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# 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 predict materials for solar thermochemical water splitting (STWS) and demonstrate the effectiveness of our materials-by-design approach by experimentally demonstrating materials with computationally predicted thermodynamic and kinetic properties.
- Utilize materials-by-design approach to rapidly computationally prototype new STWS materials and demonstrate materials with improved performance.
- Computationally prototype doped metal oxides for thermodynamic and kinetic viability and experimentally demonstrate materials with improved hydrogen productivity, reaction kinetics, and durability.

## Fiscal Year (FY) 2018 Objectives

- Utilize advanced machine-learning techniques to enable the prediction of the perovskite

crystal structures (polymorphs) relevant to STWS conditions.

- Screen materials for thermodynamic viability based on stability, oxygen vacancy formation energy ( $E_v$ ), and extent of reduction ( $\delta$ ).
- Develop and utilize an accelerated pseudo transition state approach and machine-learned models to rapidly computationally screen materials for kinetic viability.
- Experimentally demonstrate the durability and thermodynamic and kinetic water splitting behavior of new materials predicted from our computational screening using the thermogravimetric analyzer with differential scanning calorimeter (TGA/DSC) and stagnation flow reactor (SFR).
- Complete an annual status report comparing results from the different demonstrations.

## 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<sup>1</sup>:

(S) High-Temperature Robust Materials.

## Technical Targets

This project has contributed toward progress in meeting the target for “Annual Reaction Material Cost per TBD H<sub>2</sub>” 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

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

working toward the following goals to hit this target:

- Hydrogen productivity:  $>350 \mu\text{mol/g/cycle}$
- Operating temperature:  $T_{\text{red}} \leq 1,450^\circ\text{C}$  and  $\Delta T \leq 400^\circ\text{C}$
- Cycle times:  $<10$  minutes
- Stability:  $<10\%$  decrease in reactivity between cycles 100 and 200.

### **FY 2018 Accomplishments**

- Developed two machine-learned descriptors that significantly narrow the search space for candidate materials to accelerate the screening of more than 1,000,000 perovskite structures.
- Advanced the capability of materials screening for kinetic properties by developing a pseudo transition state identification approach and predicted rate-limiting step in hydrogen evolution reaction.
- Identified an important thermodynamic screening parameter necessary for determining a material's water-splitting ability.

## INTRODUCTION

STWS provides a promising route for efficient conversion of solar energy to hydrogen fuel; however, despite the significant number of materials that have been examined, an optimal 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 this year, the team has developed a machine-learned descriptor that improves the prediction of single and double perovskite stability, eliminating the need to use expensive first-principles density functional theory (DFT) quantum mechanical calculations, significantly reducing the number of potential candidate materials and reducing the computational expense of stability predictions from hours to milliseconds per material. The team has also developed a second machine-learned descriptor that predicts thermodynamic stability at relevant high-temperature conditions ( $>1,300^{\circ}\text{C}$ ), which further reduces the computational expense of accurately prototyping new materials and considerably narrows the pool of candidate materials requiring experimental testing. In addition to reducing the materials space by machine-learned descriptors, the team has also made significant advancements in high-throughput screening of materials for kinetic and thermodynamic water-splitting viability.

## APPROACH

This project will focus on the design and demonstration of mixed metal oxides for STWS with a predominant emphasis on perovskites and spinels. The redox stability of these materials at conditions at which they undergo an oxygen-vacancy-mediated STWS mechanism will be evaluated, and their thermodynamic and kinetic properties will be tuned through compositional (doping) control. We will ensure properties are evaluated with the correct topology (structure and coordination) at STWS conditions. To achieve DOE targets, materials will be designed with low thermal reduction temperatures ( $<1,450^{\circ}\text{C}$ ), high hydrogen production capacity ( $>350 \mu\text{mol H}_2/\text{g}/\text{cycle}$ ), material stability and reactivity over many cycles ( $<10\%$  loss in hydrogen production from cycles 100 to 200), and rapid reduction and oxidation kinetics (cycle times  $<10$  minutes). This work will consist of four tasks to develop novel water splitting materials.

