High Efficiency Solar Thermochemical Reactor for Hydrogen Production

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Project End Date: September 30, 2017

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 continuous operation on a solar simulator producing greater than 3 L of H_2.

Fiscal Year (FY) 2017 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)

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 2017 Accomplishments

- Discovered a novel perovskite material for solar thermochemical H_2 production. It exhibits thermodynamic cycle behavior intermediate to SLMA and CeO_2. This is desirable because a reasonable compromise between a large reduction extent at relatively low-temperature (like SLMA), and high WS favorability in the presence of steam and hydrogen (like CeO_2), will be required for commercial viability.
- Demonstrated H_2 production through solar thermochemical water splitting in Sandia's CPR^2 prototype. This was accomplished at a scale of ~3.5 kW_{th} while achieving a peak rate of 0.2 SLPM H_2. The prototype validated key design objectives important to advancing the technology readiness level of this renewable WS pathway.

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 DOE targets.

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 large number of compounds looking for redox and WS activity. A general rule has emerged where materials that exhibit a large extent of reduction ($\delta>0.2$) generally do not split water under commercially viable oxidation conditions [7]. Moreover, we have learned that compounds with thermodynamic redox properties that are intermediate between the SLMA perovskite and CeO_2 are desirable because they represent a reasonable compromise between a large reduction extent at relatively low-temperature (like SLMA) and high WS favorability in the presence of steam and hydrogen (like CeO_2).

Recently our group found a complex perovskite ($AB_{0.25}B'_{0.75}O_y$, where A=alkaline earth metal, B=rare earth metal, and B′=transition metal) that not only exhibits thermodynamic behavior between SLMA and CeO_2, but also undergoes a very interesting reversible phase transition during redox cycling that has not been reported for STCH perovskites. Firstly, in the course of investigating a family of compounds with $AB_xB'_{1-x}O_y$ ($0<x<1$) stoichiometry, we found that only the $B_{25}B'_{75}$ formulation was active for WS. Evidence for this is presented in figure 1, where the plot on the left shows a strong correlation between the amount of $B_{25}B'_{75}$ phase present in an as-synthesized sample to the total hydrogen produced during WS experiments. Samples were prepared using the sol-gel method. Various compound stoichiometries were targeted by adjusting the mass fraction of B relative to B′ in the sol-gel liquid precursors. X-ray diffraction confirmed that targeted stoichiometries ($x\neq0.25$) having excess B or B′ were comprised of various WS inactive secondary oxide phases, mainly AB_xO_y and AB'_xO_y, along with $B_{25}B'_{75}$ suggesting that $AB_{0.25}B'_{0.75}O_y$ is a line compound.

