# HydroGEN Seedling: Accelerated Discovery of Solar Thermochemical Hydrogen Production Materials via High-Throughput Computational and Experimental Methods

Ryan O'Hayre (Primary Contact), Michael Sanders
Colorado School of Mines
1500 Illinois St.
Golden, CO 80401
Phone: 303-273-3952
Email: rohayre@mines.edu

DOE Manager: Katie Randolph
Phone: 720-356-1759
Email: Katie.Randolph@ee.doe.gov

## Overall Objectives

- Theoretical stability analysis of at least 8,500 "potential" compounds, based on a combination of existing data located in material databases and new density functional theory (DFT) calculations.

- Determination of oxide formation enthalpy, bandgap, and atomic electronegativity for at least 500 theoretically stable compounds, based on a combination of existing data located in material databases and new DFT calculations.

- Determination of material properties that can be used as identifiers for water-splitting performance and verification of predictive capability experimentally.

- Production of combinatorial thin-film "libraries" for at least 20 material families that have been identified by the theoretical screening as candidate materials.

- Demonstration that thin-film compositions of candidate material families can be evaluated for Solar Thermochemical Hydrogen Production (STCH) potential using simple experimental techniques.

- Identification of at least three new materials that split water under any steam-to-hydrogen ratio with a hydrogen capacity at least equal to that of cerium oxide (ceria) under the reduction conditions of 1,350°C and oxidation temperatures of 850°C–1,000°C.

- Identification of one or more new materials that split water under steam-to-hydrogen ratios lower than 10:1 and with a hydrogen capacity under the reduction conditions of 1,350°C and oxidation temperatures of 850°C–1,000°C at least equal to that of ceria under the reduction conditions of 1,450°C and oxidation temperatures of 850°C–1,000°C.

- Characterization of final materials including cycling, durability, thermodynamic, and kinetic property investigations, and performance verification at both Colorado School of Mines and Sandia National Laboratory's (SNLs) Stagnation Flow Reactor facility.

## Fiscal Year (FY) 2019 Objectives

- Defect calculations on the $Ce_xSr_{2-x}MnO_4$ (CSM) and $Sr_{1-x}Ce_xMnO_3$ (SCM) systems for ranges of $x$ from ~0.05 to 0.25. These systems will be studied in detail in Y2 because they were demonstrated to be highly promising STCH-candidate oxides during the Y1 budget period investigations.

- Targeted computational structure search for STCH-relevant oxides containing three cations within the Ba, Ce, Mn, Nb, and V compositional space. These cations were identified as being particularly promising during the Y1 budget period investigations and are thus targeted in this Y2 focused search.

- Create a results dataset for machine-learning, compiled from new and existing charged-defect calculations.

- Produce at least 10 combinatorial thin-film "libraries" from the Ba, Ce, Mn, Nb, and V compositional space and five "libraries" to support the effort to alter the cerium content in $BaCe_{0.25}Mn_{0.75}O_3$ (BCM).

- Demonstrate production of thin-film combinatorial "libraries" of complex oxides using simple binary targets (i.e., simple, single-cation oxides).

- Demonstrate evaluation of thin-film compositions of candidate material families for STCH potential using simple experimental techniques.

## Technical Barriers

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

- High-Temperature Robust Materials.

## Technical Targets

The objective of this project is to discover new STCH materials. Those materials are necessary to meet the following DOE 2020 STCH targets:

- Target 1Cost: $2/kg of Hydrogen

- Steam to Hydrogen (STH) Efficiency: 20%.

## FY 2019 Accomplishments

- Performed defect calculations for parent-phase of CSM and SCM, $Sr_2MnO_4$ (SMO214) and $SrMnO_3$ (SMO113) and produced a phase diagram of the Sr-Mn-O system.

- Adapted existing structure search protocols to include a genetic algorithm to improve the structure prediction capabilities.

- Successfully synthesized $BaCe_xMn_{1-x}O_3$ (BCMX) and $Sr_xBa_{1-x}MnO_3$ (SBMX) combinatorial library films by pulsed laser deposition and subsequently annealed at 950°C to determine the effect of A-site and B-site cation composition on their structures.

