SAND2016-9299R

# II.C.1 High Efficiency Solar Thermochemical Reactor for Hydrogen Production

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Project Start Date: October 1, 2014

Project End Date: December 31, 2016

## Overall Objectives

- Verify the potential for solar thermochemical cycles for hydrogen production to be competitive in the long term and by 2020, develop this technology to produce hydrogen with a projected cost of \$3.00/gge at the plant gate.
- Develop a high-efficiency particle bed reactor for producing hydrogen via a thermochemical water-splitting (WS) cycle, and demonstrate eight continuous hours of operation on a solar simulator producing greater than 3 L of $H_2$.

## Fiscal Year (FY) 2016 Objectives

- Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical water-splitting cycles. (Barrier S and T)
- Construct and demonstrate a particle receiver-reactor capable of continuous operation at 3 kW thermal input. (Barrier T)
- Conduct full techno-economic, sensitivity, and trade-off analysis of large-scale hydrogen production facility using a plant-specific predictor model coupled to H2A. (Barrier X)

## Technical Barriers

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

(S) High-Temperature Robust Materials
(T) Coupling Concentrated Solar Energy and Thermochemical Cycles
(X) Chemical Reactor Development and Capital Costs

## Technical Targets

This project is conducting fundamental studies on materials for use in concentrated solar power applications and designing reactor concepts that, when combined, will produce hydrogen from thermochemical WS cycles. Insights gained from these studies will be applied toward the design and optimization of a large scale solar receiver and reactor that meets the following ultimate DOE hydrogen production targets:

- Hydrogen cost: <\$2/kg $H_2$
- Material of reaction cost: ≤\$11K/yr TPD $H_2$
- Solar-to-hydrogen (STH) conversion ratio: ≥26%
- One-sun hydrogen production rate: $\geq 2.1 \times 10^{-6}$ kg/s $m^2$

## FY 2016 Accomplishments

- Extended approach to material discovery and engineering of thermochemical properties by demonstrating an entropy engineering concept using Sr–$CeO_2$, and by applying density functional theory (DFT) to guide synthesis and characterization of binary $ABO_3$ perovskites.
- Identified key trends in material properties under thermal reduction, from approximately 200 compound formulations, that informed a heuristic approach to assessing material viability.
- Completed design of Sandia's cascading pressure receiver–reactor ($CPR^2$) moving particle bed reactor and in process of fabrication. Design choices were validated using modeling, simulation, and lab tests in order to increase the likelihood of meeting overall project objectives.
- Finalized a component-level model of Sandia's reactor concept to enable more advanced techno-economic analysis that will increase the fidelity and accuracy of H2A cost analysis and allow for detailed sensitivity and cost performance tradeoff analysis.

## Introduction

This research and development project is focused on the advancement of a technology that produces hydrogen at a cost that is competitive with fossil-based fuels for transportation. A two-step, solar-driven WS thermochemical cycle is theoretically capable of achieving an STH conversion ratio that exceeds the DOE target of 26% at a scale large enough to support an industrialized economy [1]. The challenge is to transition this technology from the laboratory to the marketplace and produce hydrogen at a cost that meets or exceeds the DOE target of <\$2/kg $H_2$.

Conceptually, heat derived from concentrated solar energy can be used to reduce a metal oxide at high temperature producing oxygen (Step 1). The reduced metal oxide is then taken "off sun" and re-oxidized at lower temperature by exposure to water, thus producing hydrogen (Step 2) and completing the cycle. Commercial success of solar thermochemical hydrogen production is contingent upon developing suitable redox active materials and incorporating them into an efficient reactor. There are numerous material chemistries that have attributes suitable for inclusion in a thermochemical hydrogen production system [2-4]. The challenge is to identify an optimally performing material. In addition, the development of redox material and reactor are not mutually exclusive, but must be conducted in parallel [5]. To maximize the probability of success, this project also addresses the reactor- and system-level challenges related to the design of an efficient particle-based reactor concept [6].

## Approach

Thermochemical WS reactors are heat engines that convert concentrated solar energy (heat) to chemical work. Our approach is to discover materials to accomplish the WS chemistry and pair these with a novel cascading pressure receiver–reactor ($CPR^2$) that, when combined, can achieve an unprecedented STH conversion ratio. The material discovery work involves expanding our understanding of the underlying thermodynamics and kinetics in order to make performance improvements and/or formulate new, more redox active compositions. Sandia's patented $CPR^2$ technology is based on a moving bed of packed particles that embodies key design attributes essential for achieving high efficiency operation: (1) sensible heat recovery; (2) spatial separation of pressure, temperature, and reaction products; (3) continuous on-sun operation; and (4) direct absorption of solar radiation by the redox active material. Research efforts are focused on demonstrating this technology in a 3 kW scale prototype.

