II.B.4 Solar Hydrogen Production with a Metal Oxide-Based Thermochemical Cycle

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Project Start Date: October 1, 2008
Project End Date: October 1, 2013

Overall Objectives

- Verify the potential for a solar thermochemical hydrogen production cycle based on a two-step, non-volatile metal oxide to be competitive in the long term.
- Develop a high-temperature solar receiver-reactor (SRR) and redox material for hydrogen production with a projected cost of $3.00/gasoline gallon equivalent at the plant gate by 2020.

Fiscal Year (FY) 2013 Objectives

- Discover and characterize novel perovskite materials for a two-step, non-volatile metal oxide water-splitting thermochemical cycle.
- Calculate theoretical system efficiency for various SRR operating scenarios that meet or exceed a solar-to-hydrogen (STH) ratio of 26%.
- Formulate particle-based SRR designs and assess feasibility.
- Construct an engineering test stand and evaluate particle conveyance and pressure separation concepts.
- Conduct H2Av3 analysis of a dish-based particle SRR producing 100,000 kg H_2/day and identify a clear path towards meeting DOE projected cost targets for H_2.

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
(T) Coupling Concentrated Solar Energy and Thermochemical Cycles
(X) Chemical Reactor Development and Capital Costs
(AC) Solar Receiver and Reactor Interface Development

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 H_2 from thermochemical water-splitting (WS) cycles. Insights gained from these studies will be applied toward the design and optimization of an SRR that meets the following ultimate DOE hydrogen production targets:

- Hydrogen Cost: $2/kg H_2
- Materials of Reaction Cost: $11 K/yr tonnes per day H_2
- STH Conversion Ratio: 26%
- 1-Sun Hydrogen Production Rate: 2.1×10^{-6} kg/s m^2

FY 2013 Accomplishments

- Synthesized 55 different oxides and screened them for WS activity.
- Discovered a $Sr_{1-x}La_xMn_{1-y}Al_yO_3$ perovskite that produces 9x more hydrogen (220-307 µmoles/g oxide) as compared to CeO_2 (32 µmoles/g) at a lower reduction temperature (T_{RED}). Finding more effective materials increases the likelihood of meeting the DOE targets for material cost and STH conversion ratio.
- Refined our thermodynamic model of the particle SRR and discovered an optimal ΔT (T_{RED}-T_{OXD}) that lies between the worst case (isothermal operation, $\Delta T = 0°C$) and the highest practical reduction temperature (T_{RED} = 1,600°C). Identifying optimal operating temperatures is key to meeting the DOE STH conversion ratio target of 26%. This result was derived for ceria, however, it is anticipated that other materials will act the same.
- Constructed an engineering test stand that operates at ambient conditions, verified that a particle conveyance rate of more than 30 g/s can be achieved which exceeds

the particle flow design requirement for a 5-kW SRR. The gas permeability of surrogate particles is also lower than that required for pressure and gas separation. Achieving these two milestones is critical to demonstrating the feasibility of the particle SRR design.

- Analyzed H_2 production costs for a parabolic-dish based particle SRR for a 100,000 kg H_2/day plant. Sensitivity analysis reveals the importance of reactor efficiency to meeting DOE ultimate cost targets.
- Designed and optimized a novel full field beam-down optical system for a 5-15 MW central receiver with a flat tower reflector. This design will form the basis of an H2Av3 cost analysis for a central receiver hydrogen production plant.

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INTRODUCTION

This research project is focused on the development of technologies that produce 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 a STH conversion ratio that exceeds the DOE target of 26% at a scale large enough to support a hydrogen economy [1]. The challenge is to engineer an SRR that will meet the DOE cost target of \$2/kg H_2.

Conceptually, heat derived from concentrated solar energy can be used to reduce a metal oxide at high temperature producing O_2 (step 1). The reduced metal oxide is then taken off sun and re-oxidized at lower temperature by exposure to H_2O, thus producing H_2 (step 2) and completing the cycle. The ultimate commercial success of solar thermochemical H_2 production is contingent upon developing suitable redox active materials and incorporating them into an efficient SRR. There is a large pallet of material chemistries that have attributes suitable for inclusion in a thermochemical H_2 production system [2-4]. The challenge is to identify an optimally-performing material. In addition, the development of redox material and SRR are not mutually exclusive, but must be conducted in parallel [5]. This project also addresses the reactor- and system-level challenges related to the design of an efficient particle-based SRR concept [6].