- Produced defect formation thermodynamic quantities for a series of CSM and SCM variants. These results are being used to validate the DFT calculations and refine target parameters.

- Tested three SCM compositions for water-splitting. $Sr_{0.60}Ce_{0.40}MnO_3$ produced 280 µmol $H_2$/g, a new project high for per-cycle production. These results, along with the thermodynamics calculations, are opening new windows into the role of structure on water-splitting performance.

## INTRODUCTION

Two-step metal oxide cycles for STCH have the potential to produce industrial-scale quantities of hydrogen. In step one, a suitable oxide is defected by driving oxygen from the lattice at high temperatures derived from concentrated solar energy. In step two, and upon exposure to steam at a lower temperature, oxygen is stripped from steam and transferred back into the oxide. This completes the cycle and results in the net production of hydrogen.

While ceria has shown itself to be the best performing and most cycle-tolerant STCH oxide, it requires very high reduction temperatures (>1,500°C) to attain sufficient per-cycle hydrogen yield. This leads to severe efficiency penalties that make the 2020 target of 20% STH efficiency unattainable. Ultimately, this work looks to culminate in the discovery and characterization of new STCH materials that can produce hydrogen at quantities to attain the 20% STH efficiency target and facilitate the production cost target of <$2/kg of $H_2$. This requires finding a material that reduces significantly at the target reduction temperature of 1,350°C under moderate oxygen partial pressures of 10–100 ppm and can split water while in the presence of hydrogen at a steam-to-hydrogen ratio of 10:1.

## APPROACH

Because STCH utilizes the full solar spectrum, it has the potential to achieve high theoretic efficiency. Despite its promise, however, surprisingly few candidate STCH materials have been uncovered that can compete with ceria, which remains the state-of-the-art. Our objective is to merge combinatorial synthesis methods with combinatorial theoretical calculations to discover new potential materials for use in two-step metal oxide

---

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

cycles for STCH. This project will make significant in-roads to replacing ceria by obtaining outcomes along several distinct fronts: combinatorial DFT screening, combinatorial thin-film production and testing, bulk powder synthesis and characterization, and the integration of experimental results into the refinement of DFT methodologies and screening criteria. By combining these capabilities with the high-throughput nature of combinatorial synthesis and testing, our goal is to not only efficiently and methodically uncover new potential materials that can meet DOE's 2020 targets, but to better understand fundamental links between oxide structure, chemical composition, and STCH performance.

As a HydroGEN Seedling Project, we are afforded the opportunity to leverage the National Labs' world-class capability and expertise. This collaboration is critical to our project, with interactions occurring with three different nodes across all three of our tasking fronts. The "First Principles Materials Theory for Advanced Water Splitting Pathways" node, led by Stephan Lany, is assisting with all DFT work and Andriy Zakutayev's "High-Throughput Experimental (HTE) Thin Film Combinatorial Capabilities" node is supplying thin films and characterization for the rapid screening effort. Finally, actual water-splitting testing is being performed using SNLs "Virtually Accessible Laser Heated Stagnation Flow Reactor for Characterizing Redox Chemistry of Materials Under Extreme Conditions" node, overseen by Anthony McDaniel.