## Results

Materials Research and Development Thrust. Over the course of this project, Sandia and collaborators have synthesized and screened a select group of compounds for redox and WS activity from perovskite, lanthanum molybdenum oxide, fluorite, and zircon-type crystal structures derived from 15 elements (Al, Ba, Ca, Ce, Fe, La, Mn, Mo, Nb, O, Sn, Sr, Ti, V, and Zr). Through this effort, guided by experience gained from investigating oxides for two-step thermochemical WS cycles and DFT, the $Ce^{3+/4+}$, $Fe^{2+/3+}$, $Mn^{2+/3+/4+}$, $Mo^{3+/4+}$, $Sn^{2+/4+}$, $Ti^{2+/4+}$, and $V^{4+/5+}$ redox couples were explored. More than 200 compounds were synthesized and screened using various thermogravimetric analysis (TGA) protocols, the most efficient of which measured oxygen evolution behavior during a single heat cycle and then inferred WS candidacy from two figures of merit: (1) a redox capacity that exceeds $CeO_2$ (0.01 mol O/mol sample), and (2) an onset temperature for oxygen release ($T_{OR}$) where the extent of oxygen non-stoichiometry ($\delta$) exceeds 0.005. Viable WS candidates have a $T_{OR}$ between $Sr_{0.6}La_{0.4}Mn_{0.6}Al_{0.4}O_3$ (SLMA6464) (850°C) and $CeO_2$ (1,350°C). Approximately 50 compounds with high figures of merit were further characterized in Sandia's stagnation flow reactor.

Shown in Figure 1 is a summary of the most relevant results from this project's material research and development thrust. The filled circles represent specific oxide formulations, for example $CeO_2$ or SLMA6464, plotted as a function of the maximum $\delta$ observed by mass loss measured using TGA ($T_{RED}$=1,350°C and $pO_2 < 10^{-8}$ atm) versus the temperature at which $\delta$ exceeds 0.005. Compound formulations known to split water upon re-oxidation with steam are found in the yellow and green shaded areas. Two key trends in material redox behavior are evident in Figure 1. First, materials that exhibit a large $\delta$ (>0.25) generally do not split water under practically accessible oxidation conditions even though the crystal structure may support a large oxygen deficiency. Second, many WS-active compounds were identified, and achieved a larger $\delta$ than $CeO_2$ at lower temperatures. However, moving from right to left along the solid green line in Figure 1, the amount of steam required to re-oxidize the material relative to the amount of $H_2$ produced increases dramatically. Going from a 1:1 $H_2O$:$H_2$ ratio at the far right (characteristic of $CeO_2$) to a value greater than 10,000:1 on the left. This means that the thermodynamic driving force to move oxygen back into the solid becomes less favorable for compounds that reduce at relatively low temperatures and support larger $\delta$s. It is unclear yet if these trends comprise a universal truth for nonstoichiometric oxides, but these results may bound the discovery space and could be leveraged in a high-throughput screening study.