APPROACH

Thermochemical WS reactors are heat engines that convert concentrated solar energy (heat) to chemical work. Our approach is to discover novel materials to accomplish the WS chemistry and pair these with a novel SRR 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 SRR technology is based on a moving bed of packed particles that embodies all of the design attributes essential for achieving high efficiency operation: 1) inherent sensible solid-solid 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 validating design concepts and deriving optimal operating conditions through detailed systems modeling.

RESULTS

Perovskite oxides are an unexplored class of materials in solar H_2 applications. Fifty-five different perovskite formulations were synthesized this FY and screened for the following attributes: 1) O_2 uptake and release, 2) onset temperature of thermal reduction, and 3) WS activity. Of those screened, three formulations of a Sr- and Mn-doped $LaAlO_3$ (SLMA) exhibited attributes that exceed the current state-of-the-art redox material, CeO_2. We found that the SLMA materials reduce to a much greater extent than CeO_2, and that the onset of thermal reduction occurs fully 300°C lower in temperature. More importantly, the SLMA family of compounds we discovered split H_2O and yield more H_2 than CeO_2. Results were reported in a high-impact journal article [4] and a patent application was filed.

Presented in Figure 1 are the H_2 production rates for SLMA perovskites and CeO_2 measured over previously reduced oxides. Nearly 9x more H_2 is produced by the SLMA compounds (220-307 µmoles/g oxide) as compared to CeO_2 (32 µmoles/g). To put this discovery in perspective, extensive efforts to improve the performance of CeO_2, focused on destabilizing the crystal structure through doping and substitution, succeeded in marginally increasing the cycle capacity [7]. Although decreasing T_{RED} while increasing cycle capacity is significant, fast oxidation kinetics are equally important because they directly influence the STH conversion ratio. Detailed numerical analysis of the H_2 production rates for SLMA1-3 found that the WS rates are comparable to CeO_2, a material noted for fast kinetics. The number of perovskite compounds that may exhibit redox and WS activity is extremely large. In fact, we discovered another material that shows WS activity comprised entirely of inexpensive earth-abundant elements ($CaTi_{1-x}Fe_xO_3$). Unfortunately this compound's redox behavior did not surpass that of CeO_2. Nonetheless, Sandia is the first to recognize the potential for these materials to achieve DOE technical targets, and we feel confident that better performing perovskites will be discovered in the near future.

In this FY, the thermodynamic model of our SRR was expanded to include a detailed accounting of the energy needed for steam production. Previously, we described the

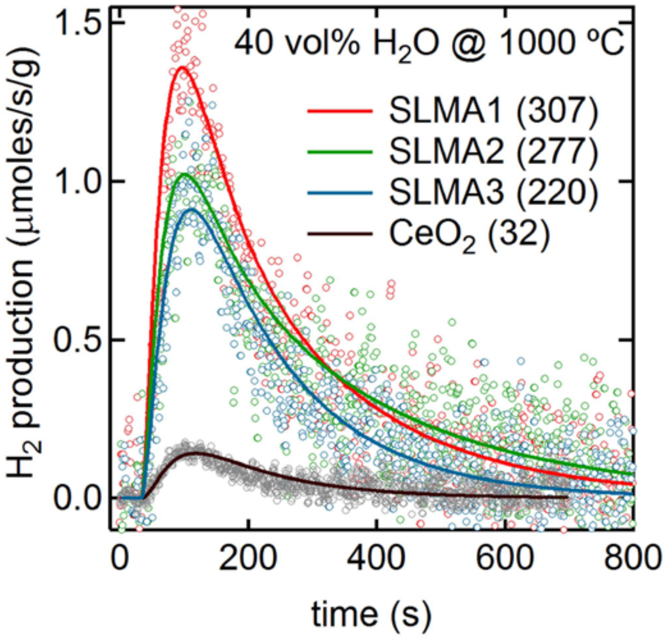

FIGURE 1. H_2 production rate as a function of time measured during oxidation in 40 vol% H_2O at 1,000°C (open symbols). SLMA1-3 and CeO_2 thermally reduced at 1,350°C in He. The total amount of H_2 produced in µmoles per g material is shown in parentheses. Solid lines are the results of detailed kinetic modeling.