## RESULTS

### Computational Effort

The phase diagram for the Sr-Mn-O composition was mapped out in chemical potential space (Figure 1), based on the calculated formation enthalpies of the different oxide phases. This mapping yields the boundaries of the O chemical potential for the respective phase stabilities. We observe that the $SrMnO_3$ (113) perovskite transforms into the brownmillerite-like $Sr_2Mn_2O_5$ (225) phase already at mildly reducing conditions ($Dm_O = -1.7$ eV), which are outside the window for the STCH redox process ($-3.0$ eV $< Dm_O < -2.5$ eV). $Sr_2MnO_4$ (214) is stable down to $-2.2$ eV, but still not within the desired range. This is consistent with our experimental observations that SMO is not STCH active.
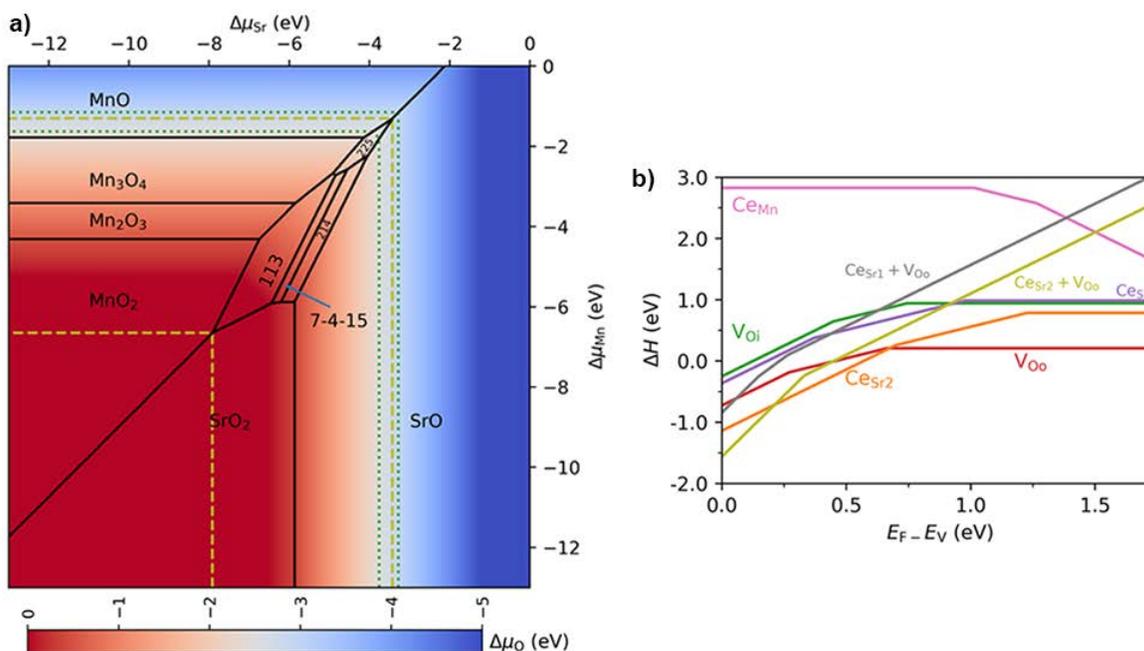


Figure 1. (left) Phase stability map for the Sr-Mn-O phases. (right) Defect formation energies in SrMnO3 at the 113/225 phase boundary.

While SMO is not STCH active, we have shown that Ce-substitution leads to the STCH-active SCM compositional family. So, what is the role of Ce? In order to model the effect of Ce substitution and as a first step towards a thermochemical model for CSM and SCM, we performed defect calculations, including the

formation of O vacancies and Ce substitution at cation sites. We find a strong preference for Ce to substitute on the Sr site rather than the Mn site. Further, the $Ce_{Sr}$ substitution results in a charge compensation between $Ce^{3+}$ (+1 relative to the substituted $Sr^{2+}$) and $Mn^{3+}$ (-1 relative to the substituted $Mn^{4+}$). Therefore, Ce doping causes a reduction of Mn. At this point, we hypothesize that the Mn reduction due to Ce addition impedes the further reduction due to $V_O$ formation.