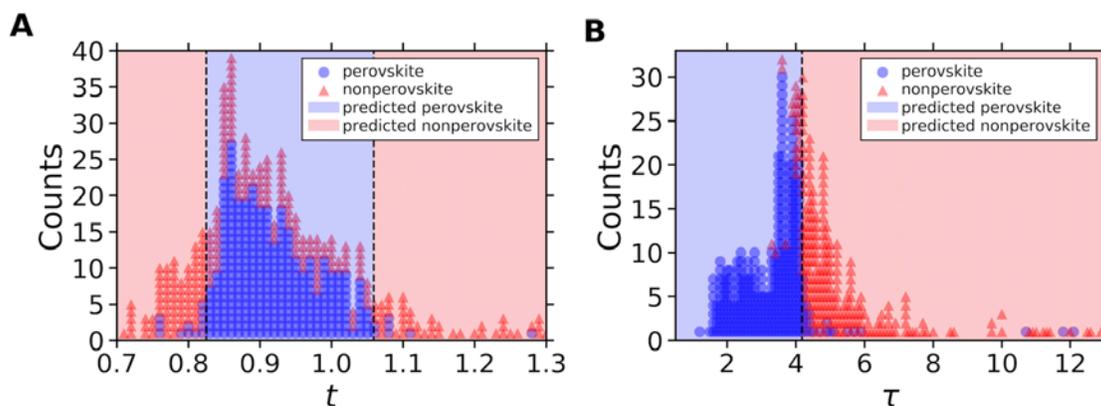
We will:

1. Develop machine-learned models for predicting phase transitions in perovskites.
2. Screen active materials for thermodynamic viability.
3. Screen active materials for kinetic viability.
4. Experimentally test promising materials for redox cycling durability and thermodynamic and kinetic performance.

## RESULTS

During FY 2018, the team developed a machine-learned descriptor that improves the prediction of single- and double-perovskite stability from 74% to 92% accuracy (Figure 1), eliminating the need to use first-principles DFT calculations for  $>1,000,000$  perovskite structures. This descriptor significantly focuses the material space and reduces the computational expense of stability predictions.

A decision tree classifier determines that the optimal bounds for perovskite formability using the Goldschmidt tolerance factor,  $t$ , are  $0.825 < t < 1.059$ , which yields a classification accuracy of 74% for 576 experimentally characterized  $\text{ABX}_3$  solids (Figure 1a). The new tolerance factor ( $\tau$ ) achieves 92% classification accuracy on the set of 576  $\text{ABX}_3$  solids based on perovskite classification for  $\tau < 4.18$ , with this decision boundary identified using a one-node decision tree (Figure 1b). This result indicates that this model is truly predictive and allows for significant generalizability to predicting experimental realization for single and double perovskites that are yet to be discovered.



**Figure 1.** Assessing the performance of the improved tolerance factor. (A) A decision tree classifier determines that the optimal bounds for perovskite formability using the Goldschmidt tolerance factor,  $t$ , are  $0.825 < t < 1.059$ , which yields a classification accuracy of 74% for 576 experimentally characterized  $ABX_3$  solids. (B)  $\tau$  achieves 92% classification accuracy on the set of 576  $ABX_3$  solids based on perovskite classification for  $\tau < 4.18$ , with this decision boundary identified using a one-node decision tree. The largest value of  $\tau$  in the experimental set of 576 compounds is 181.5; however, all points with  $\tau > 13$  are correctly labeled as nonperovskite and not shown to highlight the decision boundary. The outlying compounds at  $\tau > 10$  that are labeled perovskite yet have large  $\tau$  are  $\text{PuVO}_3$ ,  $\text{AmVO}_3$ , and  $\text{PuCrO}_3$ , which may indicate poorly defined radii or incorrect experimental characterization.

During this year, a second machine-learned descriptor was developed that predicts thermodynamic stability at relevant high-temperature conditions ( $>1,300^\circ\text{C}$ ). The sure independence screening and sparsifying operator (SISSO) approach was used to identify a simple and highly accurate descriptor for  $G(T)$ . The current descriptor for the  $G(T)$  requires only temperature, chemical formula, and DFT-calculated density to reproduce experimental  $G(T)$  with errors of  $\sim 40$  meV/atom (Figure 2).

