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

Alan W. Weimer (Primary Contact),
Charles Musgrave, Brian Ehrhart,
Ibraheam Al-Shankiti, Amanda Hoskins,
Samantha Miller, Scott Rowe, Caitlin Majlinger
University of Colorado Boulder
Campus Box 596
Boulder, CO 80309-0596
Phone: (303) 492-3759
Email: alan.weimer@colorado.edu

DOE Manager: Katie Randolph
Phone: (240) 562-1759
Email: Katie.Randolph@ee.doe.gov

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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) 2016 Objectives

- Develop and test reactive materials with high productivity and stable reactivity.
- Synthesize and characterize high temperature containment materials.
- Test containment materials for steam resistance.
- Build test system for reactor containment materials evaluation.
- Collaborate closely with joint National Science Foundation (NSF) and the Department of Energy's (DOE) materials discovery "sister" project to screen improved active materials.
- Work with the National Renewable Energy Laboratory to ready reactor for on-sun testing.
- 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 (TEA) analysis program and are outlined in Table 1.

TABLE 1. Progress toward meeting technical targets for solar-driven high-temperature thermochemical hydrogen production.

Characteristics	Units	2015 Target	2020 Target	CU 2016 Status
Solar-Driven High-Temperature Thermochemical Cycle H_2 Cost	$/kg	14.80	3.70	14.67
Active Material Cost per Year	$/yr-TPD H_2	1.47M	89K	62.7K*
STH Energy Conversion Ratio	%	10	20	9.3**
1-Sun Hydrogen Production Rate	kg/s per m^2	8.1×10^{-7}	1.6×10^{-6}	7.5×10^{-7}

CU – University of Colorado; STH – Solar-to-hydrogen ratio
*Assuming reaction material replacement lifetime of 1 yr
**Analysis uses hercynite as the active material

FY 2016 Accomplishments

- Manufactured and characterized large, spherical, highly active hercynite materials via spray drying and dynamic mixing techniques. Measurements show active materials can produce >150 µmol H_2/g active material.
- Acquired electrically heated high-temperature oxygen transport membrane and testing is underway.
- Integrated particle flow test system with transport membrane to study kinetics and mass transfer properties of test particles.
- Updated laboratory test systems used to determine production and long-term stability of active materials.
- Altered scaled-up process model to more realistically reflect reactor concept, thermodynamic efficiencies and test material characteristics.
- Collaborated with DOE/NSF sister project to screen 955 binary spinel structures and 1,343 binary perovskite materials for STWS potential. Eight materials have been synthesized for experimental validation.

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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 a small ΔT between reduction and oxidation and are highly stable over hundreds of thousands of cycles. We will develop new materials which possess these properties in conjunction with project collaborators. Initial materials development has focused on the doped-hercynite cycle (Red: $Co_{0.4}Fe_{0.6}Al_2O_4 \rightarrow Co_{0.4}Fe_{0.6}Al_2O_{4-\delta} + \delta/2\ O_2$) and perovskite structure (Red: $ABO_3 \rightarrow ABO_{3-\delta} + \delta/2\ O_2$) materials, which have both shown promise in reaching the materials 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 are developing particle fabrication procedures using spray drying technology so that the particles are flowable, reactive, and robust. Additionally, we are 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 TEA.

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 which maximizes heat flux, and minimizes heat and mass transfer limitations by fluidizing the active particles. The particles move through the reduction zone by gravity and are entrained in steam flow through the oxidation zone. Since such high-temperatures are required, the absence of moving parts greatly reduces the risk of critical reactor failure. The near-isothermal nature (ΔT < ~150°C) of the reactor design minimizes the need to reheat materials between oxidation and reduction, which leads to low efficiencies in other STWS designs. The reduction step will be carried out using inert sweep gas to achieve the low oxygen partial pressures necessary for the reduction reaction.

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. This will be used in a TEA showing that we are capable of meeting the < \$2/kg H_2 at 50,000 kg H_2/d ultimate project goals.

RESULTS

Significant progress has been made over the past year in preparing active solid spherical reactive particles via spray drying. One technique that showed very promising results for improving the morphology of spray dried particles was pH tuning, whereby the pH of suspensions is altered to match the isoelectric point of the solids. This increases particle flocculation, leading to particles that are larger, more solid, and more spherical. The use of an ultrasonic nebulizer in our spray drier has increased morphology further still. This nozzle tip uses vibration, rather than a compressed gas stream, to aerosolize the suspension. This creates larger droplets, which turn into larger particles when dried. Images of these particles in Figure 1 show a clear improvement in particle size and morphology.

