

II.B.3 Solar-Thermal Redox-Based Water Splitting Cycle

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TABLE 1. Technical Targets for Solar-Driven High-Temperature Thermochemical Hydrogen Production

Characteristics	Units	2015 Target	2020 Target
Plant Gate H ₂ Cost	\$/gge H ₂	14.80	3.70
Installed Heliostat Capital Cost	\$/m ²	140	75
Solar-to-H ₂ Energy Conversion Ratio (LHV)	%	10	20

gge – gasoline gallon equivalent; LHV – lower heating value

FY 2013 Accomplishments

- >200 μmoles/g active material was demonstrated.
- Isothermal redox was found to be more efficient than temperature-swing redox under the conditions evaluated.
- Demonstrated stable activity after the first cycle up to ~200 cycles.



Overall Objective

Develop a two-step, non-volatile metal-oxide solar-thermal water-splitting cycle to produce hydrogen.

Fiscal Year (FY) 2013 Objectives

- Demonstrate isothermal redox water-splitting in a stagnation flow reactor at a temperature of 1,350°C yielding a H₂ production per gram of total mass of active material >100 μmoles/g active material.
- Develop an understanding of temperature swing vs. isothermal redox and the relative efficiency for carrying out each.
- Demonstrate the so-called “hercynite cycle” on-sun.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Office Multi-Year Research, Development, and Demonstration Plan:

- (S) High-Temperature Robust Materials
- (U) Concentrated Solar Energy Capital Cost
- (T) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

The technical targets for solar-driven thermochemical conversion are summarized in Table 1.

INTRODUCTION

Two-step solar thermochemical processes based on non-volatile metal-oxide cycles have the potential to operate at high thermal efficiencies, are chemically simple, and require less land and water to operate than competing biomass, artificial photosynthesis, and photovoltaic-driven electrolysis. Traditionally, two types of non-volatile metal-oxide redox chemistries are utilized in solar thermochemical H₂O splitting. The first is based on non-stoichiometric oxides of which ceria is a representative example. Such redox materials are thermally reduced without undergoing phase change, as the lattice is able to accommodate the strain induced by oxygen vacancy formation. These materials are thermally quite stable, although the extent of reduction, and hence cycle capacity, is small compared to other reducible oxides.

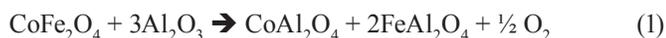
The second prototypical chemistry utilizes materials of the spinel structure that form solid solutions upon reduction. The most common are ferrites where Fe³⁺ in M_xFe_{3-x}O₄ is partially reduced to Fe²⁺; here M can be any number of transition metals that form spinel type oxides with iron, though Co, Zn, and Ni are the most studied. In these redox cycles, the ferrite spinel is heated until it decomposes into a mixture of metal-oxide solid solutions that are thermodynamically stable at temperatures above which the spinel decomposes. Thus, thermal reduction yields a solid solution of oxides with mixed valence (M²⁺, Fe²⁺, and Fe³⁺). While these materials theoretically exhibit greater redox potential than non-stoichiometric oxides, in practice deactivation induced by irreversible processes such

as sintering or the formation of liquid phases and metal vaporization lead to loss of active oxide.

We have developed a novel chemistry for a two-step, non-volatile metal-oxide H₂O splitting cycle that shuttles iron oxidation states (Fe^{2+/3+}) between CoFe₂O₄ and FeAl₂O₄ spinel compounds. This chemistry is dramatically different than current metal-oxide cycles that exploit oxygen non-stoichiometry in ceria or solid solution behavior in ferrites. The material has maintained redox productivity for over 150 thermochemical cycles. Hydrogen is produced via an isothermal two-step solar-thermal H₂O splitting cycle by removing the traditional temperature swings that are detrimental to efficiency and materials. We show that the traditional temperature swings for redox are unnecessary, and that isothermal water splitting at 1,350°C using the hercynite cycle exhibits H₂ production capacity >3 and >12 times that of the hercynite cycle and ceria, respectively, per mass of active material when reduced at 1,350°C and re-oxidized at 1,000°C. These properties provide for a technical foundation to achieve the DOE technical targets and enable the hydrogen economy.