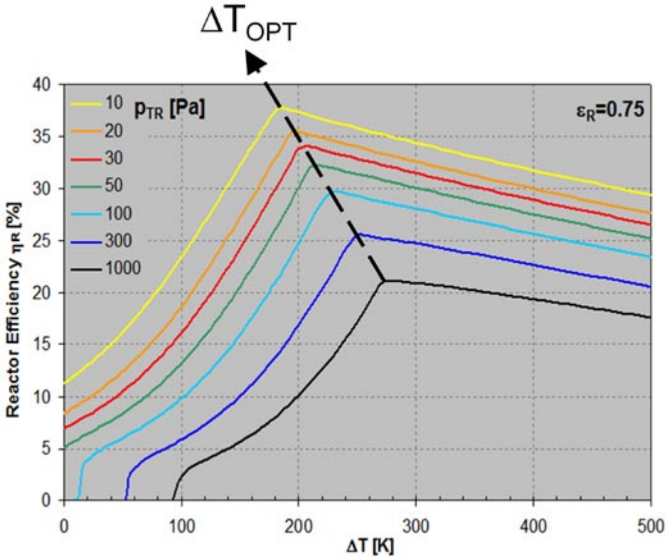

FIGURE 2. Calculated reactor efficiency (η_R) as a function of ΔT for several values of O_2 partial pressure in the reduction zone (p_{TR}) and a recuperator effectiveness (ε_R) of 0.75.

dependence of reactor efficiency on the O_2 partial pressure (p_{TR}) and recuperator effectiveness (ε_R) [6]. This analysis was conducted at a fixed value for ΔT. By extending the SRR model and relaxing the ΔT constraint, we can more thoroughly probe the thermodynamic behavior of the system. The SRR operation parameter space was explored using CeO_2 as the active oxide with special emphasis on resolving optimal values for operating points. We note that our model is easily adapted to predict the performance of other materials provided thermodynamic information on the specific redox cycle is available. To facilitate this analysis, the collection and conversion efficiencies were decoupled in the model. Thus, reactor efficiency (η_R) is reported in the subsequent figure as opposed to the STH conversion ratio. Illustrated in Figure 2 are the calculated reactor efficiencies (η_R) as a function of ΔT for several values of p_{TR} at a recuperator effectiveness of 0.75. The existence of a temperature difference value, ΔT_{OPT}, for any value of p_{TR} where η_R is greatest, is an obvious feature in the results shown in Figure 2. Additionally, it can be seen that isothermal operation (ΔT = 0) yields the lowest efficiency for any p_{TR}.

The peaks in the η_R vs. ΔT curves appear because the sensible heat of the reduced oxide is used to heat the steam to reaction temperature. Since oxide heating and steam heating are the two largest sensible heat loads, peak efficiency occurs at the point where these two terms are balanced. The reason behind poor performance at large ΔT, and even poorer performance at ΔT = 0, are easily explained. At large ΔT more sensible heat is available in the reduced oxide than is needed for heating steam, creating excess waste heat. In the isothermal operation limit, the reverse is true—no energy is needed to heat the oxide but the steam heating requirement is exceptionally large. The entirety of both these loads must be supplied by solar input, and inefficient utilization negatively impacts η_R. We also find through this expanded analysis that waste heat of sufficient quality is available to provide all of the process water via an absorption chiller; basically condense H_2O from the atmosphere. This reduces capital costs because H_2O does not have to be transported or otherwise supplied to a remote, desert location.