Figure 2a shows the performance of the SISSO-learned descriptor on the training set and Figure 2b shows distribution of residuals between the SISSO-learned descriptor and experiment on the training set. Combining this high-throughput model for the prediction of  $G(T)$  with tabulated and readily available DFT-calculated  $\Delta H_f$  and experimental Gibbs energies for the elements enables the rapid prediction of  $\Delta G_f(T)$  from a single DFT total energy calculation. Thus, reaction energetics, thermochemical equilibrium product distributions, and temperature-dependent compound stability can be assessed for the millions of structures currently compiled in materials databases. This unprecedented ability to rapidly predict reaction equilibria for reactions involving solid compounds is illustrated in Figure 3 for a small set of example reactions.

Figure 3a shows comparison of experimental reaction energetics (labels) to those predicted using the machine-learned descriptor for  $G(T)$  (dashed curves) and Figure 3b shows reaction product distributions between  $\text{MoO}_2$ ,  $\text{Mo}_2\text{N}$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$  based on Gibbs energy minimization subject to molar conservation and fixed pressure of 1 atm. In both figures, “pred” applies the SISSO-learned descriptor to  $G(T)$  of the solid phases and experimental data for all other components. This model can be trivially applied to all perovskite oxides under consideration to assess the stability (or metastability) as a function of temperature, and further reduce the space of compounds that require more sophisticated (e.g., defect) calculations.

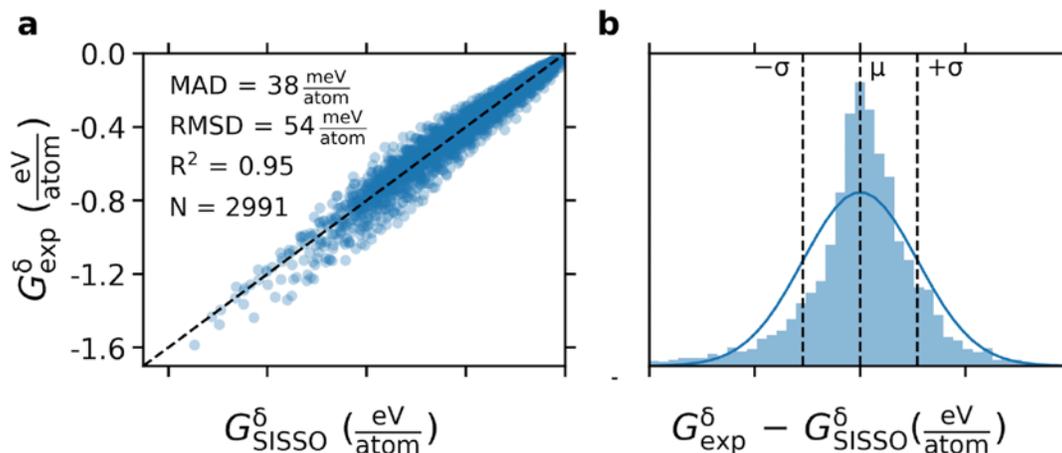


Figure 2. Descriptor performance. Performance of the SISO-learned descriptor on the training set. MAD is the mean absolute deviation, RMSD the root mean square deviation, N the number of points shown,  $\mu$  the mean deviation and  $\sigma$  the standard deviation. The curved lines are normal distributions constructed from  $\mu$  and  $\sigma$ .

