II.C.2 Flowing Particle Bed Solarthermal Redox Process to Split Water

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Project End Date: November 30, 2017

Overall Objectives

The University of Colorado's overall objective is to design and test individual components of a novel flowing particle solarthermal water splitting (STWS) system by optimizing active redox materials, reactor containment materials, and reactor design, with the ultimate goal of demonstrating our technology by producing three standard liters of hydrogen in eight hours on-sun in a prototype fluidized particle reactor.

Fiscal Year (FY) 2017 Objectives

- Develop and test reactive materials with high productivity that have stable reactivity.

- Perform kinetic studies on reactive materials of interest.

- Test reactor tubes coated with specially developed containment materials for steam resistance.

- Test compatibility of containment materials with reactive materials.

- Evaluate performance of fluidized bed with high-temperature O_2 transport membrane.

- Collaborate closely with joint National Science Foundation and the Department of Energy's (DOE's)

materials discovery "sister" project to screen improved active materials.

- Work with the NREL to demonstrate on-sun hydrogen production.

- Update process model and H2A to reflect experimental progress toward DOE goals.

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.

(S) High-Temperature Robust Materials

(W) Materials and Catalysts Development

(X) Chemical Reactor Development and Capital Costs

Technical Targets

The project's performance towards DOE's technical targets were projected using experimental results from our materials testing and thermodynamic modeling, a process model of a 50,000 kg H_2/d industrial-scale production plant, a detailed solar field model, and DOE's H2A techno-economic analysis program and are outlined in Table 1.

TABLE 1. Progress toward Technical Targets for Solar-Driven Thermochemical Hydrogen Production

Characteristics	Units	2015 Target	2020 Target	CU 2017 Status
Solar-Driven High-Temperature Thermochemical Cycle H_2 Cost	$/kg	14.80	3.70	8.79
Active Material Cost per Year	$/yr-TPD H_2	1.47M	89K	68K[a]
STH Energy Conversion Ratio	%	10	20	13.8[*]
On-Sun Hydrogen Production Rate	kg/s per m^2	8.1 x 10^{-7}	1.6 x 10^{-6}	1.1 x 10^{-6}

CU – University of Colorado; STH – solar-to-hydrogen ratio; TPD – tonne per day
[a] Assuming reactive material lifetime of 1 yr
[*] Using hercynite (FeAl$_2$O$_4$)

FY 2017 Accomplishments

- Performed long-term stability tests of reactive materials showing no loss in reactivity between 100th and 200th cycle and 2X targeted H_2 production rate.

- Developed atomic layer deposition (ALD) barriers that improve high-temperature resistance of SiC to steam by >60%, 2X targeted impact.

- Demonstrated on-sun production of 1.91 standard liters H_2 in less than three hours.

- Assessed economic viability of thermal energy storage to provide electricity for non-intermittent STWS.

- Completed study on effects of structure and magnetic ordering for 1,343 materials.

- Continued testing of high temperature O_2 transport membrane for inert gas recycle.

- Completed construction of high-flux solar simulator to test hybrid reactor concept.

✧   ✧   ✧   ✧   ✧

INTRODUCTION

In order to meet DOE targets for economical and efficient solarthermal hydrogen production at the commercial scale, advances in active redox materials and reactor fabrication materials are needed. Ideal STWS materials have high hydrogen production capacity, relatively low thermal reduction temperatures (closer to 1,200°C than 1,500°C), fast reaction kinetics, reduction enthalpies on the order of the water splitting enthalpy, are solid in both oxidized and reduced forms, operate with small ΔT between reduction and operation, and are highly stable over hundreds of thousands of cycles. We will develop new materials that possess these properties in conjunction with project collaborators. Materials development has focused on spinel structure (Red: $AB_2O_4 \rightarrow AB_2O_{4-\delta} + \delta/2\ O_2$) and perovskite structure (Red: $ABO_3 \rightarrow ABO_{3-\delta} + \delta/2\ O_2$) materials, which have both shown promise in reaching the targets. Efficient flowing particle reactors need active materials that are robust, attrition resistant and not limited by slow heat or mass transfer properties. Therefore, we have developed particle fabrication procedures for particles that are flowable, reactive, and robust, and are currently testing their performance in fluidized bed reactors. We are also evaluating reactor containment materials to ensure stability at the high temperatures at which water splitting occurs. In the end, we will produce reactor ready materials with demonstrated hydrogen productivities to drive the field closer to meeting DOE's technical targets, as determined from our process model and techno-economic analysis.

