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/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 H₂.

Fiscal Year (FY) 2017 Objectives

- Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical water-splitting cycles. (Barriers S and T)
- Construct and demonstrate a particle receiver-reactor capable of continuous operation at greater than 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.
cycle is theoretically capable of achieving a solar-to-hydrogen 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 CPR to that commonly observed in other solar thermochemical hydrogen 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 (like CeO_2).

Recently our group found a complex perovskite (AB_{0.25}B_{0.75}O_{25}, 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 perovskites capable of thermochemical water splitting. Firstly, in the course of investigating a family of compounds with AB\textsubscript{1-x}B_{y}O_{25} (0 < x < 1) stoichiometry, we found that only the AB_{0.25}B_{0.75}O_{25} 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 ≠ 0.25) having excess B or B′ were comprised of various WS inactive secondary oxide phases, mainly AB\textsubscript{O} and AB\textsubscript{O}B′\textsubscript{O}y, along with B_{25}B_{75} suggesting that AB_{0.25}B_{0.75}O_{25} is a line compound.

Secondly, during an investigation of the B_{25}B_{75} phase using thermogravimetric analysis, 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 the crystallography of B_{25}B_{75} 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 and 32 deg. 2θ) stacked atop one another with each pixel row representing a different sample temperature (298 K→1,623 K→298 K) recorded in a low O\textsubscript{2}-partial pressure helium atmosphere (i.e., during thermal reduction). It is clear by the manner in which the colored vertical bars at various 20 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 1,573 K. As mentioned previously, this chemistry does not conform to that commonly observed in other solar thermochemical hydrogen 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 not shown).

**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 (δ > 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).

**CPR\textsuperscript{2} Fabrication and Demonstration Thrust.** Sandia completed an intensive staged buildout and test campaign
of the CPR\textsuperscript{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\textsuperscript{2}, which stands \textasciitilde 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\textsuperscript{2} are a particle source chamber for pre-heating and storing \textasciitilde 70 kg CeO\textsubscript{2} particles, a four-lamp, 20 kW\textsubscript{e} solar simulator array for radiant heating of particles, a receiver/reactor or thermal reduction (TR) chamber to reduce particles and produce O\textsubscript{2}. 

FIGURE 2. Image and schematic of Sandia’s fully assembled and operational CPR\textsuperscript{2}. PS = particle source chamber, SSIM = 4-lamp, 20 kW\textsubscript{e} solar simulator, TR = thermal reduction chamber, WS = water splitting chamber, and PD = particle drain (see text for details).
II.C  Hydrogen Production / High-Temperature Thermochemical

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a pressure separation segment, a WS reactor to oxidize particles and produce H₂, and a particle drain 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 system was assembled and integrated into the CPR² for the supply and control of gases and particles, power to lamp array, and signal inputs and outputs to the reactor. The fully functional CPR² resides at the National Solar Thermal Test Facility in Albuquerque, New Mexico.

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 CeO₂ as the redox active material. A maximum thermal reduction temperature of 1,700 K was achieved in the radiant cavity receiver, and water splitting occurred at ~970 K (see data plots of temperature and instantaneous H₂ flowrate in Figure 3). The topmost image shows the receiver cavity looking through the aperture 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 H₂ production rate, a standard heat capacity-based mass flow meter and a Sandia patented solid state sensing device.

In summary, Sandia and collaborators designed, fabricated, and demonstrated H₂ production through thermochemical water splitting in the CPR² prototype. This was accomplished at a scale of ~3.5 kW_th (20 kW_el) while achieving a peak rate of 0.2 SLPM H₂. 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

**FIGURE 3.** (Left) images of the CPR² during operation. Starting from top to bottom, CeO₂ particles are heated by simulated solar radiation (~3.5 kW_th at the aperture) to ~1,700 K where O₂ is removed from the solid by vacuum pumping the TR. The radiant cavity through which CeO₂ 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 CeO₂ accumulates in the WS, steam is introduced causing the spontaneous re-oxidation of CeO₂ and production of H₂. (Right) selected excerpts of data streams from the CPR² data acquisition and control system showing temperature readings from various locations within the system and instantaneous H₂ flowrate as a function of run time during a test.
advancing the technology readiness of Sandia’s concept for implementing a high-temperature, two-step thermochemical water splitting cycle.

CONCLUSIONS AND UPCOMING ACTIVITIES

• 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 (found at http://h2awsm.org) will focus on advancing the material discovery effort.

• Establishing the CPR² as a “routine-use” R&D tool to support seedling projects in Hydrogen Advanced Water Splitting Materials Consortium 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


REFERENCES