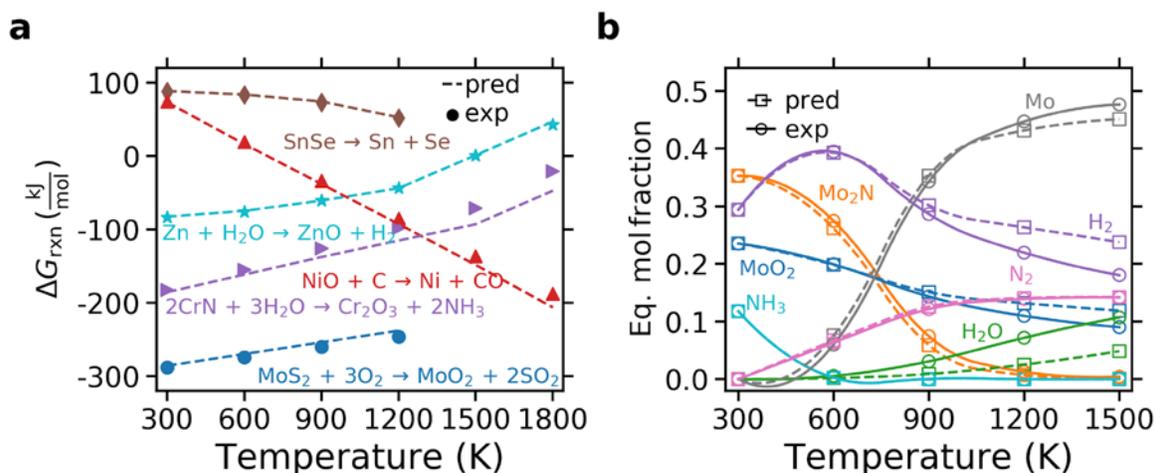


Figure 3. High-throughput reaction engineering. (a) A comparison of experimental reaction energetics (labels) to those predicted using the machine-learned descriptor for  $G(T)$  (dashed curves). (b) Reaction product distribution between  $\text{MoO}_2$ ,  $\text{Mo}_2\text{N}$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$  based on Gibbs energy minimization subject to molar conservation and fixed pressure of 1 atm. In both figures, “pred” applies the SISO-learned descriptor to  $G(T)$  of the solid phases and experimental data for all other components.

In addition to focusing the chemical space by machine-learned descriptors, the team has made significant advancements in high-throughput screening of materials for kinetic and thermodynamic viability. For the thermodynamic screening, the team utilized the machine-learned model developed for perovskite stability to screen >1,000,000 potential perovskite materials down to ~27,000 stable materials to be further evaluated using DFT. All of the 328 stable ternary ( $\text{ABO}_3$ ) perovskites and 425 stable double ( $\text{A}_2\text{BB}'\text{O}_6$ ) perovskites were evaluated for STWS based on the oxygen vacancy formation energy. Further work is now being conducted to evaluate these materials based on their stability at elevated temperatures using the machine-learned model for free energy  $G(T)$  described above. The team also evaluated the effect of charged defects on the predicted thermodynamic behavior of STWS materials. This study was completed in conjunction with Dr. Stephan Lany at the National Renewable Energy Laboratory utilizing the HydroGEN consortium computational node “First Principles Materials Theory for Advanced Water Splitting Pathways.” Through this work the team has demonstrated that charged antisite-vacancy defect pairs are critical for understanding the water splitting ability in hercynite. Future work will involve utilizing these charged and antisite defect

calculations to complete a full thermodynamic model for the equilibrium defect concentration at relevant temperatures in hercynite and hercynite alloys. For the kinetic screening, the team has identified the rate-limiting step in the hydrogen evolution reaction and developed accelerated pseudo transition state identification approaches. The rate-limiting step was identified from an initial screening of 23 perovskite/spinel materials. The full reaction pathway for the hydrogen and oxygen evolution surface reactions was evaluated in addition to the bulk kinetics for all 23 materials. The pseudo transition state identification approaches we developed significantly accelerate the kinetic screening of materials. These approaches involve estimating an upper/lower bound on transition state energies, utilizing atomic potentials to estimate transition state geometries, and recent developments allow the use of machine-learned models for rapid materials screening. These advancements not only limit the number of calculations needed to screen for kinetic viability but also significantly reduce the computation expense attributed to costly ab initio transition state calculations. Experimentally, the activity of four transition metal–hercynite alloys was measured in a stagnation flow reactor. These alloys produced  $>200 \mu\text{mol H}_2/\text{g}$  at reduction temperatures of  $1,450^\circ\text{C}$ . The Mn–hercynite alloy shows the highest hydrogen production as well as an improved peak rate over pure hercynite. The experimentally measured peak rates were accurately matched against computational predictions.

## CONCLUSIONS AND UPCOMING ACTIVITIES

The materials-by-design approach has thus far been developed to (1) significantly narrow the candidate materials space, (2) predict energetics at relevant high-temperature conditions, (3) increase the capabilities of state-of-the-art high-throughput kinetic screening, and (4) identify relevant thermodynamic screening parameters. The initial success of this approach has been demonstrated for transition metal–hercynite alloys by correctly rank ordering the experimental peak hydrogen production rate of four materials by the computational kinetic results. Additionally, four materials producing  $>200 \mu\text{mol H}_2/\text{g}$  at reduction temperatures  $\leq 1,450^\circ\text{C}$  and temperature swings  $\leq 400^\circ\text{C}$  were demonstrated.

