Final Report

Project Title: Accelerated Discovery of Solar Thermochemical Hydrogen Production Materials via High-Throughput Computational and Experimental Methods

Project Period of Performance: October 1st, 2017 – December 31st, 2021

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Executive Summary. In this project, combinatorial synthesis and testing methods were combined with high-throughput materials theory calculations to greatly accelerate the discovery of thermodynamically suitable candidates for green hydrogen production via a two-stage solar thermochemical water splitting (STCH) process. Over the course of the project, more than 8000 quinary and higher oxide compositions were computationally screened for STCH viability, and detailed stability calculations were performed for more than 30 of the most promising identified compositional archetypes. As a result, three new STCH capable compositional families were discovered and experimentally verified. The first, $Ce_xSr_{2-x}MnO_4$ (CSM), represents the first known Ruddlesden-Popper compound to show STCH activity, and thus demonstrates that perovskite-related structures may hold promise for this application. The second family, $Sr_{1-x}Ce_xMnO_3$ (SCM), is the simple perovskite sister-analog to CSM. $Sr_{0.7}Ce_{0.3}MnO_3$ (SCM30), a member of this compositional family, was found to produce the highest hydrogen yields of any compound tested in this project, exceeding the end of project milestone target of > 150 µmol H_2/gram oxide at a reduction temperature of 1350 °C, although only at steam-to-hydrogen ratios greater than 1000:1. Finally, we proved that a third novel Sr-and Mn-containing family, $Sr_{1-x}Ca_xTi_{1-y}Mn_yO_3$ (SCTM), which was identified by Materials Project tools, also splits water. The behavior of the SCTM system was found to be similar to the previously discovered $Sr_{1-x}La_xAl_{1-y}Mn_yO_3$ (SLMA) family, albeit with lower H_2 yields. Across the three thrusts of the project (computational, combinatorial, and bulk testing), five journal articles were published. As part of Program End Analysis and Data Dissemination, relevant data used for the publications was uploaded to the HydroGEN Data Hub for public access, and in certain cases, results were added to public materials databases.

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Project Objective: Because solar thermochemical hydrogen production (STCH) utilizes the full solar spectrum, it has the potential to achieve high theoretical efficiency. Despite its promise, however, surprisingly few candidate STCH materials have been uncovered that can compete with cerium oxide (CeO2), 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 cycles for STCH. This project will make significant in-roads to replacing ceria by obtaining outcomes along several distinct fronts: combinatorial density-functional theory (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.

Background: While ceria has shown itself to be the best performing and most cycle-tolerant STCH oxide, it requires very high reduction temperatures (>1500 °C) to attain sufficient per-cycle hydrogen yield. This leads to severe efficiency penalties which make the 2020 target of 20% STH efficiency unattainable.

Through collaboration with Sandia National Lab, the Colorado School of Mines (CSM) has worked at the forefront of materials development specific to STCH for the last several years. In that time, we have discovered two novel materials for STCH application. The first, $Sr_{0.6}La_{0.4}Mn_{0.6}Al_{0.4}O_{3-\delta}$ (SLMA)[1], produces much higher per-cycle hydrogen yields than ceria at lower temperatures (typically 1350 °C). However, it does not perform well under the high conversion conditions associated with realistic reactor operation, as any hydrogen that is produced dramatically hinders further water splitting. Based on the lessons learned from SLMA, we have recently developed a potential "goldilocks" material, $BaCe_{0.25}Mn_{0.75}O_{3-\delta}$ (BCM), which shows intermediate performance under high-conversion, falling between CeO_2 and SLMA, while still maintaining better hydrogen production than ceria at the lower target temperature of 1350 °C.

[1] McDaniel, A.H., et al., Energy & Environmental Science, 2013. **6**(8): p. 2424-2428.