A new reactor system was constructed for determining the long-term hydrogen production of spray dried particles. Testing is underway and we are on track to meet our go/no-

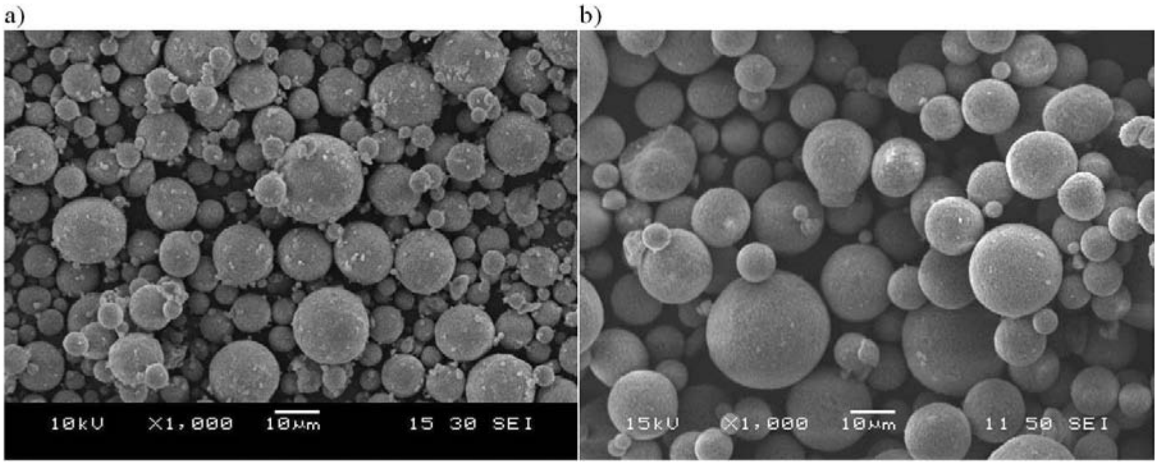

FIGURE 1. Scanning electron microscopy images of calcined hercynite spray dried particles with 20 wt% solids and no organic, made with an iron oxide nanopowder suspension and boehmite suspension in water and the solution was modified to a pH of 7.4 and sprayed using an (a) two-fluid compressed air nozzle and (b) ultrasonic nebulizer.

go target to produce at least 150 µmol H_2/g, while not losing more than 10% reactivity between cycles 100 and 200. All of the spray dried materials tested thus far have generated more than 150 µmol H_2/g, exceeding our go/no-go target as shown in Figure 2. Even materials that had not been optimized via pH tuning and ultrasonic spraying exceeded the required production.

Work to identify new candidate active materials with our DOE/NSF STWS material "sister" project is ongoing. The STWS behavior of 955 binary normal spinel materials was screened based on the oxygen vacancy formation energy determined through a fundamental material descriptor model. Investigations into the effect of spinel inversion, metal oxide structure, and magnetic ordering on density functional theory calculations indicate that all three factors are critical in accurately predicting the STWS behavior of candidate materials.

Progress on the development of stable containment materials has been focused on the growth of atomic layer deposition (ALD) films with desirable properties. During the past year we have deposited alumina and silica films on SiC and developed a method for generating mullite ($3\ Al_2O_3 : 2\ SiO_2$) ALD films. Coated particles have been thoroughly characterized to determine the quality, dispersity, and conformity of the deposited films. The transmission electron microscopy images in Figure 3 show the deposited films are conformal and cover the entire particle surface. Inductively coupled plasma analysis has confirmed we are producing the desired stoichiometry. Energy-dispersive X-ray spectroscopy has confirmed the films are uniformly dispersed and there is no preferential deposition of either alumina or silica.

The oxidation resistance of coated SiC has been analyzed via thermogravimetric analysis. We have exposed coated and uncoated SiC particles to steam at 1,000°C for 20 h

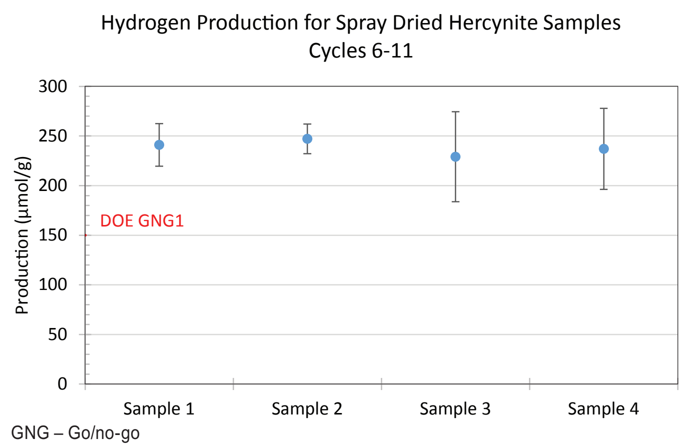

FIGURE 2. Average hydrogen production for four spray dried doped hercynite samples for cycles 6–11 with 95% confidence intervals on the mean.