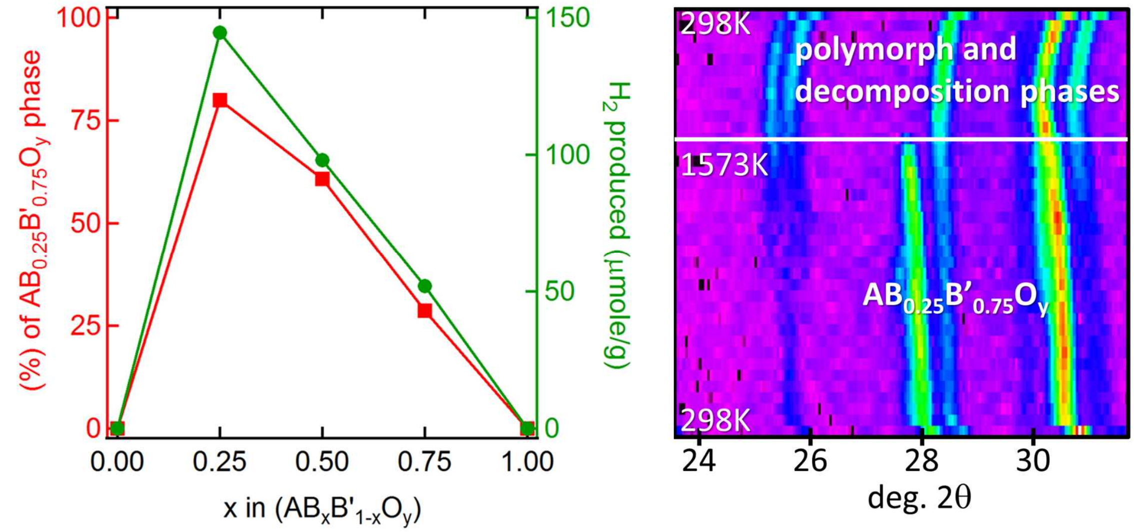

Figure 1. (Left) fractional amount of $AB_{0.25}B'_{0.75}O_y$ perovskite line compound contained in an as-prepared powder sample as a function of the target compound stoichiometry (x). The observed H_2 production capacity of a powder sample tested in the SFR is also displayed and clearly shows a strong positive correlation between $AB_{0.25}B'_{0.75}O_y$ phase fraction and total amount of H_2 produced. (Right) in-situ high-temperature X-ray diffraction lines scans between 23 and 32 deg. 2θ as a function of sample temperature measured for the $AB_{0.25}B'_{0.75}O_y$ perovskite line compound during thermal reduction. Line scan intensity reveals several diffraction peaks associated with $AB_{0.25}B'_{0.75}O_y$, polymorphs of

this perovskite, and decomposition products like AB_xO_y and AB'_xO_y. The abrupt phase transition at ~1573K is reversible, and may be responsible for maintaining WS favorability at moderate H_2O:H_2 ratios during re-oxidation.

Secondly, during an investigation of the $B_{25}B'_{75}$ oxygen redox cycle using TGA, anomalies in the reduction behavior were discovered that were dependent upon the temperature profile and the oxygen partial pressure used in the experiment (data not shown). This prompted a more thorough look into $B_{25}B'_{75}$'s crystallography during reduction using in-situ high temperature X-ray diffraction; the results of which are also presented in figure 1. The image on the right in this figure is comprised of X-ray diffraction line scans (between 23-32 deg. 2θ) stacked atop one another with each pixel row representing a different sample temperature (298K→1623K→298K) recorded in a low O_2-partial pressure helium atmosphere (i.e. during thermal reduction). It is clear by the manner in which the colored vertical bars at various 2θ scattering angles bend (indicating changes in lattice d-spacing due to thermal and chemical effects), disappear (crystal phases reacting away), and appear (new crystal phases forming) that there is complex solid state chemistry occurring in $B_{25}B'_{75}$ at a temperature of 1573K. As mentioned previously, this chemistry does not conform to that commonly observed in other STCH perovskite materials, and could impart high reduction entropy to $B_{25}B'_{75}$ that maintains WS favorability in the presence of both steam and hydrogen (data also not shown).

CPR^2 Fabrication and Demonstration Thrust. Sandia completed an intensive staged buildout and test campaign of the CPR^2 that commenced in July 2016 and concluded in May 2017. The goal was to complete construction of Sandia's moving particle bed reactor, support structure, solar simulator, and balance of plant, and then test the complete system. The assembled CPR^2, which stands ~6 m tall, is pictured in figure 2 and consists of several main components shown in a solid rendering on right, and in the photograph on left, in figure 2. Key components of the CPR^2 are: a particle source chamber (PS) for pre-heating and storing ~70 kg CeO_2 particles, a four-lamp, 20 kW_{ele} solar simulator (SSIM) array for radiant heating of particles, a receiver/reactor or thermal reduction (TR) chamber to reduce particles and produce O_2, a pressure separation segment, a water splitting (WS) reactor to oxidize particles and produce H_2, and a particle drain (PD) chamber for collecting oxidized particles. In addition, a comprehensive balance of plant subsystem inclusive of steam generator, vacuum pumps, mass flow controllers, engineered safety components, sensors, transducers, and data acquisition and control (DAC) system was assembled and integrated into the CPR^2 for the supply and control of gases and particles, power to lamp array, and signal inputs and outputs to the reactor. The fully functional CPR^2 resides at the National Solar Thermal Test Facility in Albuquerque, NM.