Project Summaries:

Task 1: Computational Effort

Computationally, the combination of increased calculation speeds and better dissemination of previous modeling results has led to a revolution in materials research. However, methods for predicting “higher-level” material behaviors (like water splitting capability), from “lower-level” materials properties (such as atomic configurations, formation enthalpies and electronic structures) directly calculable by DFT are still in their infancy. Our work on modeling SLMA suggests that proxies can be used that allow difficult-to-calculate materials behavior (such as water splitting potential) to be inferred from relatively easy to calculate material properties (such as oxygen vacancy formation energies). This sort of inference can be further strengthened by greatly increasing the number of modeled and screened materials, refining existing proxies, as well as potentially discovering new ones. This effort hoped to not only bolster the search for STCH materials, but also enhance the search for other types of materials, such as solid-oxide fuel cell electrode materials, which share a number of common desired properties with STCH materials. Some of those goals were attained, as listed below, but the computations remain challenging.

- We have developed a general and novel approach on how to incorporate repulsive interactions for modeling defective systems beyond dilute limit and at high temperature. This fills a critical knowledge gap in the computational community and should be broadly applicable for the computational defect modeling of oxide systems at high temperatures across many applications beyond STCH, including ceramic fuel cells and electrolyzers, sensors, high-temperature semiconductors, and thermal barrier coatings. A manuscript titled “Predicting thermochemical equilibria with interacting defects: $Sr_{1-x}Ce_xMnO_{3-\delta}$ alloys for water splitting” has been submitted for publication.
- The thermodynamic modeling code can predict oxygen vacancy concentration as well as off-stoichiometry as a function of temperature and oxygen partial pressure for both the reduction and oxidation step.
- We have learned that oxygen vacancy formation energy in $Sr_{1-x}Ce_xMnO_3$ (SCM) alloys depends on the ratio of Mn^{3+}/Mn^{4+}. Therefore, varying Ce concentration in the alloys provide a mechanism to tune the oxygen vacancy formation energy because of the changing Mn^{3+}/Mn^{4+} ratio. This finding is fundamentally important for optimizing the STCH performance of Mn-containing alloy’s and can likely be adopted for other Mn-based STCH alloys.
- We developed a modeling tool that helps estimate capacity as a function of steam-to-hydrogen ratio, which directly relates to the STCH performance.

Task 2: Combinatorial Thin-Film Deposition and Experimentation

High-throughput predictive theory can be used to rapidly focus experimental efforts towards the most intriguing compositional regions. Nevertheless, high-throughput experimentation is also required to further isolate high-potential STCH candidates and to help validate/refine the behavioral trends predicted by theory. Combinatorial experimental efforts (mainly the creation of pulsed-laser deposited thin films of compositional gradients of materials) were leveraged to probe the full compositional range between promising end-member compounds. It was envisioned that these films could be screened directly for thermal redox behavior by observing color changes between the oxidized and reduced states after exposing the films to the STCH conditions of interest. This vision was never fully realized, as the combinatorial films were never robust enough to handle the stresses of redox cycling at high temperatures. The results are summarized below.

- The thin-film combinatorial production of STCH materials was never able to overcome the limitations of the deposition and testing processes. The combinatorial films required complicated targets that were already close to the compositions of interest, dramatically reducing the value and throughput. The experimental conditions were also too demanding for the films, and most were irreversibly destroyed or reacted with the substrates.
- The optical screening method was also never able to overcome the limitations. While it was shown that some materials do demonstrate a reversable color change during redox, the film challenges made it unlikely that for new compounds, any changes could be solely attributed to redox activity.
- The combinatorial films did however continue to show their usefulness when investigating a specific system, in this case, phase and structure analysis of the (Ba,Sr)MnO_3 perovskites. The ability to create large compositional gradients and investigate these compositions rapidly gave insight into the role of Ce in the structure and whether it was possible to have the dopant sit on both the a- and b-sites simultaneously. The results of that study were published in 2021 (doi.org/10.1021/acsenergylett.1c01214).

