

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

Alan W. Weimer (Primary Contact),
 Charles Musgrave, Brian Ehrhart,
 Ibraheam Al-Shankiti, Christopher Muhich,
 Amanda Hoskins, Samantha Miller, Barbara Ward
 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: (720) 356-1759
 Email: Katie.Randolph@ee.doe.gov

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 National Renewable Energy Laboratory (NREL)
 Golden, CO

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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) 2015 Objectives

- Demonstrate activity of initial formulation spray dried redox materials
- Finish construction and demonstrate operation of lab-scale flowing particle bed redox system
- Collaborate closely with National Science Foundation (NSF) materials discovery "sister" project to screen improved active materials
- Work with NREL to ready reactor for on-sun testing
- Design test system for reactor containment materials evaluation
- Update process model and Hydrogen Analysis (H2A) model 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

Using experimental results from our materials testing and thermodynamic modeling, a process model of a 50,000 kg H₂/day industrial-scale production plant, a detailed solar field model, and DOE's H2A techno-economic analysis program, our performance in the DOE technical target categories is projected, 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 Boulder 2015 Status
Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost	\$/kg	14.80	3.70	14.67
Annual Reaction Material Cost per TPD H ₂	\$/yr-TPD H ₂	1.47 M	89 K	62.7 K*
Solar to Hydrogen (STH) Energy Conversion Ratio	%	10	20	9.3
1-Sun Hydrogen Production Rate	kg/s per m ²	8.1 x 10 ⁻⁷	1.6 x 10 ⁻⁶	7.5 x 10 ⁻⁷

*Assuming reaction material replacement lifetime of 1 year
 TPD - Tonnes per day

FY 2015 Accomplishments

- The project manufactured and characterized spherical spray dried doped-hercynite active particles. Preliminary measurements suggest that spray dried active materials can produce >150 μmol H₂/g active material.
- Construction and start-up of lab-scale flowing particle redox test system capable of cycling >1 g spray dried active particles is nearly complete.
- The team completed an upgrade and successfully tested a laboratory test system to incorporate new, state-of-the-art mass spectrometers and more precise steam feeders.

- The scaled-up process model was expanded to include more detailed thermodynamic and kinetic models of active material performance and improved solar field and reactor design.
- The project team collaborated with NSF sister project to screen 1,678 of the 2,156 potential binary water splitting active materials in silico. Of those, 420 perovskites and 260 spinels were found to show potential for STWS.



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 need to be made. Ideal STWS materials have high H₂ production capacity, low thermal reduction temperatures, fast reaction kinetics, reduction enthalpies on the order of the water splitting enthalpy, are solid in both oxidized and reduced forms, operate isothermally or near-isothermally, and are highly stable over hundreds of thousands of cycles. We will develop new materials which possess the materials properties outlined above in conjunction with project collaborators. Initial materials development will be based on the doped-hercynite cycle (Red: Co_{0.4}Fe_{0.6}Al₂O₄ → Co_{0.4}Fe_{0.6}Al₂O_{4-δ} + δ/2 O₂) and perovskite structure (Red: ABO₃ → ABO_{3-δ} + δ/2 O₂) materials which have shown promise in reaching materials targets. The nature of efficient flowing particle reactors requires that the material is formed into particles that are robust, attrition resistant, and possessing of rapid heat and mass transfer properties. Therefore, we will develop particle formation procedures and formulations based on spray drying technology so that the particles are flowable, reactive, and robust. Additionally, we will evaluate reactor containment materials because the active redox materials must be compatible with the reactor materials of construction at the high temperatures at which water splitting occurs. In the end, we will produce reactor ready materials with demonstrated H₂ 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 maximize heat flux to the reactive materials, and optimize mass transfer while minimizing sources of heat loss in a scalable and mechanically sound design. We are designing a novel beam-up, fluidized particle based reactor which maximizes heat flux to the reactor due to its beam-up configuration, and minimizes heat and mass transfer limitations due to the fluidized particles. The particles are moved through the

reduction and oxidation zones by gravity and in entrained steam flow, respectively. The lack of moving parts at temperatures over 1,000°C greatly reduces the risk of critical reactor failure. The isothermal (or near-isothermal) nature of the reactor design minimizes the need to reheat material from the oxidation temperature to the reduction temperature found in many STWS designs. The reduction step will either be carried out at low pressure with vacuum pumping or using inert sweep gas to achieve the low O₂ partial pressures necessary for the reduction reaction.

In this project we will examine the individual components of the reactor system (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 O₂ removal following reduction, and solar concentration modeling) to determine their individual feasibilities and efficiencies. Using this information we will construct and operate a solar powered system producing three liters of H₂ in an eight-hour day. By the end of the project, we will have tested and modeled the individual portions of the reactor system and combined them into an overall system Aspen model which will be evaluated via technoeconomic analysis showing that we are capable of meeting the <\$2/kg H₂ at 50,000 kg H₂/day ultimate project goals.