APPROACH

A highly efficient STWS reactor must have a scalable and mechanically sound design that maximizes heat flux to the reactive materials and optimizes mass transfer. We are designing a novel reactor that maximizes heat flux, and minimizes heat and mass transfer limitations by fluidizing the active particles. The reduction step will be carried out using inert sweep gas to achieve the low oxygen partial pressures necessary for the reduction reaction. The particles are contained in fluidized bed reactors that switch between inert flow during reduction and steam flow during oxidation, and there is minimal temperature difference between oxidation and reduction, i.e., near isothermal operation. Since such high temperatures are required, the absence of moving parts greatly reduces the risk of critical reactor failure. The small ΔT between reduction and oxidation minimizes the need to reheat materials between oxidation and reduction, which leads to reduced efficiencies in other STWS designs.

In this project, we are examining the individual components of the reactor system to determine their feasibility and efficiency. These include kinetic and thermodynamic behavior of spray dried redox materials in a fluidized system, performance of coated reactor containment materials, effect of vacuum pumping vs. inert gas flow for oxygen removal following reduction, and solar concentration modeling. Using this information, we are constructing and operating a solar-powered system that can produce at least three liters of hydrogen in eight hours on-sun. By the end of the project, we will have an Aspen model that integrates the individual portions of the reactor system. We will use this in a techno-economic analysis showing that we are capable of meeting the <$2/kg H_2 at 50,000 kg H_2/d ultimate project goal.

RESULTS

A key goal of our research is to produce redox materials that can maintain high STWS activity over time. Specifically, we pursued the goal of fabricating particles that can produce at least 150 µmol H_2/g/cycle and not lose more than 10% of reactivity between the 100th and 200th redox cycles. In the past year, we have met this goal. We tested the long-term hydrogen production of a spray dried cobalt doped hercynite in a stagnation flow reactor system over 200 cycles. The active particles produced an average of 299 µmol/g/cycle over Cycles 93 through 99 and 303 µmol/g/cycle over Cycles 201 through 208, demonstrating no loss in activity between the 100th and 200th cycles. This exceeds the target of 150 µmol/g/cycle at 10% loss in reactivity. H_2 production before Cycle 100 and after Cycle 200 are shown in Figure 1. Each cycle consisted of a 15-min oxidation step at 1,350°C using 50% H_2O or CO_2 in argon at a flow rate of 300 sccm and a 30-min reduction step at 1,500°C using argon at a flow rate of 300 sccm. Control runs without the active oxide were conducted at the same reaction conditions and the average production over 10 blank cycles was subtracted from each of the experimental H_2 generation cycles to account for water splitting on the surface of the reactor. While Cycles 92–99 and 201–208 were conducted as H_2O splitting experiments to directly measure the H_2 production, CO_2 splitting experiments were conducted for the remainder of the cycles
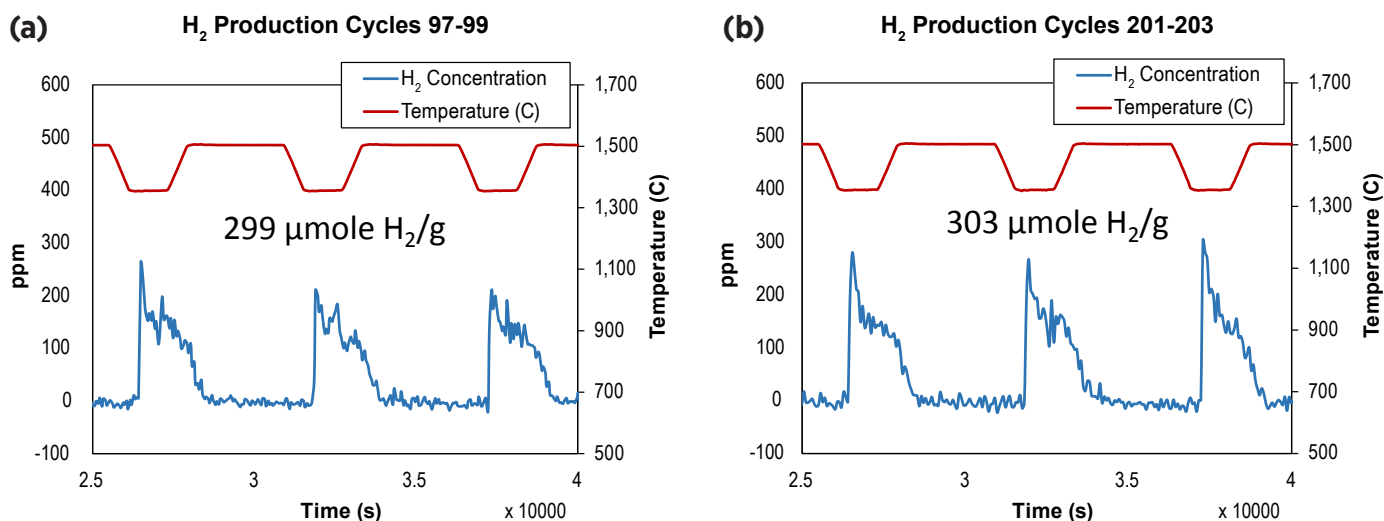
(a)