Task 3: Bulk Testing

Finally, follow-up quantitative testing needed be applied to the most promising compositions by bulk synthesis and characterization of specific compositions. A screening protocol was developed centering on temperature programed reduction and oxidation (TPR/TPO) studies using thermogravimetric analysis (TGA) to track the

reduction behavior of candidate materials and to determine oxidation reversibility upon reexposure to ambient air. We have found that materials that reduce at lower temperatures or have very large extents of reduction typically cannot split water, since in such cases the oxygen vacancy formation energy is too low and does not provide sufficient driving force for water splitting. Thus, materials that do not exhibit sufficient redox reversibility even under air re-oxidation will not be suitable for STCH. Any compositions that showed promise after screening were to be sent to Sandia's Virtually Accessible Laser Heated Stagnation Flow Reactor for Characterizing Redox Chemistry of Materials Under Extreme Conditions node (SFR) for validation. Plausible STCH candidates will split water under any steam-to-hydrogen ratio with a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C. This criterion covers most of the STCH candidates found to date.

With the difficulties in the previous two thrusts of the project, more traditional materials discovery methods were also employed, which had promising results, as detailed below. More in-depth investigation of two of the compounds was also performed to better understand the role of both compositional and structural variation on reduction thermodynamics and therefore STCH performance.

- Discovered three STCH capable compositional families. The first, $Ce_xSr_{2-x}MnO_4$ (CSM) is the first Ruddlesden-Popper compound to show thermochemical activity and demonstrates that perovskite-related structures may hold promise. Those results were published in 2019 (doi.org/10.1021/acs.inorgchem.8b03487). The second, $Sr_{1-x}Ce_xMnO_3$ (SCM) is the simple perovskite sister-composition to CSM. SCM30 produced the highest hydrogen yields of any compound tested in this project. Finally, we also proved that a third Sr-Mn family, $Sr_{1-x}Ca_xTi_{1-y}Mn_yO_3$ (SCTM), which was identified by Materials Project tools, also splits water. Its behavior was found to be similar to that of SLMA with lower yields.
- Published in late 2021 (doi.org/10.1002/ente.202100515), an in-depth thermodynamics study of the SCM/CSM families showed the role that both doping and structure play in tuning the redox thermodynamics. The ceria additions were seen as mainly structural stabilizers and a tool to shift the initial Mn^{3+}/Mn^{4+} ratio. It does not appear that the Ce plays any direct role in the thermochemical activity.
- Temperature Programmed Thermal Reduction (TPTR), a screening technique used since the inception of the project, was codified in standardized protocol form and was published for use by the wider STCH community (doi.org/10.3389/fenrg.2022.856943).

Conclusions.

- $Ce_xSr_{2-x}MnO_4$ (CSM), $Sr_{1-x}Ce_xMnO_3$ (SCM), and $Sr_{1-x}Ca_xTi_{1-y}Mn_yO_3$ (SCTM) are identified as STCH-capable perovskite or perovskite-related oxide systems. Of the three, the SCM compositional family gives the highest per-cycle H_2 productivity, with $Sr_{0.7}Ce_{0.3}MnO_3$ (SCM30) exceeding the end of project milestone target of > 150 µmol H_2/gram oxide at a reduction temperature of 1350 °C.
- None of the identified compositions retain their water splitting capability at the low steam to hydrogen ratios that are likely needed in a practical STCH process reactor design. H_2 productivity is observed to fall off dramatically below 1000:1 steam to hydrogen ratios, while a target steam to hydrogen ratio of 10:1 is likely needed for practical application.
- A novel, easy-to-implement Temperature Programmed Thermal Reduction (TPTR) technique was developed in this project to enable rapid experimental screening of candidate STCH materials. This new experimental method has been codified in standardized protocol form and has been published in the academic literature for use by the wider STCH community.
- On the computational front, thermodynamic modeling code was developed that can predict oxygen vacancy concentration as well as off-stoichiometry as a function of temperature and oxygen partial pressure for both the reduction and oxidation step. Accurate predictions require that defect-defect interactions beyond the dilute limit and at high temperature are properly accounted for. This fills a critical knowledge gap in the computational community and should be broadly applicable for the computational defect modeling of oxide systems at high temperatures across many applications beyond STCH, including ceramic fuel cells and electrolyzers, sensors, high-temperature semiconductors, and thermal barrier coatings.
- From DFT-modeling of the highest-performing $Sr_{1-x}Ce_xMnO_3$ (SCM) compositional family, we discovered that the oxygen vacancy formation energy depends on the ratio of Mn^{3+}/Mn^{4+}. Therefore, varying the Ce concentration in this system provides a mechanism to tune the oxygen vacancy formation energy because of the changing Mn^{3+}/Mn^{4+} ratio. This finding is fundamentally important for optimizing the STCH performance of Mn-containing alloys and can likely be adopted for other Mn-based STCH alloys.