In parallel with our detailed DFT investigations of the known STCH-active SCM and CSM families, we continue to pursue structure-search calculations to identify other potentially STCH-active compounds. To improve the results from these preliminary structure searches, we have incorporated a genetic algorithm (GA) structure search [1] methodology in our workflow. The success of this methodology was tested in finding a phase-stable structure for $Ba_2MnVO_6$ composition. Figure 2 shows that GA finds a structure that is ~28 meV/atom away from being phase stable. This is a marked improvement from other methods as the random search and prototyping techniques only find a structure that is ~80 meV/atom from stability. It is important to note that the GA uses seeds from both random and prototyping procedures. This suggests that GA, coupled with random prototyping, is a more robust structure search technique than either individual approaches. Hence, we have implemented GA in our workflow for all our structure search efforts going forward. This refined methodology opens new capabilities for probing potential compositions containing large numbers of cations, without foreknowledge of the stable structure or the bias introduced by only looking at a couple of predetermined structures.
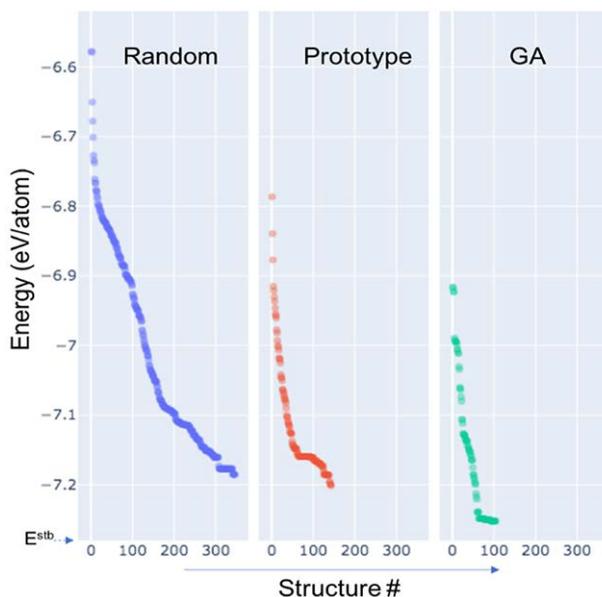


Figure 2. Structure search methodologies were tested for $Ba_2MnVO_6$. A genetic algorithm (GA) approach coupled with random and prototyping searches yields a 50 meV/atom more stable structure than individual techniques. The bottom of the y-axis, marked as $E^{stb}$, corresponds to the minimum energy (eV/atom) needed to find a phase-stable structure for this composition.

## Experimental Combinatorial Effort

As the role of Ce becomes better understood, the next challenge is to identify ways to adjust the concentration of Ce in STCH-active oxides to tune the water-splitting performance. This can be difficult if the cerium addition leads to material stability only at fixed concentrations. This is the case for BCM, which is a line compound. Figure 3(a) shows a ternary plot of diffraction angle for compositionally graded $BaCe_xMn_{1-x}O_3$ films synthesized by utilizing $BaMnO_3$ (BMO), BCM, and $CeO_2$ targets via PLD. The composition XRD profile in the region of interest, $31 - 32°/2\theta$, indicates the primary peaks of BMO and BCM phases. The primary peak position of $BaMnO_3$ ($a$ = 5.667 Å, $c$ = 18.738 Å, $P6_3/mmc$ (194)) was indexed at $31.6°/2\theta$, while that of $Ba_5(Ce_{1.25}Mn_{3.75})O_{15}$ ($a$ = 5.786 Å, $c$ = 23.902 Å, $P6_3/mmc$ (194)) was indexed at $30.9°/2\theta$ by ICSD database. Figure 3(a) shows the BMO preserved in lower Ce fraction (0 – 4%) as phase pure. However, as the

Ce fraction increase, the primary peak position consistently shifted to a lower angle, indicating the formation of the BCM phase. Much higher Ce fractions could possibly be observed with the segregation of the BCM films to BMO and $CeO_2$ phases.
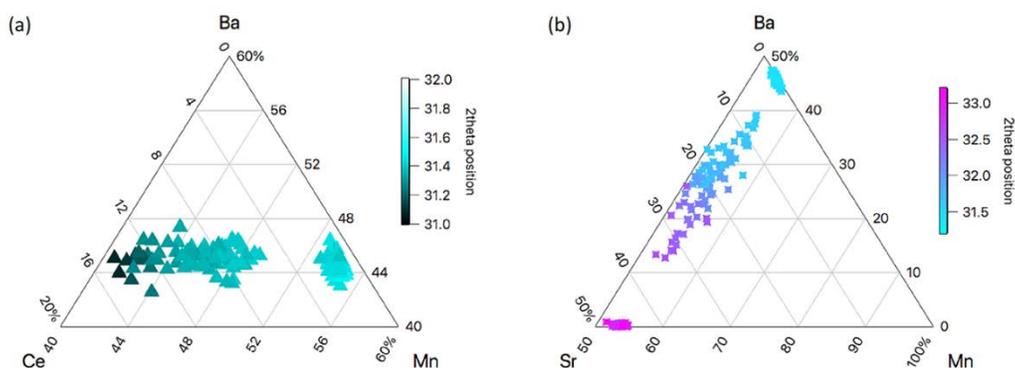