APPROACH

The hercynite cycle reduction chemistry occurs via a reaction between decomposition products of the CoFe₂O₄ and Al₂O₃, forming the corresponding stable aluminates CoAl₂O₄ and FeAl₂O₄ according to the following oxygen evolution reaction:



During subsequent oxidation by H₂O, the cobalt ferrite spinel and alumina reform and H₂ is produced:



The oxygen evolution reaction (Equation 1) occurs to a greater extent at a temperature 150°C lower than a similarly prepared CoFe₂O₄-coated m-ZrO₂ (conventional ferrite) because compound formation is thermodynamically more favorable than solid solution formation. While lowering the reduction temperature is an important consideration for solar thermochemical technologies, perhaps more intriguing is the idea of binding the reduced iron in a compound that is more stable than a solid solution.

RESULTS

We used a hercynite cycle active material (47% active by mass) composed of 19.8 wt% CoFe₂O₄ on Al₂O₃ in a stagnation flow reactor to establish the baseline for comparison of temperature-swing water splitting (TSWS) to isothermal water splitting (ITWS). In TSWS, the active materials are reduced (Reaction 1) under inert gas flow (He) at 1,350°C and 101.3 kPa for 60 min, before being cooled to

1,000°C for water re-oxidation (Reaction 2). A gas stream of 50% by volume steam in inert He was used to oxidize the reduced materials for 25 min producing 31.4 ± 2.3 μmol of H₂ per gram of total material. The extent of reduction and water splitting capacity depends on the reduction temperature. Higher temperatures lead to a larger fraction of reduced Fe²⁺ ions. The number of available Fe²⁺ ions dictates the total H₂ generating capacity of the active material with a maximum ratio of one H₂ molecule produced to every two Fe²⁺ cations. Oxidation at 1,000°C was characterized by a slow rate of reaction (a peak H₂ generation rate of 0.06±0.04 μmol/g/s) and is likely surface-reaction limited. Because the oxidation reaction is slow, it is unlikely that most of the Fe²⁺ ions are re-oxidized to Fe³⁺ during the 25 min, which limits the total H₂ production capacity of the 1,350/1,000°C TSWS cycle.

Higher TSWS reduction and oxidation temperatures result in increased H₂ and O₂ production capacity and water splitting rates. Active material cycled between 1,500 and 1,200°C produced 93.7 ± 19.2 μmol of H₂/g with a peak rate of 0.32 μmol H₂/g·s. The higher reduction temperature resulted in more complete reduction of the active material and a larger thermodynamic driving force for H₂O splitting. The higher rates of H₂ generation at 1,500/1,200°C resulted from two factors: 1) the intrinsically higher reaction rates which arise from carrying out a kinetically limited process at a higher temperature, and 2) the larger thermodynamic driving force for oxidation which comes from the larger extent of reduction. The ability to perform water oxidation at temperatures above the onset of reduction suggests that isothermal water splitting is possible and that the current understanding of the thermodynamics of solar-thermal water-splitting is incomplete.

Hercynite cycle materials split water in a two-step isothermal redox cycle as exemplified by the 1,350°C ITWS results shown in Figure 1. H₂ generation under ITWS conditions was achieved at a temperature above the minimum reduction temperature by first flowing an inert gas through the reactor to sweep away O₂ generated during the reduction step and subsequently injecting steam during the oxidation step to produce H₂. For 1,350°C ITWS, the active particles produced 45.1 ± 7.6 μmol O₂/g during 1 hour of reduction and 102 ± 18 μmol H₂/g total (>200 μmol H₂/g active material) during a 25 min exposure to 50 vol% steam in He. During reduction, the initial O₂ plateaus arise from incomplete H₂O removal from the system. Once all steam is swept from the reactor, the O₂ peak occurs as the materials reduce followed by the normal exponential decay as the reaction goes to completion. 1,350°C ITWS produces substantially more O₂ and H₂ than 1,350/1,000°C TSWS and slightly more O₂ and H₂ than 1,500/1,200°C TSWS. The slight deviation of the 2.26:1 H₂ to O₂ ratio from the expected 2:1 ratio, though within the error, likely arises from slight differences in the sensitivities and response times of the mass spectrometer used for measuring H₂, and the O₂ analyzer. The higher gas splitting production capacity of ITWS was