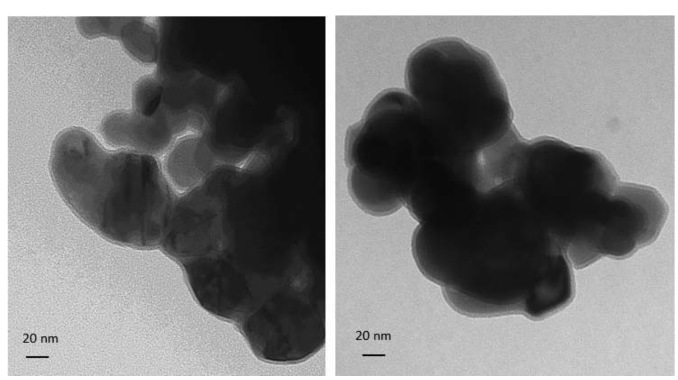

FIGURE 3. Transmission electron microscopy images of zirconia particles coated with 50 cycles mullite ALD.

and recorded the percent mass gain. The results show that alumina films of equal thickness outperform initial mullite films. The best performing sample shows a 10% improvement over uncoated SiC. Since we expect boron nitride films to outperform Al_2O_3 films significantly, we believe to be on track for meeting our go/no-go target of 25% improvement by the end of September 2016.

Over the past year, a fluidization test system has been built to study kinetic and thermodynamic behavior of our redox materials. This system operates using an inert gas sweep to achieve low oxygen partial pressures. Coupled with this system is a selective, high-temperature oxygen transport membrane used to remove oxygen after reduction. In a scaled-up system the inert gas could be recycled, greatly reducing operating costs. Initial testing of the membrane shows promising results. The oxygen content of an O_2/He mixture was reduced from 1.03 mass% O_2 to 15 ppm at 1 SLPM with 21% efficiency.

Computational modeling of our proposed reactor system is ongoing. A method to couple ray tracing (RT) and finite volume (FV) radiation models at an arbitrary surface via spatial as well as angular discretization was developed. The interfacing method was validated by comparing its results with full RT simulations of a compound parabolic concentrator as well as a large-scale solar-thermal reactor, as shown in Figure 4. The validated model was used to investigate the effects of SiC tube radius on the efficiency

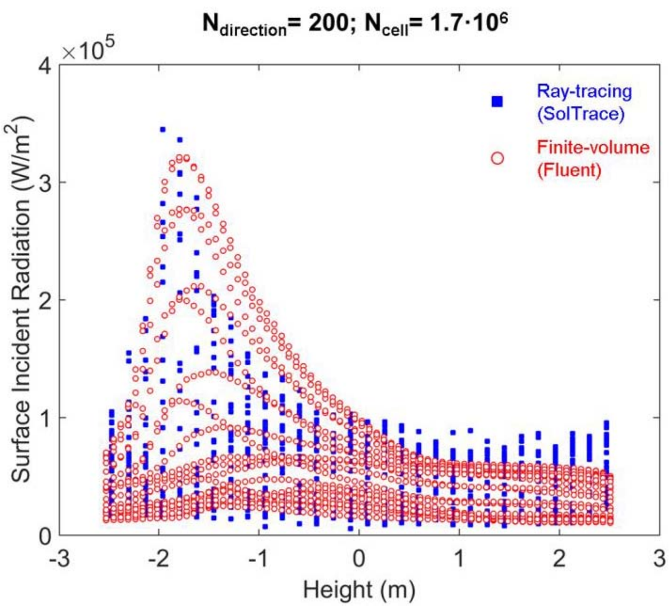

FIGURE 4. Comparison of RT and FV radiation model predicted surface incident radiation profiles along a single reactor tube. Radiation was simulated in the complete reactor geometry by both models. RT and FV predicted total radiative power on the reactor tube are 4.73·105 and 4.69·105 W, respectively. RT predicted peak flux of 3.45·105 W/m^2 (uncertainty ±5%) is ~7% higher than that from the FV simulations (3.21·105 W/m^2).

of ceria reduction. Decreasing the reactor tube radius from 25–5 cm reduced the total ceria production rate but increased the extent of conversion when the particle bed velocity was maintained.