Figure 3. Ternary plots of XRD diffraction angle for (a) BCM and (b) SBM library films.

Interestingly, the key to increasing the Ce content may lie in the other cation. The Ce in BCM sits on the B-sites of the perovskite, while it sits on the A-site in the Sr containing CSM and SCM variants. So, our current investigations are studying the use of both cations simultaneously as a way to increase the available range of Ce doping. $Sr_xBa_{1-x}MnO_3$ (SBM) thin films were grown by using BMO and $SrMnO_3$ (SMO) targets to determine the effect of A-site cation on the structure. Figure 3(b) shows a ternary plot of diffraction angle for compositionally graded SBM films. The composition XRD profile indicates that the BMO peak positioned at 31.6°/2θ is steadily shifted to a higher angle to be an SMO structure as increasing the Sr fraction. Both BMO and SMO were indexed to a hexagonal *2H* structure (space-group *P6₃/mmc*). Considering the A-site ionic radius of the $Ba^{2+}$ ($r_{Ba2+}$ = 1.60 Å) and $Sr^{2+}$ ($r_{Sr2+}$ = 1.440 Å), this result shows the importance of the size of the 12-coordinated alkaline-earth ion on $ABX_3$ hexagonal perovskite stability.

## Bulk Materials Effort

In support of the validation of the computational component of this project, the oxygen vacancy defect thermodynamics have been determined using thermogravimetric analysis. The partial quantification of the difference in reduction thermodynamics between CSM and SCM has led to some interesting insights. Preliminary fits of the data show that the structure strongly influences the enthalpy of vacancy formation, but not the entropy. In comparing the enthalpy results with the aforementioned theoretical calculations, there is reasonable agreement between the SCM10 (200 kJ/mole or 2.1 eV/atom) and the 1.9 eV/atom for the SMO113. However, the enthalpy difference of approximately 50 kJ/mol between CSM and SCM is about a factor of eight larger than the 60 meV/atom that is predicted. At this point, it is important to remember that the calculations are for the non-cerium containing parent materials. As the computational work has predicted, the enthalpy is expected to increase as Ce is introduced to both materials.
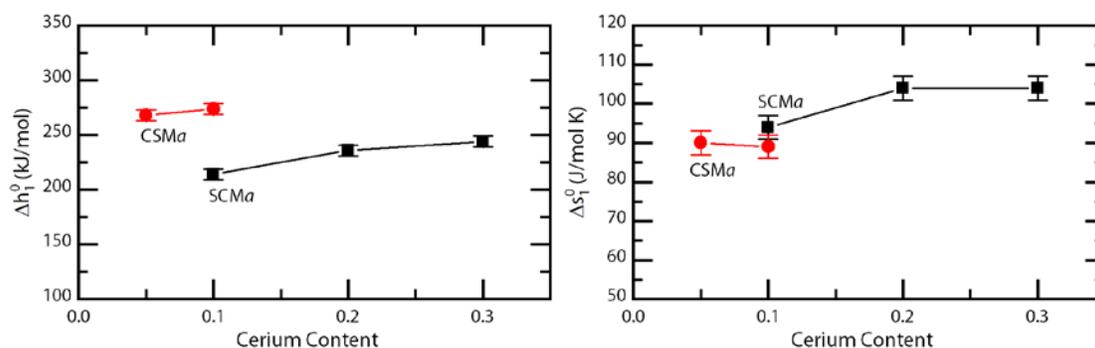


Figure 4. The effects of Ce content on the oxygen vacancy defect formation energy for CSM and SCM compositions.