(b)

FIGURE 1. STWS activity of cobalt-doped hercynite material in long-term activity tests. (a) H_2 production for Cycles 97 through 99. (b) H_2 production for Cycles 201 through 203.

to avoid technical difficulties with long-term use of the steam generator. However, all conditions remained consistent between the H_2O and CO_2 experiments and properties between these two redox processes have been shown to be similar.

Another key challenge in the field of STWS that we wish to address is the stabilization of ceramic materials in the presence of steam. SiC has favorable mechanical and thermal properties at the temperatures required for STWS, but will react with steam to form a SiO_2 layer that eventually degrades the material and severely limits its lifetime. To address this issue, we are using particle ALD to study the stabilization effects of nanoscale diffusion barriers with atomic growth control to prevent the oxidation of SiC. Mullite ($3Al_2O_3 \colon 2SiO_2$) and BN have been identified as promising coating materials using density functional theory calculations. Mullite, alumina, BN and hybrid mullite/Al_2O_3 films of various thicknesses were deposited on high surface area SiC particles using ALD. All films were then annealed at 1,500°C for 20 h in order to crystallize the films.

To test the effectiveness of the films, uncoated and ALD coated SiC particles were exposed to high temperature steam at 1,000°C for 20 h in a thermal gravimetric analyzer using an evaporation rate of 3 g/h. Water vapor was introduced to the thermogravimetric analyzer furnace once the temperature had reached 1,000°C. In all of these experiments mass change of the sample over the course of the steam exposure was monitored. Mass gains during these experiments are attributed to silica growth on the surface due to oxidation. A summary of the performance of all films to date is presented in Figure 2.

The figure shows that significant improvements have been made to the oxidation resistance of SiC. Depositing

a coating of only 10 nm reduced the oxidation of SiC by ~50%. Although alumina films outperformed mullite films, mullite is preferred because its thermal expansion coefficient matches well with that of SiC. Mullite films are capable of matching the performance of alumina films by increasing the thickness. This is expected based on theoretical results, even though the thicknesses of mullite films are nanometer. All but two of the films tested have met or surpassed the goal of this work, which was to improve the oxidation resistance of SiC by 25%. The highest performing film improved the oxidation resistance of SiC by 64%, far surpassing the project goal.

Hercynite is a spinel material that is highly active for STWS. Since it consists of iron and aluminum oxide, it also has the benefit of being much cheaper than most STWS materials, which often contain rare earth metals. As kinetics can have a profound effect on system efficiency, we are interested in determining the reaction rates and mechanisms of hercynite reduction.