In this FY, Sandia constructed an engineering test stand, shown schematically in Figure 3c, in order to validate two critical design concepts, 1) particle elevation using an Olds lift, and 2) pressure separation using a packed particle bed. The data in Figure 3a shows a linear correlation between mass flow rate of particles and the rotational velocity of the chamber wall for a prototype double-helix auger designed for efficient solid-solid heat recuperation. The mass conveyance rate for this auger greatly exceeds the requirement for a 5-kW SRR, which is our design target for a high-temperature test stand. In addition, the gas permeability of a ~3-m column of surrogate steel grit particles is sufficient to stand-off an atmosphere of pressure, therefore validating our pressure separation concept at this length scale. Taken together, these results indicate no major technical barriers will prevent operation of a 5-kW, high-temperature test stand. We are currently modifying this unit to operate under vacuum at high-temperature.

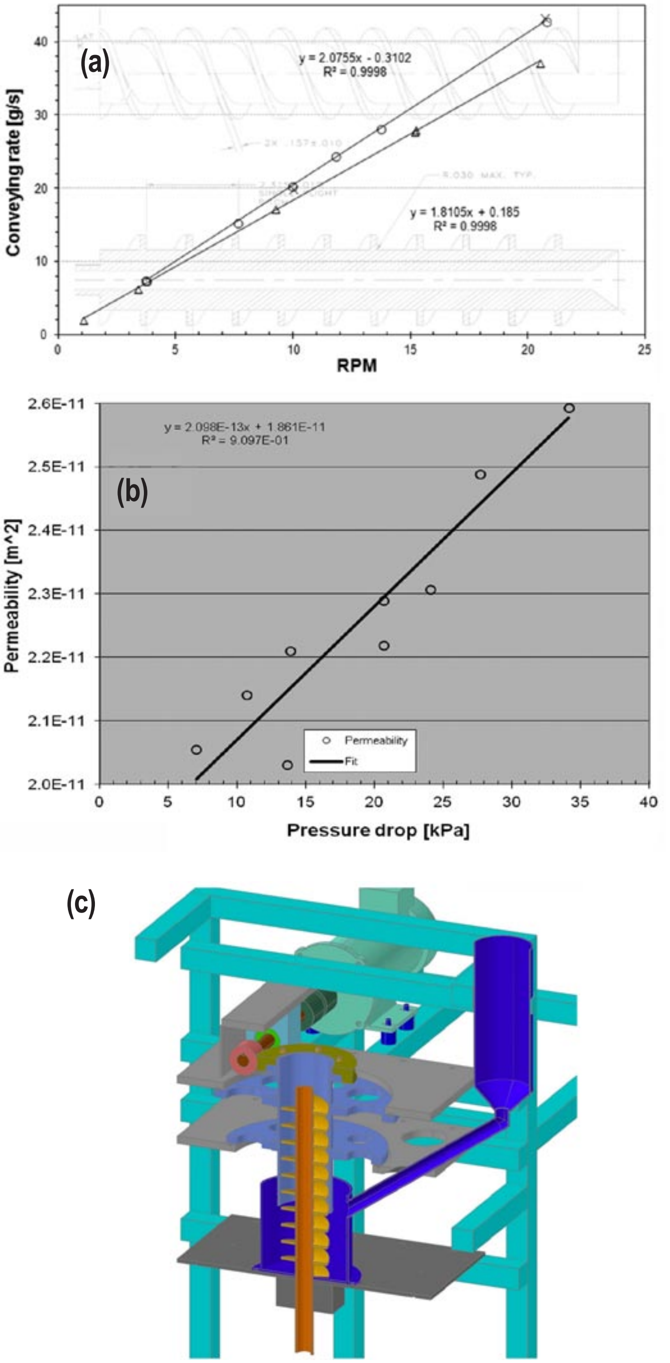

FIGURE 3. (a) The mass transport rate of particles as a function of revolutions per minute (RPM) measured in the engineering test stand at ambient conditions. (b) The gas permeability as a function of pressure drop across a packed bed of surrogate particles measured in the engineering test stand. (c) A schematic of the engineering test stand designed to operate at ambient conditions and test particle conveyance.