Three SCM compositions have been tested using SNLs stagnation flow reactor node to assess their water-splitting performance, SCM20, SCM30, and SCM40. While all three variants split water, the higher Ce containing SCM40 had the best yield. The 280 µmol $H_2$/g, a new project high for per-cycle production. This $H_2$ yield is around 15% higher than the CSM2 composition reported last year. Unfortunately, preliminary testing indicates that it is unlikely to retain its high production capability under the more stringent low steam-to-hydrogen ratio testing conditions of the 2020 milestone.

## CONCLUSIONS AND UPCOMING ACTIVITIES

While this year has not seen the discovery of a "break-through" STCH material, the understanding provided by the work across all three efforts has greatly informed the search. This is especially true for our studies of the relationship between defect thermodynamics and structure. Previously, the search for STCH materials has assumed a structure and looked for stable compositions within that space. Only now are we beginning to understand that nearly the same composition can have very different STCH performance depending on the crystal structure.

Computationally, studies planned for FY20 will address the consequences of the Ce addition in CSM and SCM on the phase stability, as well as the defect formation energy. We are also exploring other tools, such as machine learning, to accelerate the structure search.

While part of the combinatorial film effort will continue to explore ways to adjust Ce content in BCM, most of the work will center on producing new combinatorial libraries of compositional families recommended by DFT results. Along with STCH testing, these films can also be used to inform the computational work on what structures are stable for a wide range of unknown chemical compositions. This is important because the structure search is computationally expensive, however, with combinatorial techniques we can allow nature to do much of the heavy lifting.

Finally, the bulk effort will continue to produce thermodynamic data and perform more detailed water-splitting experiments on the materials in the CSM and SCM compositional space. Work will also include the production of PLD targets and synthesis of new predicted STCH materials.

## FY 2019 PUBLICATIONS/PRESENTATIONS

1. D.R. Barcellos, F.G. Coury, A. Emery, M. Sanders, J. Tong, A. McDaniel, C. Wolverton, M. Kaufman, R. O'Hayre. "Phase Identification of the Layered Perovskite $Ce_xSr_{2-x}MnO_4$ and Application for Solar Thermochemical Water Splitting." *Inorganic Chemistry* 58, no. 12 (2019): 7705-14.

2. R. O'Hayre, M. Sanders, D. Barcellos, C. Duan, J. Huang, M. Papac, V. Stevanovic, N. Kumar, A. Zakutayev, S. Lany, A. Emery, C. Wolverton, C. Borg, A. McDaniel. "The 'Perovskite Playground'—Engineering Defect Chemistry in Doped Perovskite and Perovskite-Related Oxides for High Temperature Redox-Active Chemical and Electrochemical Applications." Invited Presentation. 2019 Spring MRS, Phoenix AZ.

3. M. Sanders, A. Bergeson-Keller, N. Kumar, J. Pan, D. Barcellos, V. Stevanovic, S. Lany, R. O'Hayre. "The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides." Presentation. 2019 Spring MRS, Phoenix AZ.

4. A. Bergeson-Keller, D. Barcellos, M. Sanders, R. O'Hayre. "Study of the Reduction Thermodynamics of $Sr_{1-x}Ce_xMnO_3$ Perovskites for Solar Thermochemical Hydrogen Production." Presentation. 2019 Spring MRS, Phoenix AZ.

5. R. O'Hayre, M. Sanders. "P165 Accelerated Discovery of STCH Hydrogen Production Materials via High Throughput Computational and Experimental Methods." Presentation. DOE Annual Merit Review 2019.

6. M. Sanders, A. Bergeson-Keller, N. Kumar, Y. Xu, J. Pan, D. Barcellos, A. Zakutayev, V. Stevanovic, S. Lany, R, O'Hayre. "The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides." Invited Presentation. Colorado Center for Advanced Ceramics 2019 Internal Conference, Golden CO.

## REFERENCES

1. A. Oganov, C. Glass. "Crystal structure prediction using ab initio evolutionary techniques: Principles and applications." *J Chem Phys 124* (2006): 244704