RESULTS

Progress on the development of active redox materials during this fiscal year has focused on thermodynamic modeling of hercynite materials, process efficiency calculations, synthesizing and characterizing preliminary spray dried particles, and building research systems. Generating spherical particles is important for promoting flowability and attrition resistance of the active materials, and having robust particles that do not degrade during fluidization is key to maintaining low active material replacement costs. Figure 1 shows scanning electron microscope images of spray dried hercynite particles. They appear spherical, with a particle size distribution around 10 μm. Spray dried particles have also been characterized using X-ray diffraction and elemental analysis to verify that they possess the desired crystal structure and stoichiometric composition. Spray dried particles are currently being tested for hydrogen production activity, and we are on track to meet our go/no-go target to produce more than 150 μmol H₂/g of active material by the end of September 2015.

Activity testing is also ongoing for new candidate active materials identified by our NSF STWS materials "sister" project. In order to make computational evaluations of candidate materials, a criteria based on the reaction thermodynamics was established to analyze the reaction mechanism and predict STWS behavior. The initial experimental work performed this year on spinel aluminate

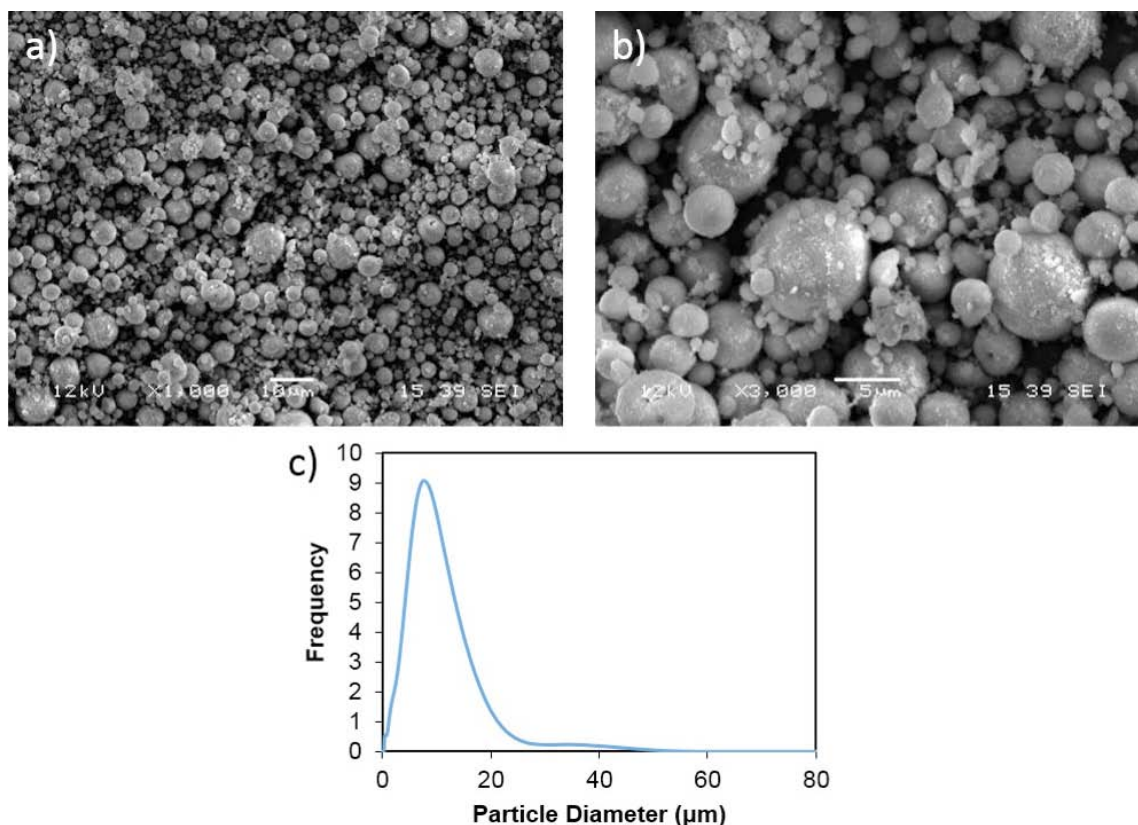


FIGURE 1. Scanning electron microscope images of preliminary spray dried hercynite particles at magnifications of (a) 1,000x and (b) 3,000x with (c) the particle size distribution shown

materials indicates that density functional theory can be used to accurately predict redox properties, and thus STWS behavior, of metal oxides based on their reduction enthalpies.

