

II.E.3 Solar Hydrogen Production with a Metal Oxide-Based Thermochemical Cycle

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Fiscal Year (FY) 2012 Objectives

- Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical cycles.
- Design and test particle conveying concepts for a novel reactor/receiver concept.
- Test construction materials for compatibility between ceria and reactor components at high temperature and low oxygen partial pressure.
- Calculate theoretical system efficiency for various reactor/receiver operating scenarios.
- H₂A technoeconomic analysis of dish-based particle reactor/receiver concept.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

This project is conducting fundamental studies on materials suitable for use in concentrated solar power applications and designing reactor concepts that when combined will produce H₂ from thermochemical water splitting cycles. Insights gained from these studies will be applied toward the design and optimization of solar-driven reactors that meet the following DOE hydrogen production targets:

- Cost: \$2-\$4/gasoline gallon equivalent H₂
- Process energy efficiency: >35%

FY 2012 Accomplishments

- Developed a detailed kinetic model for ceria redox that can be used to establish theoretical cycle performance metrics in SNL-designed reactors.
- Synthesized and characterized transition metal-doped ceria materials which demonstrate increased redox capacity and lower effective thermal reduction temperature compared to undoped ceria.
- Validated particle conveyor concept by demonstrating a sustained mass flow rate of 30 g/s particles for 1 hour.
- Verified no adverse reactivity between ceria (active material) and materials of construction such as alumina (to 1,550°C), SiC (to 1,400°C), or Haynes 214 alloy (to 1,200°C) for a period of 3 hours.
- Evaluated theoretical system efficiency under low direct normal insolation (DNI). Particle reactor design achieves efficiencies that meet the 2012 DOE target of 30% for DNI between 400 W/m² and 1,000 W/m².
- Initiated H₂A analysis of a 100,000 kg/day H₂ plant based on 22,000 dish-type receivers.



Introduction

The conversion of solar radiation into a chemical fuel such as hydrogen is an engineering challenge, however, unlike solar-derived electricity or heat, it is easier and more efficient to transport and store hydrogen. This point is important because energy demand is rarely matched to incident solar radiation, either spatially or temporally. Two-step solar-driven thermochemical cycles based on non-volatile metal oxides are an attractive technology for producing hydrogen because of the potential to operate

at high solar-to-chemical conversion efficiency with moderate operational demands on land and water resources. Conceptually, heat derived from concentrated solar energy thermally reduces a metal oxide at temperatures between 1,300°C and 1,500°C, producing O₂ (step 1). The reduced metal oxide is then taken off sun and oxidized at temperatures below 1,000°C by exposure to H₂O, thus producing H₂ fuel (step 2) and completing the cycle. The ultimate commercial success of solar thermochemical hydrogen production is contingent upon developing suitable redox active materials and incorporating them into an efficient solar reactor/receiver.

Approach

Thermochemical reactors are heat engines that convert concentrated solar energy (heat) to chemical work. Our approach is to use a novel reactor design that achieves unprecedented solar-to-hydrogen fuel conversion efficiency. It is based on a moving bed of packed particles that embodies *all* of the design attributes essential for achieving high efficiency: (1) inherent sensible solid-solid heat recovery between the reaction steps; (2) spatial separation of pressure, temperature, and reaction products within the device; (3) continuous on-sun operation; and (4) direct absorption of solar radiation by the redox active material. In addition, the design is mechanically simple and can accommodate virtually any reactive material in particle form.

We are currently developing a high-temperature particle conveying and reactor system, and discovering active materials suitable for two-step cycle chemistry. Recent efforts have focused on ferrites and cerium oxide, which are representative of two important material classes that are defined by how the metal oxide chemistry is manifested in the solid state. The material discovery work involves expanding our understanding of the underlying thermodynamics and kinetics in order to make performance improvements and/or formulate new compositions that directly impact overall process efficiency. Additional research efforts are directed towards system-level challenges associated with dish and central-receiver based thermochemical platforms, which we address through system performance calculations and economics models.

Results

Materials Development: Cerium oxide has recently gained attention as a suitable material for use in high-temperature thermochemical water splitting cycles [1,2]. Originally disregarded because of the high temperature required to operate the cycle stoichiometrically ($T > 2,000^\circ\text{C}$), it was later discovered that the non-stoichiometric oxide could be marginally effective at lower temperatures ($T \sim 1,500^\circ\text{C}$) due to fast redox kinetics and high thermal stability. However, even at the lower reduction temperature,

it is not likely that unmodified ceria used as a working fluid in a two-step thermochemical cycle will be able to achieve the DOE cost targets for H₂ production because the redox capacity is too low. Therefore, we have been investigating the use of transition metal dopants to: (1) destabilize the ceria crystal structure in order to decrease the temperature required for effective thermal reduction, and (2) increase the redox capacity (i.e., H₂ production rate per cycle) by synthesizing ceria solid solutions with other redox active cations.