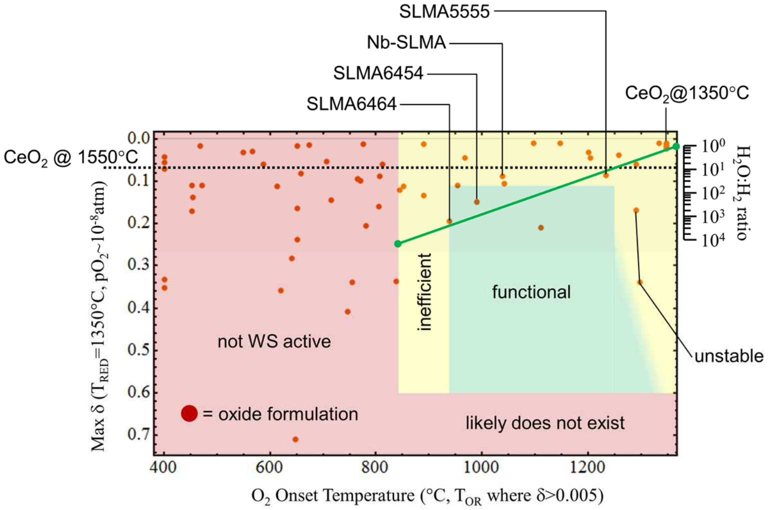

Figure 1. Graphic summarizing pertinent results from this project's materials discovery effort. Each filled circle represents a specific compound formulation that was synthesized and tested for redox activity and WS efficacy using TGA and stagnation flow reactor techniques. The ordinate is the maximum oxygen nonstoichiometry ($\delta$) inferred by mass loss measured under reduction at 1,350°C and $pO_2 \sim 10^{-8}$ atm using TGA. The abscissa is the temperature at which $\delta$ exceeds a value of 0.005. The horizontal black, dashed line is the maximum $\delta$ for $CeO_2$ at 1,550°C, which we believe is a practical operating limit for concentrated solar powered reactors. New materials have potential if their maximum $\delta$ is below the black, dashed line. The green solid line is a trend in the $H_2O$:$H_2$ ratio that fixes the gas-phase oxygen chemical potential required to achieve full re-oxidation at temperatures between 800-1,000°C. Values closer to unity are considered more commercially viable.

During this project year, we also extended our approach to engineering of thermochemical properties and material discovery by: (1) demonstrating an entropy engineering concept, using Sr-doped $CeO_2$ as a model compound, to effectively increase hydrogen production by 10% relative to undoped $CeO_2$ through lattice softening induced by aliovalent substitution, and (2) by applying a high-throughput DFT approach to screen 5,329 cubic and distorted binary $ABO_3$ perovskite formulations for WS activity. Using DFT, we identified 139 materials as potential candidates for WS, and tested 10 of them. No *new* commercially viable WS oxides were discovered.

*CPR$^2$ Fabrication and Demonstration Thrust.* By the conclusion of this project, this team will demonstrate continuous operation of a 3 kW prototype thermochemical WS reactor capable of producing >0.3 L/min $H_2$. The salient components of the CPR$^2$ are shown in Figure 2. Starting from top to bottom in the numbered schematic (particles flow by a combination of gravity and "slip-stick" action): 1-particle supply chamber that stores enough redox active material for 10 h of operation, holding high vacuum at ~800°C; 2-solar simulator module comprised of multiple lamps each producing a peak flux of ~1,000 kW/m$^2$ (Figure 3 shows the design and measured irradiance of the simulator modules in greater detail); 3-solar receive/reactor (TR chamber) where particles are brought to temperatures in excess of 1,500°C by exposure to simulated solar radiation, and reduced in high vacuum; 4-heat rejection chamber where the particle temperature is lowered to <1,000°C under high vacuum; 5-pressure separation segment capable of withstanding a 200× pressure differential between the TR and WS without fluidizing the packed particle bed; 6-WS chamber where particles are re-oxidized by steam at near ambient pressure and 800°C; and 7-particle reservoir chamber where fully oxidized material accumulates for return to the supply chamber. The schematic in Figure 2 shows a single TR configuration. A second TR chamber and simulator will be added at the conclusion of this project.

