on both the high-throughput thermodynamic screening and the deep-dive hercynite study.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. C.J. Bartel, C. Sutton, B.R. Goldsmith, R. Ouyang, C.B. Musgrave, L.M. Ghiringhelli, M. Scheffler, "New tolerance factor to predict the stability of perovskite oxides and halides," *Science Advances* 5, no. 2: eaav0693

2. Musgrave, C., C. Bartel, C. Sutton, B. Goldsmith, A. Holder, "Discovery of New Halide Double Perovskite Photovolatic Materials Using Machine Learning and Electronic Structure Theory," *American Chemical Society Spring National Meeting*, Orlando, FL, March, 2019.

3. Musgrave, C., S. Millican, Ryan Trottier, Aaron Holder and C. Bartel, "Ab Initio and Machine Learned Modeling, Design and Discovery of Water Splitting Materials," *Materials Research Society Spring National Meeting*, Phoenix, AZ, March 2019.

4. Musgrave, C., "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.

5. Musgrave, C., "Machine Learning and Ab Initio Methods to Discover and Design Novel Materials and Catalysts," *Department of Chemical Engineering, University of Massachusetts*, Amherst, MA, December 2018.

6. S.L. Millican, I. Androshchuk, A.W. Weimer, and C.B. Musgrave. "Computational Discovery of Materials for Solar Thermochemical Hydrogen Production," *American Institute of Chemical Engineers Annual Meeting*, Pittsburgh, PA, October, 2018.

7. S.L. Millican, A.M. Deml, M. Papac, R. O'Hayre, A.M. Holder, V. Stevanovic, and C.B. Musgrave. "Predicting Point Defect Concentrations in Complex, Disordered Oxides," *American Institute of Chemical Engineers Annual Meeting*, Pittsburgh, PA, October, 2018.