Our H2A has been updated to reflect advances in the project. Rather than using vacuum pumping to achieve low O_2 partial pressures, an inert gas sweep was used. This was coupled with an oxygen transport membrane, using experimentally-determined efficiencies. Aspen's fluidized bed model was used to determine the size of reactors. Sensitivity analysis identified heliostat cost, material replacement frequency, and SiC cost as the biggest cost drivers. Although last year's analysis identified heat exchanger effectiveness as the biggest driver, the changes made to the model give a higher overall STH efficiency, which reduced the dependency on heat exchanger effectiveness. Overall, the TEA predicts an a hydrogen cost of $2/kg in 2025.

CONCLUSIONS AND FUTURE DIRECTIONS

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

- Spray dried particles are able to produce well above the go/no-go goal.
- Ultrasonic nebulizer and pH tuning of the spray dry suspension led to the largest and most solid spherical particles in spray drying.
- Mullite ALD has been shown to produce conformal films with the desired stoichiometry.
- Thermogravimetric analysis of ALD-coated SiC shows a 10% improvement in oxidation resistance in a high temperature steam environment.
- Experimental efficiencies of oxygen transport membrane are likely to be sufficient to meet the DOE cost target of $2/kg H_2.
- Modeling demonstrates reactor tube diameter is positively correlated with hydrogen production and negatively correlated with extent of conversion.
- TEA shows capability of process to produce hydrogen for $2/kg using 2025 DOE targets.

Future work will include:

- Pursuing further experimental validation of high-performance STWS materials predicted by density functional theory.
- Demonstrating long-term stability of active particles that lose no more than 10% of reactivity between 100th and 200th redox cycle.
- Developing containment materials that provide a 25% increase to the stability of SiC under redox conditions.

- Updating TEA based on results of theoretical and experimental studies.
- Studying the kinetic behavior of hercynite for both reduction and oxidation.
- Producing three standard liters of hydrogen during eight hours on-sun at the National Renewable Energy Laboratory's high-flux solar furnace using a lab-scale reactor and fabricated particles.

FY 2016 PUBLICATIONS/PRESENTATIONS

Publications:

1. Muhich, C.L., B. Ehrhart, V. Witte, S.L. Miller, E. Coker, C.B. Musgrave, A.W. Weimer, "Predicting the Solar Thermochemical Water Splitting Ability and Reaction Mechanism of Metal Oxides: a Case Study of the Hercynite Family of Water Splitting Cycles," *Energy and Environmental Science*, 8, 3687–3699 (2015). DOI: 10.1039/C5EE01979F

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

3. Muhich, C.L., Erhardt, I. Al Shankiti, B.J. Ward, C.B. Musgrave and A. W. Weimer, "A Review And Perspective of Efficient Hydrogen Generation Via Solar Thermal Water Splitting," *WIREs Energy and Environment*, 5 (3), 261–287 (2016). DOI: 10.1002/wene.174

Presentations:

1. Muhich, C., B. Ehrhart, S. Miller, V. Witte, B. Ward, C. Musgrave, A. Weimer "Active and Flowable Doped-Hercynite Materials for Solarthermal Redox Processing to Split Water," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.

2. Trottier, R., S. Miller, C. Muhich, C. Musgrave and A. Weimer "Rapid Computational Screening of Metal Oxides for Water Splitting: Kinetics of H2 Production," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.

3. Miller, S., R. Trottier, C. Muhich, C. Musgrave and A. Weimer "Screening of Metal Oxide Materials for Solar Thermochemical Water Splitting," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.

4. Witte, V., B. Ehrhart, B.J. Ward, A. Weimer "Hydrogen Fuel Production Using Reactive Metal Oxides in a Solar Thermal Water Splitting (STWS) Cycle," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.

5. Groehn, A., A. Weimer "Efficiency and Design of High-Temperature Solar-Thermal Reactors," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.

6. Ehrhart, B., I. Al-Shankiti, A. Weimer "Impact of Reduction of Flowing Particles on System Efficiency for Solar Thermochemical Hydrogen Production," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.

7. Ehrhart, B., I. Al-Shankiti, A. Weimer "Reduction of Flowing Particles for Efficient Solar Thermochemical Hydrogen Production," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015.