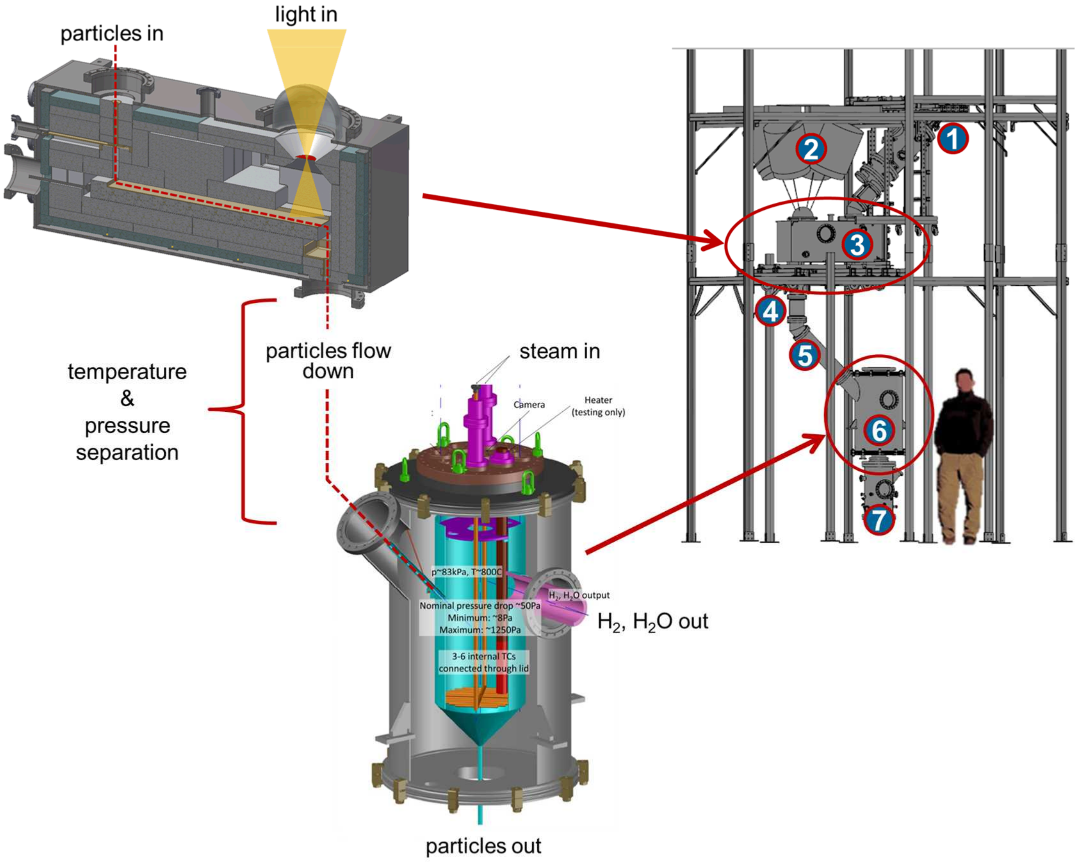

Figure 2. Detailed CPR$^2$ schematics for TR and WS chambers, as well as a numbered list of major system components (see text for discussion). In one year our team went from notional concepts of component design to fabrication and assembly of the CPR$^2$. Particles flow through system by a combination of gravity in vertical components, and “slip-stick” action along horizontal plates in the TR chambers. This design enables precise control of the particle flow rate and residence time under irradiance. The system will demonstrate Sandia’s patented technology (i.e., pressure separation via moving particle bed and pressure cascade for high efficiency) and will be capable of producing >0.3 L/min $H_2$ continuously.