Solid-state kinetics can be classified into two methods: model-fitting and model-free (isoconversional) methods. In the model-fitting method, different models are fit to experimental data. The model with the best statistical fit is chosen, and the pre-exponential factor and activation energy can be calculated from the fit. Isoconversional methods calculate the activation energy as a function of conversion without modelistic assumptions.

We conducted several thermogravimetric analysis experiments with different heating rates (3°C/min, 4°C/min, and 5°C/min) for materials containing aluminum oxide and iron oxide, and used isoconversional methods to analyze the data. We can see from Figure 3a that there are two distinct slopes in the mass loss signal and two O_2 peaks in the mass spectrometry signal, which indicates two different

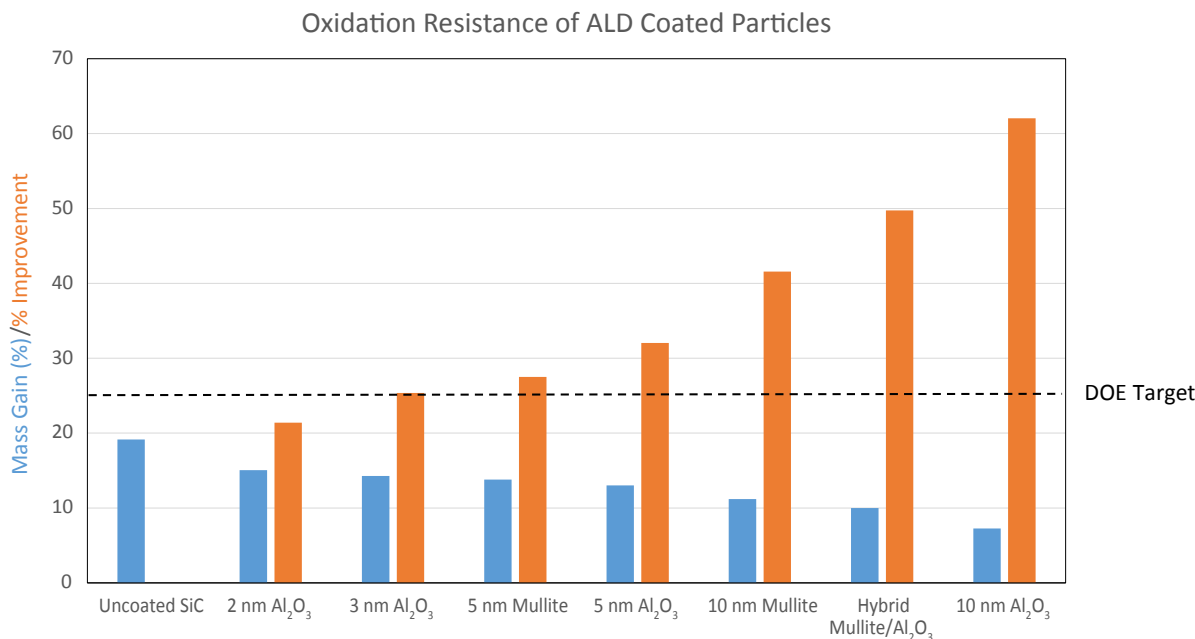Oxidation Resistance of ALD Coated Particles