Future work by the University of Colorado team includes:

- Utilizing the charged and antisite defect calculation in a thermodynamic model to compute the equilibrium defect concentrations at relevant temperatures and pressures.
- Screening candidate perovskite materials using free energy model for stability at elevated temperatures.
- Continuing deployment of pseudo transition state approaches for rapid kinetic screening that will feed into the development of machine-learned models.

## FY 2018 PUBLICATIONS/PRESENTATIONS

### Publications

1. C.J. Bartel, C. Sutton, B.R. Goldsmith, R. Ouyang, C.B. Musgrave, L.M. Ghiringhelli, and M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” *Science Advances* (Accepted), <https://arxiv.org/abs/1801.07700>.
2. C.J. Bartel, S.L. Millican, A.M. Deml, J.R. Rumpitz, W. Tumas, A.W. Weimer, S. Lany, V. Stevanovic, C.B. Musgrave, and A.M. Holder, “Physical descriptor for the Gibbs energy of inorganic crystalline solids and temperature-dependent materials chemistry,” *Nature Communications* 9, no. 1: 4168.

### Presentations

1. C.J. Bartel, C. Sutton, B.R. Goldsmith, R. Ouyang, C.B. Musgrave, L.M. Ghiringhelli, and M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” European Materials Research Society, September 2018.
2. R. Trottier, S.L. Millican, Z.J. Bare, and C.B. Musgrave, “Rapid Kinetic Profiling of Bulk Diffusion Barriers for Solar Thermal Water Splitting Materials,” 21<sup>st</sup> International Conference on Ternary and Multinary Compounds, September 2018.

3. C.J. Bartel, C. Sutton, B.R. Goldsmith, R. Ouyang, C.B. Musgrave, L.M. Ghiringhelli, and M. Scheffler, “New tolerance factor to predict the stability of perovskite oxides and halides,” 21<sup>st</sup> International Conference on Ternary and Multinary Compounds, September 2018.
4. S.L. Millican, A.M. Deml, A.M. Holder, V. Stevanovic, and C.B. Musgrave, “Modeling Point Defect Concentrations in Complex Materials Beyond Dilute Defects,” International Conference on Ternary and Multinary Compounds, September 2018.
5. C.J. Bartel, C. Sutton, B.R. Goldsmith, R. Ouyang, C.B. Musgrave, L.M. Ghiringhelli, and 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.
6. S.L. Millican, I. Androschuk, 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.
7. C.J. Bartel, C. Sutton, B.R. Goldsmith, R. Ouyang, C.B. Musgrave, L.M. Ghiringhelli, and M. Scheffler, “Improved tolerance factor for classifying the formability of perovskite oxides and halides,” American Physical Society Annual Meeting, March 2018.
8. C.J. Bartel, S.L. Millican, A.M. Deml, J.R. Rumpitz, W. Tumas, A.W. Weimer, S. Lany, V. Stevanovic, C.B. Musgrave, and A.M. Holder, “Machine learning the Gibbs energies of inorganic crystalline solids,” American Physical Society Annual Meeting, March 2018.
9. S.L. Millican, I. Androschuk, 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.
10. S.L. Millican, I. Androschuk, A.W. Weimer, and C.B. Musgrave, “Screening Metal Oxides for Solar Thermochemical H<sub>2</sub>/CO Production,” American Institute of Chemical Engineers Annual Meeting, October, 2017.
11. S.L. Millican, I. Androschuk, A.W. Weimer, and C.B. Musgrave, “Assessing the Thermodynamic Viability of Mixed Metal Oxides for Solar Thermochemical Water Splitting,” American Institute of Chemical Engineers Annual Meeting, October 2017.
12. S.L. Millican, A.L. Hoskins, C.E. Czernik, I. Alshankiti, J.C. Netter, C.B. Musgrave, and A.W. Weimer, “Complete Approach to Hydrogen Production via Solar Thermochemical Water Splitting,” American Institute of Chemical Engineers Annual Meeting, October 2017.
13. C.J. Bartel, S.L. Millican, A.M. Deml, J.R. Rumpitz, W. Tumas, A.W. Weimer, S. Lany, V. Stevanovic, C.B. Musgrave, and A.M. Holder, “Machine learning the thermochemistry of inorganic crystalline solids,” American Institute of Chemical Engineers Annual Meeting, October 2017.