Preliminary results of this effort are illustrated in Figure 1 for a 10 mol-% mixture of Fe₂O₃ in CeO₂. Samples prepared by the sol-gel method were reduced and oxidized in a stagnation flow reactor equipped with a 500 W CW near-infrared diode laser for sample heating (thermal flux closely approximates conditions found in solar concentrators). Here the O₂ production rate was measured as a function of time and temperature during thermal reduction *after* oxidation by O₂ (red curve) or H₂O (blue curve) at 800°C. The O₂ redox capacity of the material can be measured by the area under each curve, and by proxy the H₂ production rate inferred. It is clear by the data presented in Figure 1 that adding iron oxide to ceria increases the total amount of O₂ evolved and decreases the temperature at which O₂ evolution begins (see dashed lines with arrows). Unfortunately this behavior is only evident for O₂ redox cycles and not H₂O redox cycles, which indicates that this particular dopant is not an effective additive for water splitting. We have characterized the effects of doping several aliovalent first-row transition metal cations into ceria, as well as mixtures of ceria and zirconia, with mixed results. We find that certain compound formulations do indeed increase the H₂ production capacity, but reduce thermal stability by inducing sintering and slow the oxidation

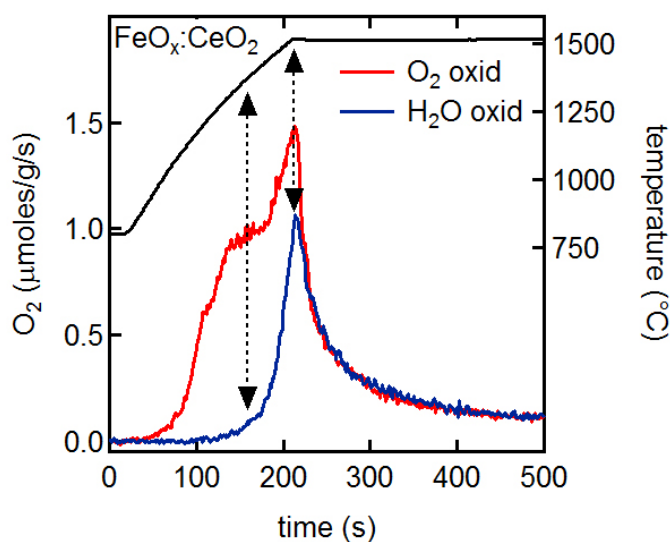


FIGURE 1. The rate of oxygen production measured during thermal reduction as a function of time after O₂ oxidation (red curve) and H₂O oxidation (blue curve) for iron oxide doped ceria

kinetics. In the future, we will investigate non-stoichiometric oxides in the perovskite family of materials.

Reactor Development: Significant progress in the development of the elevator/recuperator section of the reactor was achieved by adopting an innovative nested auger design for vertical conveyance of particles (Figure 2), and testing multiple surrogate materials (75- μm silica sand, 200- μm sand, corn flour, and corn grits). Conveying efficiency was found to differ considerably between materials depending on cohesive strength, internal friction, and wall friction of the material. The surrogate materials were chosen to test different particle sizes, effective densities, and cohesive strengths, which are all known to effect particle transport. In addition, experiments with return particle flow through a finned tube representative of a heat exchanger showed a critical dependence on particle size. Flow was essentially unimpeded for larger particles (75 μm), but was completely hindered for smaller particles (5 μm) except under severe mechanical agitation. We are now able to specify an optimal particle size for conveyance in a bench-scale prototype.

We also investigated the compatibility of ceria with prospective reactor materials, specifically, alumina and alumina-coated silicon carbide. Alumina was found not to react with ceria up to 1,550°C in stagnant air. Alumina-coated silicon carbide was tested up to 1,450°C, and also found to be unreactive. These experiments showed that a minimal thickness of alumina coating is needed before the surface can be passivated. When coating thickness is insufficient, ceria reacts vigorously with the underlying SiC/SiO₂. However, thicker coatings were found to be increasingly unstable. The optimal coating thickness and deposition method will need to be determined if SiC is to be used as a reactor material.

The most relevant performance metric that impacts H₂ production cost is the annual average efficiency. We have previously calculated this efficiency using a simple model



FIGURE 2. Nested auger design prototype for particle conveyance

for the reactor operating at off-design point conditions, i.e., low or high DNI. To better estimate the annual average efficiency we improved the design-point efficiency model, which has enabled the assessment of multiple off-design point performance parameters. The results of these calculations are summarized in Figure 3. The main conclusion from these calculations is that increased efficiency under low DNI can be achieved due to the opposing dependencies of radiation losses, recuperator effectiveness, and thermal reduction pressure. As the oxide flow rate is decreased to maintain the thermal reduction temperature, heat recovery effectiveness increases and oxygen partial pressure (p_{O_2}) decreases, leading to an increased extent of reduction of the oxide. At the same time, the *absolute* amount of power lost through the aperture via radiation remains constant (i.e. the *relative* radiation loss increases). Therefore, for a wide range of DNI the gains from increased heat recovery effectiveness and increased extent of reduction more than offset the increase in the relative radiative losses. This yields a substantially flat solar efficiency making the reactor exceptionally well-suited for real world operation.