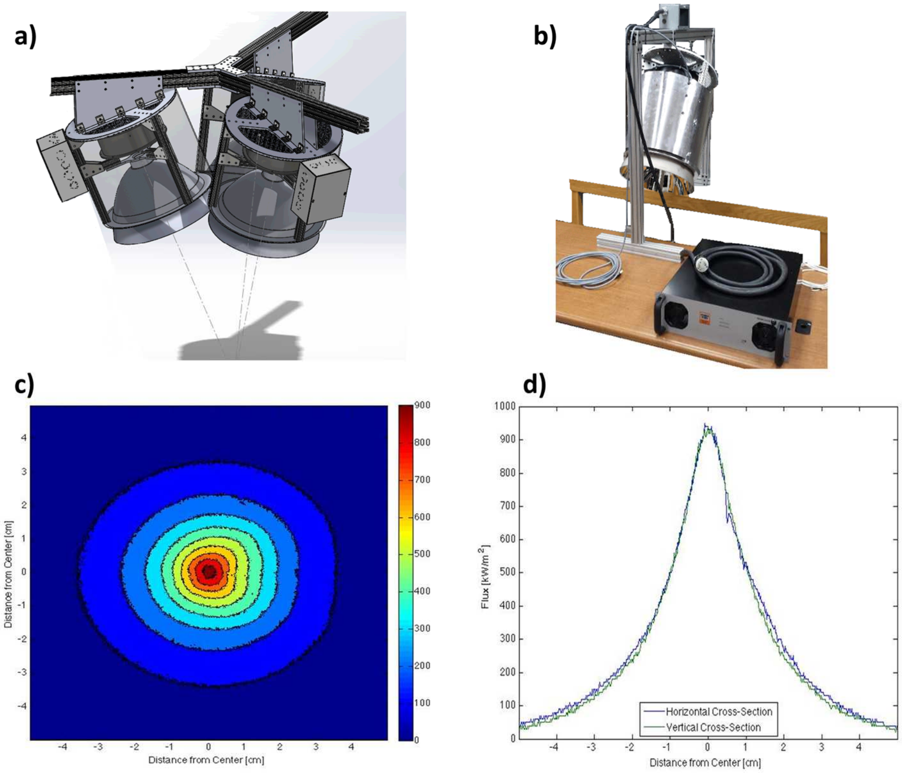

Figure 3. a) Solid model of Bucknell's three-lamp simulator module that will be used to power one of the TR chambers in the CPR$^2$. A four-lamp module will also be used, for a total of 7 kW of radiant energy delivered to two separate TR chambers. b) A photograph of a single lamp module and ballast controller. c) Flux map for a single lamp module. d) Plot of radiative flux as a function of distance along horizontal and vertical centerlines taken from the flux map in (c). These flux maps were imported into ray-tracing models and used to design the lamp layout and predict the performance of the multi-lamp arrays, as well as explore the expected thermal behavior of the radiant cavity housed within each TR chamber (e.g., locate potential hot spots).

During the last 12 months, our project team progressed from notional concepts of the CPR$^2$ to fabrication and assembly. Innumerable design choices were considered for each critical component and system operation, ultimately vetted using detailed modeling and experiments on suitable proxies for subcomponents to ensure feasibility, robustness, and high-efficiency operation at this scale. The entire system is a blend of steel, ceramic, and glass that meets the following key design criteria: (1) direct irradiation of redox material without particle shading, (2) precise control of particle flow rate and residence time in the TR chambers, (3) pressure separation without internal mechanical components like valves, (4) counter-flow mass exchange between steam and particles in WS chamber (i.e., no mixing or fluidization during re-oxidation), and (5) eight hours of continuous operation producing at least three liters of hydrogen. Thus far we have incorporated our extensive understanding of this process into the design of a 3 kW-scale reactor. The CPR$^2$ is a one-of-a-kind instrument that will be used to evaluate all reactor functions, inclusive of hydrogen production and material durability. Data collected from this instrument will be used to further refine reactor designs, and analytically up-scale Sandia's technology to a multi-megawatt centralized tower system.

*Technoeconomic Analysis Thrust.* We have finalized a design of a baseline model for a single centralized tower receiver (~29 MW) that, when combined with ~82 others, will constitute a 100 mt $H_2$/day solar thermochemical water splitting plant. The tower receiver model, shown in Figure 4a, is comprised of 14 major components that represent mass and energy flows between solar field, solar receivers, TR, WS, heat exchangers, recuperators, condensers, and pumps. The complexity and interdependency of this system is evident from the colored lines that crisscross the figure connecting one component to another. Accurately capturing system behavior is necessary to better inform H2A, as well as conduct time and DNI-dependent analysis. Engineering Equation Solver™ is used to exercise the one-dimensional steady state quasi-equilibrium model, which is capable of calculating system cost and STH efficiency, as well as perform sensitivity and tradeoff analysis. The latter is done through changing the system design configuration, component-level parameters, and state point values to affect system-level metrics.