FIGURE 2. Oxidation resistance of various ALD-coated particles over 20 h of steam exposure at 1,000°C. Percent mass gain is attributed to oxidation of SiC. Most materials exceeded DOE target.
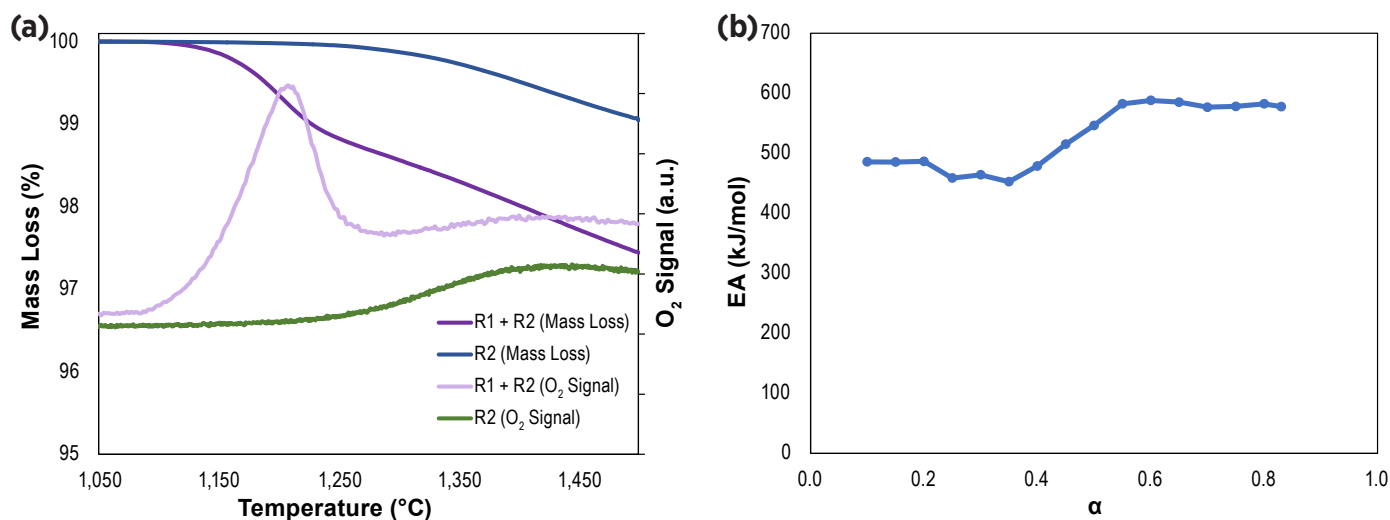

FIGURE 3. (a) Mass loss curves and O_2 mass spectrometry signals for hercynite kinetics experiments. The dark purple line shows the mass loss for the first cycle, when two reactions were occurring: the formation and reduction of hercynite. The light purple line shows the O_2 mass spectrometry signal associated with the two reactions. The blue line shows the mass loss for the reduction of hercynite. The green line shows the O_2 mass spectrometry signal for this reaction. (b) Activation energy of the formation and reduction of hercynite as a function of conversion, calculated using isoconversional methods.

rate-limiting steps. Figure 3b shows the apparent activation energies of hercynite reduction as a function of conversion (α). The formation of hercynite has an apparent activation energy of 472 kJ/mol, while the hercynite reduction reaction has an apparent activation energy of 582 kJ/mol.

The final deliverable of this research project is the production of three standard liters of H_2 in under eight hours on-sun. To achieve this goal, we are collaborating with