In addition to the thermodynamic modeling of active material behavior, a more general thermodynamic model for redox cycle efficiency has been developed this year. This model calculates heat requirements and benefits within the system and compares different operating conditions and assumptions. The model compares the chemical energy contained in a mole of hydrogen to the solar energy needed to make it; this ratio is the STH efficiency, or η_{STH} . The results of interest have been a comparison of vacuum and an inert sweep gas for the reduction reaction. The STH efficiency values have been calculated for both the vacuum pumping and recycled inert sweep gas cases, and the results are shown in Figure 2.

As can be seen, the efficiency values for vacuum pumping are drastically lower than for the recycled inert gas case. This is because the pump work increases exponentially at lower pressures, while simultaneously becoming exponentially less efficient at lower pressures. This means that the pump work increases dramatically at the pressure assumed in Figure 2 (10 Pa). By contrast, the recycled inert gas sweep looks promising, with optimal efficiency values of

over 30%. This is consistent with work by others who have also suggested inert gas sweep [1].

The 2015 fiscal year was the start-up year for this three-year project, and has thus seen numerous improvements to our existing lab test system. We met our first quarter milestone of purchasing new, more precise steam feeders and upgraded quadrupole mass spectrometers for the four redox test systems dedicated to this project. The new equipment has been installed in the stagnation flow reactor, where it is producing improved quality mass spectrometer data during redox runs of manufactured spray dried hercynite particles.

Work is in progress to complete the construction of the electrically heated particle flow redox test system, which will enable us to test the fluidization and redox behavior of spray dried particles under various reactor configurations. This test stand will allow us to run the reduction reaction either at a reduced pressure, or with an inert sweep gas using a high temperature oxygen transport membrane, allowing for a direct theoretical/experimental comparison between these alternate O_2 removal processes. The power required to run the two electrical furnaces has been installed. A gas flow system with mass flow controllers, pressure controllers and pneumatic valves has been installed. Work is in progress to integrate the reactor system with the computer through

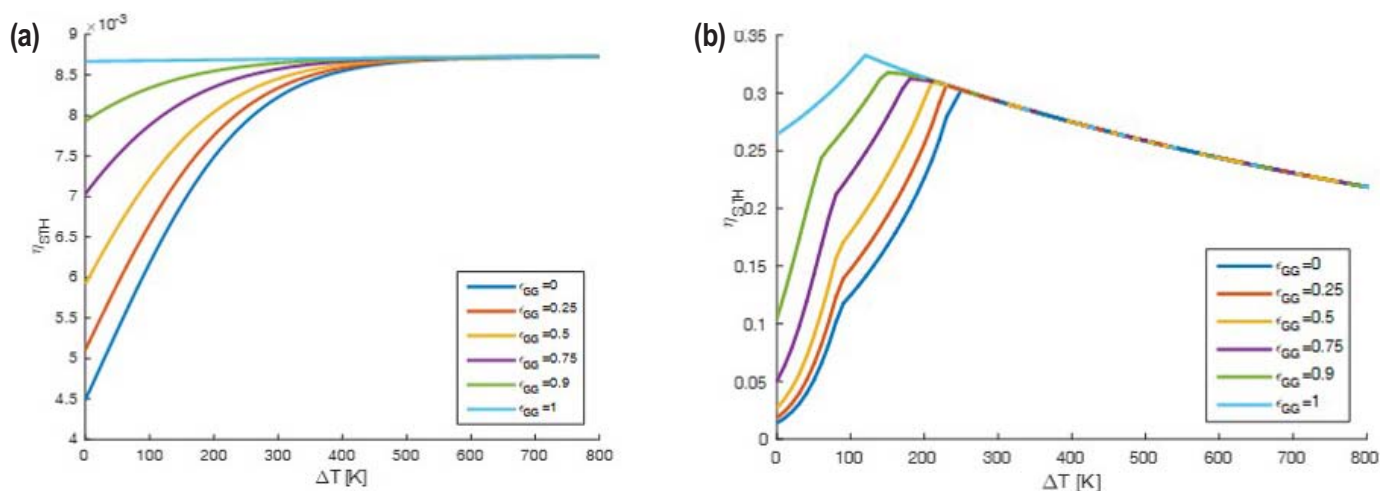


FIGURE 2. STH efficiency values for a system using ceria using (a) a vacuum pump and (b) a recycled inert sweep gas. Both sets of values are given for various ΔT values (difference between reduction and oxidation temperatures) and ϵ_{GG} values (gas heat recuperation effectiveness).



FIGURE 3. Photograph of the existing state of the flowing particle reactor test system

National Instruments data acquisition system (DAQ). The LabVIEW code to control and automate the reactor system has been completed and it will be tested once the interface between the DAQ system and equipment is finished. The current hood setup with mounted reactors, the gas flow system, the new downstream mass spectrometer, steam feeder, and vacuum pump is shown in Figure 3.