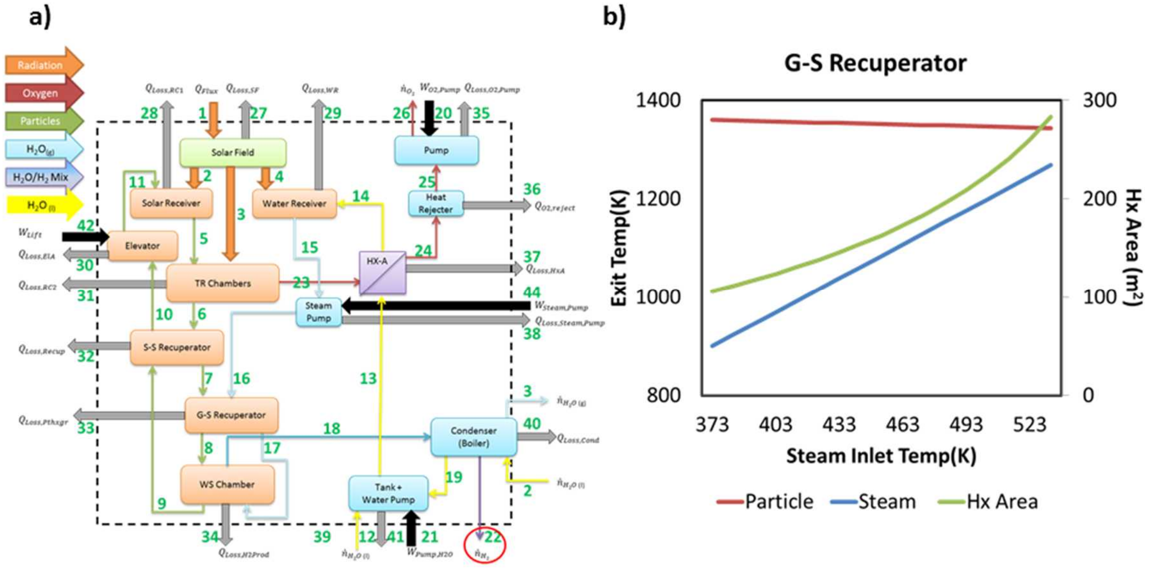

Figure 4. a) Component diagram for a single tower, multiple receiver (Solar Receiver + TR Chambers), concentrated solar powered thermochemical WS system using a non-volatile metal oxide in a two-step process. This diagram represents the minimum number of unit operations needed to implement our thermochemistry. We envision this tower running at 29 MW, and that approximately 82 such towers will be needed to produce 100 mt $H_2$/day. b) Model predictions showing how the heat exchanger surface area scales with process parameters for the gas-solid (G-S) recuperator. While desirable to have particle and steam temperature as close to each other as possible, the recuperator surface area becomes too large, thus requiring a decision between operational efficiency and capital cost (see text).

A representative example of component interdependency, and hence system complexity, is illustrated using the G-S Recuperator. Two variables of interest are the steam flowrate entering G-S (16) and recuperator surface area (Hx Area). The particle flow rate (7) is dependent on the instantaneous solar flux (1), and we want the recuperator exit temperature of both streams (8, 17) to be as close as possible. The data in Figure 4b shows that Hx Area will grow unrealistically large if we attempt to bring the exit temperatures of steam and particle to the same value, and therefore the existing steam flow (16) is not sufficient to cool the particles to the desired WS temperature. Simply increasing steam flow into G-S is not an option because of other upstream interdependencies. As such, we must consider inserting another heat exchanger between G-S and WS, or expect suboptimal STH efficiency because particles entering the WS chamber are too hot.

Herein lies the crux of tradeoff analysis, taking the lesser cost penalty between increased investment and lower operational efficiency. Upon completion of this project, we will combine our analysis with H2A to produce a roadmap from 2015 to the "Ultimate" case identifying system and material requirements needed to meet DOE cost targets for hydrogen production.

## Future Directions

- Produce ~150 kg of pelletized $CeO_2$ redox material for full scale $CPR^2$ tests.
- Produce at least three standard liters of hydrogen in eight continuous hours of operation of $CPR^2$.
- Complete techno-economic and cost-performance tradeoff analysis for a 100 mt $H_2$/day solar-thermochemical production plant.
- Disseminate project results through publications in peer-reviewed journals.