NREL to use their High-Flux Solar Furnace to heat two fluidized bed reactors filled with hercynite. In the past year, we have made significant progress toward meeting this goal. On the best day of testing, approximately 80 g of hercynite was redox cycled two times over the course of 2 h 45 min. The hydrogen concentration and normal incident power are shown in Figure 4 as a function of time. This test included two reduction cycles and two oxidation cycles. The first
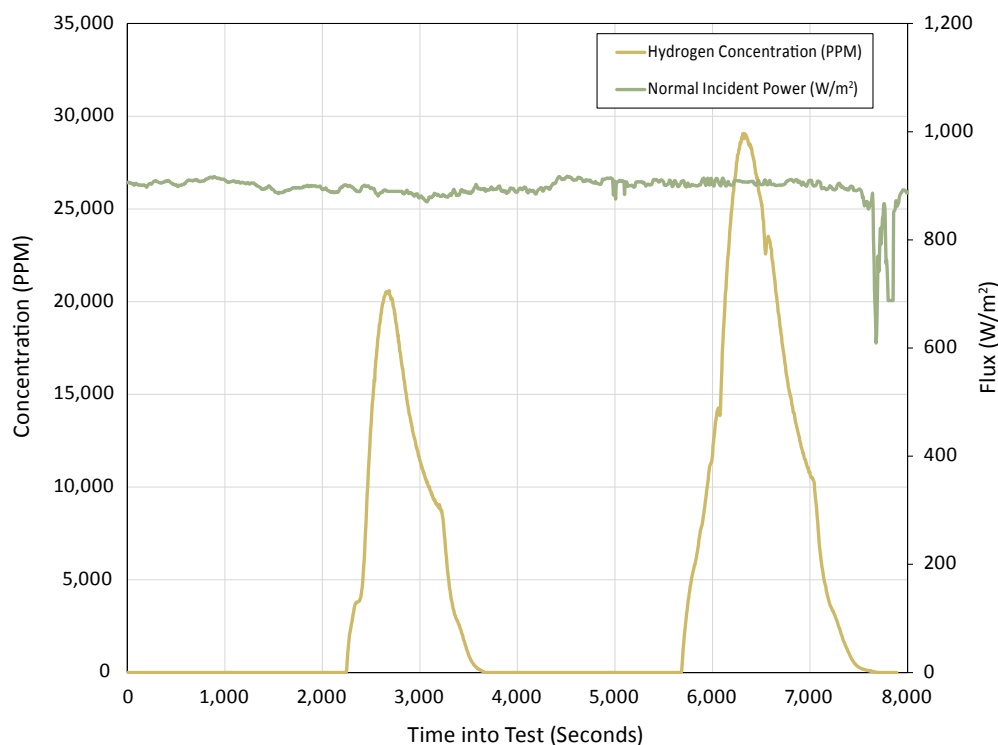
FIGURE 4. H_2 concentration and normal incident power for on-sun test at NREL's High-Flux Solar Furnace.

oxidation cycle produced 0.66 standard liters of H_2 and the second produced 1.25 standard liters of H_2, giving a total of 1.91 L. If this production rate was sustained over four cycles, the total amount of H_2 produced would be 3.81 L and the total time would be 5 h 30 min. This demonstrates that we are on target to meet our end-of-project goal.

CONCLUSIONS AND UPCOMING ACTIVITIES

After the completion of the second year of the project, several conclusions can be drawn:

- Tested redox materials can maintain high H_2 production (~300 µmol/g/cycle) over hundreds of cycles.

- ALD coatings confer substantial oxidation resistance to SiC in the presence of steam at high temperatures (1,000°C).

- Undoped hercynite undergoes an O_2 vacancy mechanism during reduction up to 1,700°C.

- Project is on target for meeting end-of-project goal of producing 3 L of H_2 in less than 8 h.

Future work will include:

- Detailed thermodynamic and kinetic studies of active materials.

- Computation work of a sister National Science Foundation project.

- Operate reduction reactor tube under vacuum and evaluate diffusional limitations.

- Develop a reactor concept for hybrid solar–electric water splitting.

- Synthesize ALD films on three SiC tubes having different thicknesses of coating material.

- Test coated tubes for stability in high temperature steam environment, and evaluate tested tubes using scanning electron microscopy, X-ray diffusion, and inductively coupled plasma optical emission spectroscopy.

- Further refine the AspenPlus model and H2A with experimental thermodynamic and kinetic results and optimal operating conditions.

FY 2017 PUBLICATIONS/PRESENTATIONS

Publications

1. A.J. Groehn, A. Lewandowski, R. Yang, A.W. Weimer. 2016. "Hybrid radiation modeling for multi-phase solar-thermal reactor systems operated at high-temperature." *Solar Energy*, *140*, 130–140.

2. C.L. Muhich, V. Poole-Aston, R.M. Trottier, A.W. Weimer, C.B. Musgrave. 2016. "A First Principles Analysis of Cation Diffusion in Mixed Metal Ferrite Spinels." *Chemistry of Materials*, 28 (1), 214–226. DOI: 10.1021/acs.chemmater.5b03911.

3. B.D. Ehrhart, C.L. Muhich, I. Al-Shankiti, A.W. Weimer. 2016. "System efficiency for two-step metal oxide solar thermochemical hydrogen production—Part 1: Thermodynamic model and impact of oxidation kinetics." *International Journal of Hydrogen Energy*, 41 (44), 19881–19893.