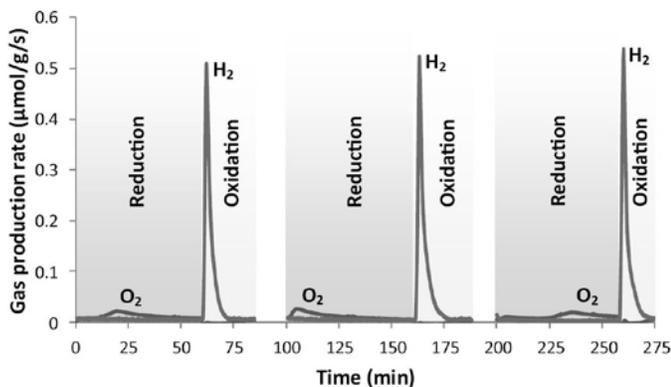


FIGURE 1. Isothermal Water Splitting at 1,350°C

accompanied by a higher H_2 production rate of 0.55 ± 0.16 $\mu\text{mol } H_2$ per gram/s. ITWS's higher rate of H_2 generation and its lack of irreversible heat losses associated with the changes in temperature between oxidation and reduction steps (which is required for TSWS) results in ITWS having a higher theoretical efficiency than TSWS with the conditions examined in this study.

Traditional TSWS thermodynamic theory uses a closed-system model in which an oxidation temperature lower than the reduction temperature raises the chemical potential of the oxidizing gas and reduced metal oxide above that of the product gases and oxidized material in order to drive the oxidation reaction. In contrast, ITWS is an open system that uses swings in the partial pressure of the oxidizing gas to produce the chemical potential differences that drive the oxidation and reduction steps. To form a two-step water-splitting closed-cycle system, a process for the recombination of H_2 and O_2 must be included, such as a fuel cell. In the ITWS process, the partial pressure of generated gaseous reduction and oxidation products remains low by sweeping them from the reactor. The low chemical potential of O_2 during reduction and high H_2O and low H_2 chemical potentials during oxidation drive the respective reactions forward to enable ITWS. Furthermore, sweeping the product gases away from the metal-oxide prevents reverse reactions from occurring.

Not only are redox reactors open systems, but the reactions take place between gases adsorbed on the surface of the solid phase. Thus, the chemical potential and the coverage gas molecules adsorbed on the surface are the relevant quantities to consider for analyzing redox reaction thermodynamics. Because the coverage of adsorbates and, therefore, their chemical potentials are related to partial pressure, the oxidation reaction is driven by increasing the H_2O partial pressure and maintaining a low H_2 partial pressure. Therefore, ITWS relies on a chemical potential difference derived from readily adjustable gas phase partial pressures, rather than having to depend on the problematic large temperature changes of TSWS.