## FY 2016 Selected Publications/Presentations

1. I. Ermanoski, J. Grobbel, A. Singh, J. Lapp, S. Brendelberger, M. Roeb, C. Sattler, J. Whaley, A. McDaniel, N.P. Siegel, Design and Construction of a Cascading Pressure Reactor Prototype for Solar-Thermochemical Hydrogen Production. In *AIP Conference Proceedings*; Cape Town, South Africa, 2016; Vol. 1734, p 120001.
2. W.C. Chueh, Electrochemical Redox of Late Transition Metal Perovskite Oxides, American Chemical Society National Meeting. Mar. 15, 2016. San Diego, USA (Invited).
3. A. M. Deml, R. O'Hayre, C. Wolverton, V. Stevanovic, "Predicting DFT total energies and enthalpies of formation of metal-nonmetal compounds by linear regression", Phys. Rev. B. 93, 085142, (2016).
4. A. M. Deml, A. M. Holder, R. P. O'Hayre, C. B. Musgrave, and V. Stevanović, "Intrinsic Material Properties Dictating Oxygen Vacancy Formation Energetics in Metal Oxides", J. Phys. Chem. Lett., 6, 1948−1953 (2015).
5. A. McDaniel, D. Barcellos, M. Sanders, J. Tong, R. O'Hayre, N. Ahlborg, C.B. Gopal, W. Chueh, A. Emery, C. Wolverton, J. Miller, "Solar Thermochemical Water Splitting: Advances in Materials and Methods", Invited Talk, 6th ECI Conference on Nonstochiometric Compounds, Santa Fe, New Mexico, USA, Sept 5th-9th, 2016.
6. R. O'Hayre, "Materials for Solar Thermochemical Hydrogen Production: Can We Beat Ceria?", Presentation to the Board of The Edward Orton Junior Foundation, Columbus, Ohio. June 17th, 2016.
7. R. O'Hayre, "Materials for Electrochemical Energy Conversion", Materials Science and Engineering Departmental Seminar, The Ohio State University, Columbus, Ohio. June 16th, 2016.
8. A. Deml, A. Holder, V. Stevanovic, and R. O'Hayre, "Incorporating Finite Temperature Effects into Materials by Design: Complex Functional Oxides", Invited Talk, 2nd International Conference on Functional Oxide Thin Films for Advanced Energy and Information Technology, Cancun, Mexico, March 5th-8th, 2016.
9. R. O'Hayre, C. Duan, M. Sanders, D. Clark, M. Shang, D. Diercks, B. Gorman, S. Ricote, and J. Tong, "Materials for Electrochemical Energy Conversion", Invited Seminar, Korea Institute of Materials Science, South Korea, August 10th, 2015.
10. R. O'Hayre, C. Duan, M. Sanders, D. Clark, M. Shang, D. Diercks, B. Gorman, S. Ricote, and J. Tong, "Materials for Electrochemical Energy Conversion", Invited Seminar, Korea Tech, South Korea, August 6th, 2015.

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## References

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2. W.C. Chueh and S.M. Haile, *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.*, **368**, 3269–3294 (2010).
3. R.B. Diver, J.E. Miller, M.D. Allendorf, N.P. Siegel, and R.E. Hogan, *J. Sol. Energy Eng.*, **130**, 041001(1)-041001(8) (2008).
4. A.H. McDaniel, E.C. Miller, D. Arifin, A. Ambrosini, E.N. Coker, R. O'Hayre, W.C. Chueh, and J. Tong, *Energy Environ. Sci.*, **6**, 2424–2428 (2013).
5. J.E. Miller, A.H. McDaniel, and M.D. Allendorf, *Adv. Energy Mater.*, **4**, 1300469 (2014).
6. I. Ermanoski, N.P. Siegel, and E.B. Stechel, *J. Sol. Energy Eng.*, **135**, 31002 (2013).

## Acronyms

| | |
|---|---|
| $CPR^2$ | cascading pressure receiver-reactor |
| DFT | density functional theory |
| FY | fiscal year |
| G-S | gas-solid recuperator unit operation |
| SFR | stagnation flow reactor |
| SLMA | general term to describe $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$ perovskite compositions |
| SLMA6464 | $Sr_{0.6}La_{0.4}Mn_{0.6}Al_{0.4}O_3$ |
| STH | solar-to-hydrogen |
| TGA | thermogravimetric analyzer |
| $T_{OR}$ | onset temperature for oxygen evolution measured during thermal reduction |
| TR | thermal reduction chamber |
| $T_{RED}$ | the oxide thermal reduction temperature, usually in the range 1300-1600°C |
| WS | water-splitting |
| $\delta$ | extent of oxygen non-stoichiometry in, for example, $ABO_{3-\delta}$ or $CeO_{2-\delta}$ |
| L | liter |
| $CeO_2$ | Cerium(IV) oxide |
| MW | megawatt |
| ~ | approximately |

## Figure Captions

Figure 1. Graphic summarizing pertinent results from this project's materials discovery effort. Each filled circle represents a specific compound formulation that was synthesized and tested for redox activity and WS efficacy using TGA and stagnation flow reactor techniques. The ordinate is the maximum oxygen nonstoichiometry ($\delta$) inferred by mass loss measured under reduction at 1,350°C and $pO_2 \sim 10^{-8}$ atm using TGA. The abscissa is the temperature at which $\delta$ exceeds a value of 0.005. The horizontal black, dashed line is the maximum $\delta$ for $CeO_2$ at 1,550°C, which we believe is a practical operating limit for concentrated solar powered reactors. New materials have potential if their maximum $\delta$ is below the black, dashed line. The green solid line is a trend in the $H_2O:H_2$ ratio that fixes the gas-phase oxygen chemical potential required to achieve full re-oxidation at temperatures between 800-1,000°C. Values closer to unity are considered more commercially viable.

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