Figure 2. Image and schematic of Sandia's fully assembled and operational CPR^2. PS = particle source chamber, SSIM = 4-lamp, 20 kW$_{ele}$ solar simulator, TR = thermal reduction chamber, WS = water splitting chamber, and PD = particle drain (see text for details).

Figure 3 consists of selected photographs and data plots that document a successful demonstration of Sandia's moving particle bed solar-driven thermochemical WS reactor technology. The demonstration was conducted in a single pass, once-through mode using CeO_2 as the redox active material. A maximum thermal reduction temperature of 1700K was achieved in the radiant cavity receiver, and water splitting occurred at ~970K (see data plots of temperature and instantaneous H_2 flowrate in figure 3). The topmost image shows the receiver aperture/cavity during simulator illumination. Owing to the high-temperature incandescence and reflection from the quartz dome covering the aperture, it is difficult to observe particle flow in the receiver itself. However, the diffuse glow of incandescent particles falling from the receiver through a translucent alumina tube, and a small windowed chamber positioned beneath it, attest to hot particles falling into the WS. Two different techniques were used to measure H_2 production rate, a standard heat capacity-based mass flow meter and a Sandia patented solid state sensing device.

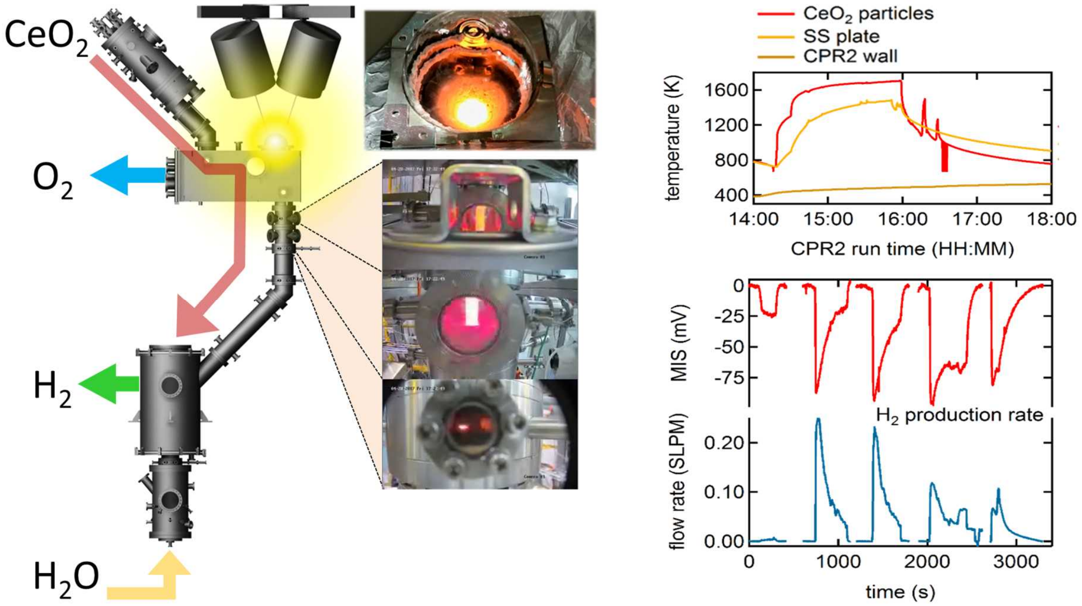

Figure 3. (Left) images of the CPR^2 during operation. Starting from top to bottom, CeO_2 particles are heated by simulated solar radiation (~3.5 kW$_{th}$ at the aperture) to ~1700K where O_2 is removed from the solid by vacuum pumping the TR. The radiant cavity through which CeO_2 particles flow is seen looking through the quartz dome in topmost picture. Particles then move by gravity through connecting chambers and collect in the WS. Incandescence from falling particles is clearly visible through viewports on the connecting chambers. Once a sufficient amount of reduced CeO_2 accumulates in the WS, steam is introduced causing the spontaneous re-oxidation of CeO_2 and production of H_2. (Right) selected excerpts of data streams from the CPR^2 DAC showing thermocouple readings from various locations within the system and instantaneous H_2 flowrate as a function of run time during a test.