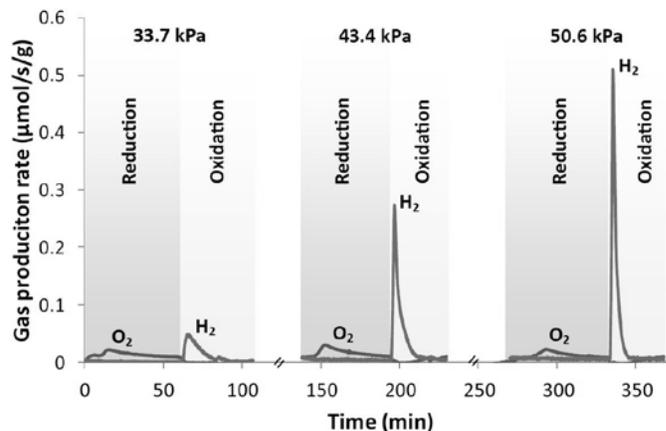


FIGURE 2. The Effect of Steam Pressure on 1,350°C ITWS

This analysis suggests that by increasing the partial pressure of the oxidizing gas, we can drive the water splitting reaction further toward the products. Indeed, an increased partial pressure of water resulted in higher H_2 production capacities at higher rates (see Figure 2). For 1350°C ITWS, steam concentrations in He of 33, 43 and 50% (overall pressure held at 101.3 kPa) correspond to H_2 production capacities of 40 ± 9 , 72 ± 8 , and 102 ± 18 $\mu\text{mol } H_2/\text{g}$ and peak production rates of 0.06 ± 0.02 , 0.15 ± 0.07 , and 0.55 ± 0.16 $\mu\text{mol } H_2/\text{g}\cdot\text{s}$, respectively. The increased peak production rates correspond to shorter oxidation times, as expected. The higher steam pressure results in a higher water chemical potential on the active material's surface, which provides a higher thermodynamic driving force for oxidation. Additionally, the higher steam concentrations increase the overall rate of reaction by increasing the reactant concentration. This result suggests that decreases in the time required for the oxidation step and possible increases in the ITWS temperature can be achieved by increasing the partial pressure of the oxidizing gas. Furthermore, as shown in Figure 3, the ITWS hercynite cycle produces >6 times more H_2 on a total mass basis and >12 times more H_2 on an active materials basis (47% active) compared to the 1,350/1,000°C ceria redox cycle which is considered the current state-of-the-art material for TSWS redox processing. In addition to ITWS's favorable kinetics and thermodynamics demonstrated in Figure 3, ITWS reduces both irreversible heat losses and thermal shock concerns that limit the efficiency and operations of traditional TSWS.

As can be seen from Table 2, our analysis, although simple, shows that the hercynite cycle-based ITWS is more efficient than TSWS for the conditions investigated. Because radiation losses scale as temperature to the fourth power, the solar heat required to maintain a 1,350°C reduction temperature is much less than a 1,500°C reduction temperature. This gives 1,350°C ITWS a substantial advantage over 1,500/1,000°C TSWS even though they produce similar quantities of H_2 per cycle. For all cases

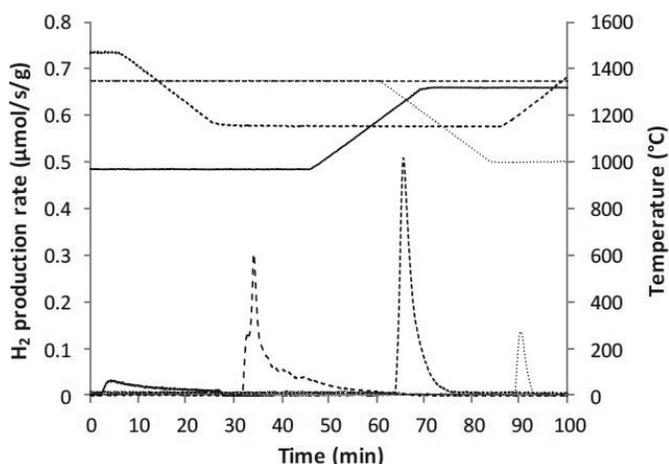


FIGURE 3. A comparison of solar-thermal water splitting. H₂ production curves are shown for hercynite cycle-based 1,350°C/1,000°C TSW (solid line), 1,500°C/1,200°C TSW long dashed line, 1,350°C ITWS (short dashed line), and ceria-based 1,350°C/1,000°C TSW (dotted line).

studied, the heat input required to counteract the radiation losses during the oxidation step was small in comparison to the other losses. The difference between emission losses during reduction and oxidation for ITWS arises from the comparatively longer reduction time, despite identical reduction and oxidation temperatures. While the decrease in temperature diminishes the radiative heat losses incurred during oxidation for the TSW cycles (and therefore the solar heat required to maintain the oxidation temperature), the

much shorter time required for ITWS oxidation keeps the total solar duty of the oxidation step low, even though ITWS’s oxidation step has a higher rate of heat loss.