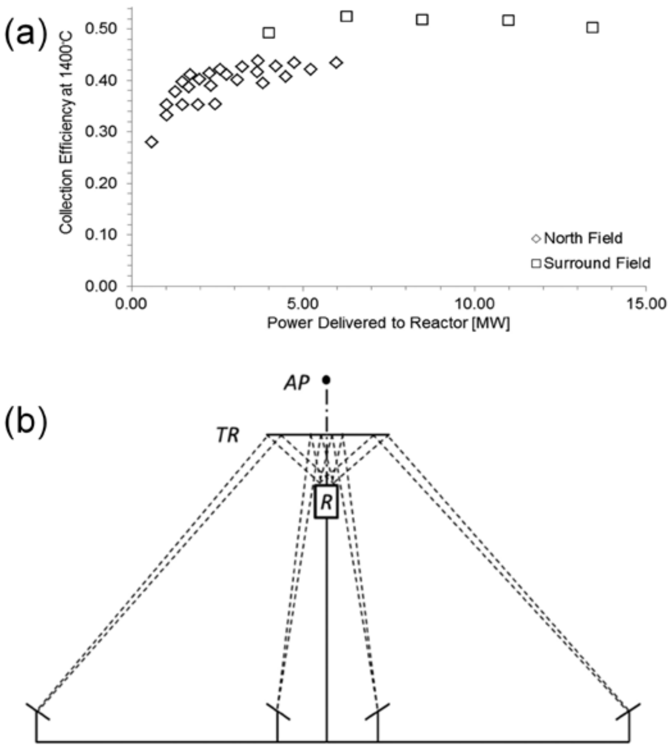

FIGURE 4. (a) The solar collection efficiency predicted for an optimal heliostat field design as a function of power delivered to the reactor aperture using a novel beam-down design. (b) A schematic of the full-field beam-down collector design. TR is the terminal reflector (flat mirror), AP is the aim point of the field, and R is the solar receiver-reactor.

Significant progress was also achieved in the design and technoeconomic analysis of large-scale H_2 production plants based on Sandia SRR technology. Namely, the design and H2Av3 analysis of a dish-based H_2 production plant capable of producing 100,000 kg H_2/day, and the design and optimization of a full-field collector array for a central receiver capable of delivering up to 15 MW to an SRR aperture. The H2Av3 work was conducted in collaboration with Strategic Analysis, Inc. (Arlington, VA). Results indicated a projected high volume cost of \$8.56/kg H_2 (produced, but not delivered or dispensed) in 2020 based on a conventional reactant material like ceria operating at an STH conversion ratio of 16.6%. The cost is projected to be near the ultimate DOE production cost target of \$2/kg H_2 for an advanced material operating in an advanced SRR at an STH conversion ratio of 34.3%. In addition, the H2Av3 analysis shows that the major contributors to capital cost are, in order, 1) STH conversion ratio, 2) collector cost, 3) SRR cost, and 4) electrical power generation cost. Research described herein addresses both the STH conversion ratio and SRR cost.

H2Av3 analysis will continue next FY using the central receiver production platform shown in Figure 4b. In this case the SRR is located on a tower as opposed to a dish, and requires a novel beam-down optical design. The collector layout was optimized using Delsol to evaluate the highest annual field efficiency for a given power level. Both north field and surround field configurations were considered.

The collection efficiencies at 1,400°C for these designs are plotted in Figure 4a. A peak collection efficiency of 53% can be achieved with a surround field design having an outer radius of 115 m providing 6.3 MW to the SRR from 9,642 heliostats. A less efficient configuration, at 50%, provides nearly 13.5 MW of power to the SRR from a total of 21,719 heliostats in a field with an outer diameter of 130 m. We will consider both cases in the pending H2Av3 study.

CONCLUSIONS AND FUTURE DIRECTIONS

- Discover additional perovskite and phase-change type oxides for improved WS activity.
- Construct a high-temperature SRR test stand sized for 5 kW.
- Conduct H2Av3 analysis of central-receiver based SRR platforms.

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12. "Nonstoichiometric Perovskite-Type Oxides for Solar Thermochemical Fuel Production", J. Tong, invited talk at the National Institute of Materials Science, Tsukuba, Japan, 12 June 2013.

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