Patents: None

Publications / Presentations:

Debora R. Barcellos, Francisco G. Coury, Antoine Emery, Michael Sanders, Jianhua Tong, Anthony McDaniel, Christopher Wolverton, Michael Kaufman, Ryan O'Hayre, *Phase identification of the layered perovskite $Ce_xSr_{2-x}MnO_4$ and application for solar thermochemical water splitting*, **Inorganic Chemistry,** 2019, 58, 12, 7705-14.

Ryan O'Hayre, Michael Sanders, Debora Barcellos, Chuancheng Duan, Jake Huang, Meagan Papac, Vladan Stevanovic, Nitin Kumar, Andriy Zakutayev, Stephan Lany, Antione Emery, Chris Wolverton, Chris Borg, Anthony McDaniel, *The "Perovskite Playground"—Engineering Defect Chemistry in Doped Perovskite and Perovskite-Related Oxides for High Temperature Redox-Active Chemical and Electrochemical Applications* **2019 Spring MRS, Phoenix AZ**

Michael Sanders, Anyka Bergeson-Keller, Nitin Kumar, Jie Pan, Debora Barcellos, Vladan Stevanovic, Stephan Lany, Ryan O'Hayre *The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides* **2019 Spring MRS, Phoenix AZ**

Anyka Bergeson-Keller, Debora Barcellos, Michael Sanders, Ryan O'Hayre *Study of the Reduction Thermodynamics of Sr_{1-x} Ce_xMnO_3 Perovskites for Solar Thermochemical Hydrogen Production* **2019 Spring MRS, Phoenix AZ**

Ryan O'Hayre and Michael Sanders, *P165 Accelerated Discovery of STCH Hydrogen Production Materials via High Throughput Computational and Experimental Methods* **DOE Annual Merit Review 2019**

Michael Sanders, Anyka Bergeson-Keller, Nitin Kumar, Yun Xu, Jie Pan, Debora Barcellos, Andriy Zakutayev, Vladan Stevanovic, Stephan Lany, Ryan O'Hayre *The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides* **Colorado Center for Advanced Ceramics 2019 Internal Conference, Golden CO**

Su Jeong Heo, Michael Sanders, Ryan O'Hayre, and Andriy Zakutayev, *Double-site Ce Substitution of $(Ba,Sr)MnO_3$ Perovskites for Solar Thermochemical Hydrogen Production,* **ACS Energy Letters,** 2021, 6, 9, 3037–3043.

Anyka Bergeson-Keller, Michael Sanders, and Ryan O'Hayre, *The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides*, **Energy Technology,** 2022 10, 1, 2100515.

Michael Sanders, Anyka Bergeson-Keller, Eric Coker, and Ryan O'Hayre, *Using Temperature Programmed Thermal Reduction as Screening Method for STCH Active Compositions*, **Frontiers in Energy Research – Article Collection on Advanced Water Splitting Technologies Development: Best Practices and Protocols**, 2022, 10, 856943.