As expected, the sensible heat necessary to heat the oxidized material back to the reduction temperature exceeds all other energy requirements considered in the simplified analysis. The solar input required ranges from 28% of the total energy required to produce a mole of H₂ in the best scenario modeled here (95% recuperation under 1,500/1,200°C TSW conditions) to 77% in the worst scenario modeled here (90% recuperation under 1,350/1,000°C TSW conditions). It is important to note that even the worst case scenario provides a generous coefficient of heat recuperation, which is more typical of fluid phase heat transfer than of solid systems. Additionally, it is worth pointing out that 1,350/1,000°C TSW suffers from two negative effects: in addition to requiring a significant amount of heat to change temperatures between 1,350 and 1,000°C, the total amount of H₂ that 1,350/1,000°C TSW can produce is small and therefore it requires multiple cycles to produce an equivalent quantity of H₂ as 1,350°C ITWS or 1,500/1,200°C TSW can achieve in a single cycle. This necessitates more cycles, and associated temperature swings, which results in higher heat losses per mole of H₂ produced.

ITWS’s higher solar efficiency and specific H₂ production capacity as compared to TSW for the conditions examined here, suggests that ITWS has the potential to be a game changing technology in the renewable energy and, particularly, H₂ economy fields.

TABLE 2. A simplified comparison of efficiencies of hercynite cycle-based ITWS and TSW operating conditions using the experimental results. This comparison is made up of the relative H₂ production per mass of material and solar energy inputs required for each step of the ITWS and TSW reactions reported in kJ/mol H₂ produced in a cycle.

Reduction/Oxidation temperature (°C)		1,350/1,350°C ITWS	1,350/1,000°C TSW	1,500/1,200°C TSW
Oxidation Time (min)		12	24	21
Relative H ₂ generation*		1.0	0.27	0.79
Solid material heat recuperation efficiency	Reaction step	Solar heat input		
	ΔH_{red} (kJ/mol H ₂)	286.4	286.4	287.8
	$Q_{rad,R}$ (kJ/mol H ₂)	101.8	101.8	171.5
	$Q_{rad,O}$ (kJ/mol H ₂)	20.4	15.4	28.6
	Q_{solids} (kJ/mol H ₂)	0.0	665.8	191.2
	Q_{tot} (kJ/mol H ₂)	408.6	1,069.5	678.9
$\epsilon_s = 0.95$	ΔH_{red} (kJ/mol H ₂)	286.4	286.4	287.8
	$Q_{rad,R}$ (kJ/mol H ₂)	101.8	101.8	171.5
	$Q_{rad,O}$ (kJ/mol H ₂)	20.4	15.4	28.6
	Q_{solids} (kJ/mol H ₂)	0.0	1,331.7	382.5
	Q_{tot} (kJ/mol H ₂)	408.6	1,735.3	870.2
	$\epsilon_s = 0.90$	ΔH_{red} (kJ/mol H ₂)	286.4	286.4
$Q_{rad,R}$ (kJ/mol H ₂)		101.8	101.8	171.5
$Q_{rad,O}$ (kJ/mol H ₂)		20.4	15.4	28.6
Q_{solids} (kJ/mol H ₂)		0.0	1,331.7	382.5
Q_{tot} (kJ/mol H ₂)		408.6	1,735.3	870.2

*Relative H₂ generation is based upon the total H₂ that can be produced by the same amount of material in an eight-hour day in the same reactor.

CONCLUSIONS AND FUTURE DIRECTIONS

- The hercynite cycle active materials can be operated under isothermal conditions, reducing irreversible heat losses and thermal shock concerns that limit efficiency and operations of traditional temperature-swing water splitting cycles.
- The hercynite cycle active materials can be improved to be greater than 47% active, thus increasing H₂ production, and work is underway to develop such materials.

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