4. B.D. Ehrhart, C.L. Muhich, I. Al-Shankiti, A.W. Weimer. 2016. "System efficiency for two-step metal oxide solar thermochemical hydrogen production—Part 2: Impact of gas heat recuperation and separation temperatures." *International Journal of Hydrogen Energy,* 41 (44), 19894–19903.

5. B.D. Ehrhart, C.L. Muhich, I. Al-Shankiti, A.W. Weimer. 2016. "System efficiency for two-step metal oxide solar thermochemical hydrogen production—Part 3: Various methods for achieving low oxygen partial pressures in the reduction reaction." *International Journal of Hydrogen Energy,* 41 (44), 19904–19914.

6. I. Al-Shankiti, B.D. Ehrhart, A.W. Weimer. 2017. "Isothermal redox for H_2O and CO_2 splitting – A review and perspective." Solar Energy, http://dx.doi.org/10.1016/j.solener.2017.05.028.

7. "Methods and apparatus for gas-phase reduction/oxidation processing," U.S. Patent 9,399,575 (2016).

Presentations

1. Samantha L. Miller, Ryan Trottier, Kevin Sun, Alan W. Weimer, and Charles B. Musgrave, "Evaluating the Effect of Modeling Variables and Experimental Conditions on Material Development for Solar Thermochemical Water Splitting," American Institute of Chemical Engineering Annual Meeting, San Francisco, CA, November 2016.

2. Amanda Hoskins, Aidan Coffey, Charles B. Musgrave, and Alan W. Weimer, "Stabilizing SiC for Solar Thermal Water Splitting Applications," American Institute of Chemical Engineering Annual Meeting, San Francisco, CA, November 2016.

3. Amanda Hoskins, "Nano-Structured Ceramic Coatings to Stabilize SiC Against Reaction in High Temperature Steam," Paper presented at the 2017 American Ceramics Society International Conference and Expo on Advanced Ceramics and Composites, Daytona Beach, Florida, January 22–27, 2017.

4. Ibraheam Al-Shankiti, Yahya Al-Salik, Hicham Idriss, and Alan W. Weimer, "Reduction Kinetics of Iron Aluminate ($FeAl_2O_4$) for Solar Thermochemical H_2O Splitting," American Institute of Chemical Engineering Annual Meeting, San Francisco, CA, November 2016.

5. Samantha L. Miller, Kevin Sun, Charles B. Musgrave, and Alan W. Weimer, "Finite temperature modeling of metal oxides for solar thermochemical water splitting," American Chemical Society Spring Meeting, San Francisco, CA, April 2017.

6. Ryan Trottier, Samantha Millican, Christopher Bartel, Aaron Holder, Alan W. Weimer, and Charles B. Musgrave, "Rapid Computational Screening of Materials for Water Splitting Using Ab Initio and Machine Learned Models: Thermodynamic and Kinetics of Solar Thermal H_2 Generation," The 231st Electrochemical Society Meeting, New Orleans, May 2017.

7. Samantha L. Millican, Ryan Trottier, Christopher Bartel, Alan W. Weimer, and Charles B. Musgrave, "Incorporating Spin Disorder, Phase and High Temperature Free Energy into Rapid Computational Screening of Redox Materials for Water Splitting," Keynote Talk, The 21st International Conference in Solid State Ionics, Padova, Italy, June 2017.

8. Alan W. Weimer, "Solarthermal Chemistry–The Path Forward," Keynote Address - presented at the American Society of Mechanical Engineers (ASME) Power and Energy Conference, Charlotte, NC (June 30, 2016).

9. Alan W. Weimer, "Solarthermal Chemistry – The Path Forward," invited Plenary Lecture (Thermochemistry) presented at the Asia Pacific Solar Research Conference, Canberra, Australia, ACT (December 1, 2016).

10. Alan W. Weimer, "Solarthermal Chemistry – The Path Forward," University Distinguished Lecture presented at Texas A & M University at Qatar, Doha, Qatar (March 23, 2017).