H2A Systems Analysis: Analysis for the particle bed reactor includes several elements that build on one another to produce the final economic model. We begin with an annual average efficiency calculation of a single dish-based particle reactor operating in Daggett, CA. The reactor uses an 88-m² parabolic dish collector with optical performance modeled after the pre-commercial units developed by Stirling Energy Systems at SNL over the last decade. The reactor uses cerium oxide particles as the reactive media and we assume sensible heat recuperation of 90%. This level of recuperation is only possible in the particle reactor concept since it includes counterflow heat transfer between solids (absolutely unique to this reactor design).

The system-level hydrogen production is assumed to be 100,000 kg/day, requiring a total of over 22,000 dishes.

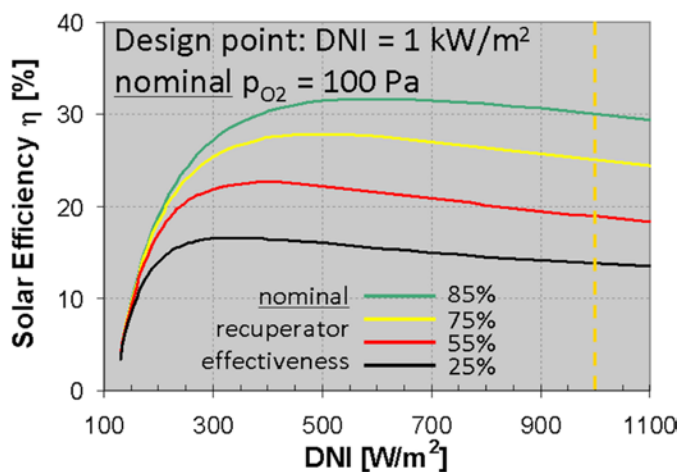


FIGURE 3. Efficiency of the particle reactor under decreased DNI (for detailed discussion see text)

Each of these dishes is connected to a central facility by hydrogen and water piping. Water is delivered under pressure to each dish, and hydrogen is pumped from each dish to the central facility at a pressure of 300 psia. The energy losses associated with pumping both the water and the hydrogen through the field are accounted for in the resultant cost of electricity on an annual basis. Economic assumptions and capital cost estimates are included to complete the model. Our baseline assumptions are consistent with those reported by TIAX [3]. Although our economic analysis is not yet complete, preliminary results indicate a significant amount of uncertainty in the projected cost of H_2 . This is also consistent with other results derived from the TIAX report, e.g. the ferrite process proposed by the University of Colorado is predicted to have a hydrogen cost between \$2.7-\$15.02/kg H_2 [3]. In this case as in ours, most of the uncertainty is tied to the performance of the reactor itself, which is an issue we need to formally address as we continue our assessment of the particle reactor concept.

Conclusions and Future Directions

- Screen a large family of perovskite-type oxides for use in two-step, high-temperature thermochemical water splitting cycles.
- Continue with the staged development of a high-temperature reactor prototype sized for 5 kW_{th} that will be tested on-sun at the National Solar Test Facility.
- Design beam-down optics for both dish and central-receiver based reactors.

FY 2012 Publications/Presentations

1. Scheffe, J.R.; McDaniel, A.H.; Allendorf, M.D.; Weimer, A.W. “Kinetic analysis of the oxidation of $Co_{0.9}Fe_{2.1}O_4/ZrO_2$ for thermochemical H_2 production.” In review at E&ES.
2. Arifin, D.; Aston, V.A.; Liang, X.; McDaniel, A.H.; Weimer, A.W. “ $CoFe_2O_4$ on porous Al_2O_3 nanostructure for solar thermochemical CO_2 splitting.” In revision at E&ES.
3. N.P. Siegel, J.E. Miller, I. Ermanoski, R.B. Diver, and E.B. Stechel, “System Performance Estimation of Two-Step Solar Thermochemical Fuel Production processes”, in preparation.
4. I. Ermanoski, N.P. Siegel, and E.B. Stechel, “A New Reactor Concept for Efficient Solar Thermochemical Fuel Production”, submitted to Journal of Solar Energy Engineering.
5. I. Ermanoski and N.P. Siegel, “Packed Bed Reactor for Solar Thermochemical Fuel Production”, presented at IEA SolarPACES 2011.

References

1. W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S.M. Haile, and A. Steinfeld, *Science*, 2010, 330, 1797–1801.
2. W.C. Chueh and S.M. Haile, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 2010, 368, 3269–3294.
3. “Support for Cost Analyses on Solar-Driven High Temperature Thermochemical Water-Splitting Cycles”, DOE report number DE-DT0000951, prepared by TIAX LLC, 2011.