Milestone Schedule							
Milestone #	**Project Milestones**	**Type**	**Task Completion Date (Project Quarter)**				**Progress Notes**
			Original Planned	**Revised Planned**	**Actual**	**Percent Complete**	
1.1	Complete theoretical stability analysis (via the application of convex hull methodology) of at least 4250 compounds, based on a combination of existing data located in material databases and new DFT calculations.	Milestone	3/31/2018		3/31/2018	100%	Complete
GNG1.3	**Experimentally validate method to qualitatively predict thermodynamic trends in oxide reduction (and hence potential STCH suitability) as a function of oxide composition by DFT across five different families and within at least one compositional family.**	**Go/No-Go**	**9/30/2018**		**9/30/2018**	**100%**	**Complete -- Compositional family related to compound X bulk screen testing complete**
1.4	Complete calculations for at least 6 compositions (3 from each system)	Milestone	11/30/2019	—	—	40%	Folded into 1.9
1.7	Validation of defect calculations by comparison with experimental results from Task 3.4.	Milestone	2/28/2020	—	—	10%	Folded into 1.9
1.9	Validate predicted off-stoichiometry behavior of six CSM/SCM compositions with experimental data for delta vs temperature (800 °C – 1400 °C) and oxygen partial pressure (pO2 = 1E-5 – 1E-2 atm).	Milestone	6/30/2021	12/31/2021	—	80%	Failed — Calculations are ongoing. Results will be published in mid 2022.
1.10	Identify at least five new candidates for bulk synthesis. Candidates should come from at least 3 different compositional families.	Milestone	3/30/2021	9/30/2021	—	50%	Failed — Two candidates were found but nonviable.
1.11	Produce a plot of average computation time per compound on Y-axis broken out by number of elements in formula unit vs. project quarter (or less if more applicable). Plot a secondary Y-axis of total compounds searched for that quarter. For quarters that utilized Random-Smart, plot both average computation time and estimated time if Random-Smart was not used. Annotate significant discontinuities in the trends.	Milestone	6/30/2021	9/30/2021	—	25%	Failed — Random-Smart work was abandoned by researcher and no data was transferred to project.
2.1	Produce a work instruction outlining the best evaluation techniques for evaluating the combinatorial PLD films for potential water splitters. Techniques will be determined by analysis of PLD films of known STCH materials and known inert and non-water-splitting compounds.	Milestone	12/31/2017		6/30/2018	100%	100% films needed to develop techniques complete, 50% complete on other process plans.

Milestone Schedule							
Milestone #	**Project Milestones**	**Type**	**Task Completion Date (Project Quarter)**				**Progress Notes**
			Original Planned	**Revised Planned**	**Actual**	**Percent Complete**	
2.3	Structure/property relationships demonstrated for at least one PLD combinatorial thin-film library by spatially measuring structure (by XRD), and composition (by XRF)	Milestone	6/30/2018		6/30/2018	100%	Complete – Ten library films made and delivered for testing
2.4	Perform blind study on films of known STCH and non-STCH materials and accurately determine STCH active areas	Milestone	8/30/2019	—	—		Failed – Films were never capable of reversable redox behavior
2.9	Disseminate combinatorial BSCM film results	Milestone	12/30/2020	3/30/21	3/30/21	100%	Complete
GNG3.2	**Bulk testing demonstrates that at least one material composition splits water with a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C, under any steam-to-hydrogen ratio.**	**Go/No-Go**	**9/30/2018**		**9/30/2018**	**100%**	**Complete -- $Ce_xSr_{2-x}MnO_4$ (Compound X) exceeds performance target**
3.4	Completion of extent-of-reduction testing and simple thermodynamic modeling of CSM/SCM system	Milestone	5/30/2019		5/30/2019	100%	Complete
GNG3.5	**Bulk testing demonstrates that at least one material composition splits water under steam-to-hydrogen ratios lower than 10:1 and with a hydrogen capacity under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C at least equal to that of ceria under the reduction conditions of 1450°C and oxidation temperatures of 850°C-1000°C.**	**Go/No-Go**	**02/28/2020**	**—**	**—**	**0%**	**Removed**
5.1	Verify all project data has been uploaded to the HydroGEN Data Hub and relevant data has been made available to the public.	Milestone	9/30/2021	12/31/2021	12/31/2021	100%	Most relevant data is uploaded to hub. Public release has not been requested to date.