CONCLUSIONS AND FUTURE DIRECTIONS

- Preliminary spray dried redox particles are spherical and form material composition of interest. Research in the next year will focus on assessing and improving the activity and flowability of spray dried particles.
- Computational thermodynamic models can accurately predict H_2 production capacity of materials, which has been validated experimentally. The Musgrave group at the University of Colorado Boulder has been awarded an NSF grant to continue materials discovery screening using these computational techniques; and in the following year, we will conduct tests to experimentally validate the material models and identify new materials of interest.
- Reactor test system upgrades carried out this year will improve data collection in 2016.
- Thermodynamic efficiency calculations predict that reducing active materials in an inert gas sweep will achieve a higher STH efficiency than vacuum reduction.
- A flowing particle test system will allow for comparison of different system configurations and is on track for completion by September 2015. It will be used to compare the performance of vacuum and inert gas O_2 removal methods in the coming year.
- A focus on robust reactor containment materials will launch in FY 2016. We will be depositing alumina and mullite protective coatings on silicon carbide using atomic layer deposition (ALD) to assess the feasibility and reactivity of protective ALD coatings on potential reactor materials.
- In the next fiscal year, we will construct and demonstrate an on-sun redox fluidized bed test system at NREL's high flux solar furnace facility in order to begin assessing our technologies under concentrated sunlight.
- Experimental results will continue to be incorporated into our commercial scale process model and techno-economic calculator to monitor the effects of

experimental progress on our progress toward overall efficiency and economic goals.

FY 2015 PUBLICATIONS/PRESENTATIONS

Publications

1. Muhich, Christopher L., Brian D. Ehrhart, Ibraheam Alshankiti, Barbara J. Ward, Charles B. Musgrave, and Alan W. Weimer. 2015. “A Review and Perspective of Efficient H₂ Generation via Solar Thermal Water Splitting.” *Wiley Interdisciplinary Reviews: Energy and Environment*, doi: 10.1002/wene.174.

2. Muhich, Christopher L., Kayla C. Weston, Darwin Arifin, Anthony H. McDaniel, Charles B. Musgrave, and Alan W. Weimer. 2015. “Extracting Kinetic Information from Complex Gas-Solid Reaction Data.” *ACS Industrial & Engineering Chemistry*, 54, 4113–4122.

Presentations

1. Brian D. Ehrhart, Christopher L. Muhich, Ibraheam Alshankiti, and Alan W. Weimer. 2014. “Solar Thermochemical Hydrogen Production Efficiency with Kinetic Limitations.” Presented at American Institute of Chemical Engineers (AIChE) Annual Meeting, Atlanta, GA, November.

2. Christopher L. Muhich, Kayla Weston, Darwin Arifin, Anthony H. McDaniel, Eric Coker, Brian D. Ehrhart, Vanessa Witte, Charles B. Musgrave, and Alan W. Weimer. 2015. “The Mechanism of the Doped-Hercynite Cycle for Solar-thermal Water Splitting.” Presented at ACS Spring Meeting, Denver, CO, March.

3. Christopher L. Muhich, Kayla Weston, Brian D. Ehrhart, Vanessa Witte, Darwin Arifin, Anthony H. McDaniel, Eric Coker, Charles B. Musgrave, and Alan W. Weimer. 2014. “The Chemistry and Thermodynamics of the Hercynite Cycle Solar-thermal Water Splitting Reaction.” Presented at AIChE Annual Meeting, Atlanta, GA, November.

4. Christopher L. Muhich, Brian D. Ehrhart, Kayla Weston, Ibraheam Alshankiti, Darwin Arifin, Anthony H. McDaniel, Charles B. Musgrave, and Alan W. Weimer. 2014. “Extracting Kinetic Information from Complex Gas-solid Reaction Data: the Kinetics of Hercynite Materials for Solar Thermal CO₂ Splitting.” Presented at AIChE Annual Meeting, Atlanta, GA, November.

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7. Christopher L. Muhich, Brian D. Ehrhart, Ibraheam Al-Shankiti, Barbara J. Ward, Samantha L. Miller, Charles M. Musgrave, and Alan W. Weimer. 2015. “Near-isothermal Doped-hercynite Redox Cycle for Solar-thermal Water Splitting.” Presented by A.W. Weimer at the 227th Meeting of the Electrochemical Society, Chicago, IL, May 27.

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1. Krenzke, P.T. and J.H. Davidson. 2015. “On the Efficiency of Solar H₂ and CO Production via the Thermochemical Cerium Oxide Redox Cycle: The Option of Inert-Swept Reduction.” *Energy & Fuels*. **29**(2): 1045-1054.