In summary, Sandia and collaborators designed, fabricated, and demonstrated H_2 production through thermochemical water splitting in the CPR^2 prototype. This was accomplished at a scale of ~3.5 kW$_{th}$ (20 kW$_{ele}$) while achieving a peak rate of 0.2 SLPM H_2. In so doing, our prototype validated the following design objectives: 1) continuous and direct irradiation of redox material without particle shading, 2) precise control of particle flow rate and residence time in the TR, 3) pressure separation without internal mechanical components like valves, and 4) counter-flow mass exchange between steam and particles in WS (i.e. no mixing or fluidization during re-oxidation). Successful validation of these design objectives builds on knowledge needed to verify the potential for this hydrogen production technology to be cost competitive in the future, and critical to advancing the technology readiness of Sandia's concept for implementing a high-temperature, two step thermochemical water splitting cycle.

Future Directions

- Discovering a redox material that will meet or exceed DOE cost and performance targets. We anticipate that investments made by DOE's Hydrogen Advanced Water Splitting Materials Consortium (H_2 AWSM, found at http://h2awsm.org) will focus on advancing the STCH material discovery effort.
- Establishing the CPR^2 as a "routine-use" R&D tool to support seedling projects in H_2 AWSM as well as engage commercial interest and investment.
- Publish all project results in peer-reviewed journals.

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FY 2017 Selected Publications/Presentations

1. Ermanoski et. al, "Design of a particle bed reactor for solar water splitting", presented at SolarPACES 2016, October 11-14, 2016, Abu Dhabi, United Arab Emirates.
2. McDaniel et. al, "A brightly-lit pathway towards decarbonizing the US energy infrastructure", presented by invitation to the Mechanical Engineering Department at University of Florida, November 15, 2016, Gainesville, FL.
3. McDaniel et. al, "A novel solar thermochemical water splitting perovskite for hydrogen production", presented at 12th Pacific Rim Conference on Ceramic and Glass Technology hosted by ACS, May 21-26, 2017, Kona, HI.
4. Ermanoski, "Metal oxides in solar-thermochemical cycles: gaining breathing room through reactor design", presented at 21st International Conference on Solid State Ionics, June 18-23, 2017, Padua, Italy.
5. A.H. McDaniel, "Renewable energy carriers derived from concentrating solar power and nonstoichiometric oxides", *Current Opinion in Green and Sustainable Chemistry*, **4**, 37 (2017).
6. A. Singh, J. Lapp, J. Grobbel, S. Brendelberger, J.P. Rheinhold, L. Olivera, I. Ermanoski, N.P. Siegel, A.H. McDaniel, M. Roeb, C. Sattler, "Design of a pilot scale directly irradiated, high temperature, and low pressure moving particle cavity chamber for metal oxide reduction", under review in *Solar Energy*. (2017).

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Acronyms

$B_{25}B'_{75}$	general term to describe $AB_{0.25}B'_{0.75}O_y$, perovskite composition
CeO_2	Cerium(IV) oxide
CPR^2	cascading pressure receiver-reactor
DAC	LabVIEW-based data acquisition and control system
DNI	direct normal insolation
FY	fiscal year
PS	particle source chamber
PD	particle drain chamber
SFR	stagnation flow reactor
SLMA	general term to describe $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$ perovskite compositions
SLPM	standard liter per minute
SSIM	4-lamp, 20 kW$_{ele}$ solar simulator

STH	solar-to-hydrogen
TGA	thermogravimetric analyzer
TR	thermal reduction or thermal reduction chamber
WS	water-splitting or water-splitting reactor
δ	extent of oxygen non-stoichiometry in, for example, $ABO_{3-\delta}$ or $CeO_{2-\delta}$
~	approximately