

II.F.4 Solar-Thermal ALD Ferrite-Based Water Splitting Cycle

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A recent report on H₂A cost analyses for solar-driven thermochemical conversion [1] included an analysis of the developed ferrite cycle. The key figures of merit used for this study are summarized in Table 1. The projected thermal efficiency for the developed process is 55.5% LHV, thus exceeding the >35% figure of merit for the 2025 case. For a solar-to-receiver annual average efficiency of 40.2%, the overall solar to H₂ efficiency is estimated at 22.3% (LHV). Furthermore, the \$6/kg H₂ plant gate cost for the central 100,000 kg H₂/day facility 2015 case should be easily achieved for the \$126.50/m² installed heliostat cost. The \$3/kg H₂ plant gate cost for 2025 for a \$90/m² installed heliostat field may be achievable.

TABLE 1. Key Figures of Merit Used for Cost Analyses for 2015 and 2025 for Solar-Driven High-Temperature Thermochemical Hydrogen Production [1]

Characteristics	Units	2015	2025
Plant Gate H ₂ Cost Projections	\$/kg H ₂	\$6	\$3
Installed Heliostat Capital Cost	\$/m ²	\$126.50	\$90
Process Energy Efficiency (thermal)	%	30	> 35

Fiscal Year (FY) 2011 Objectives

- Finalize the ferrite process flow diagram and H₂A economic analysis.
- Determine the most cost effect design and construction materials for the FY 2010 conceptualized scalable central solar reactor/receiver per H₂A guidance on economics.
- Demonstrate suitable materials for robust redox/thermochemical cycling.

Technical Barriers

This project addresses the following technical barriers from page 3.1-26 of the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

The technical targets are the cost of hydrogen and the process energy efficiency.

- For 2017, these are \$3.00 per gasoline gallon equivalent (gge) H₂ and >35% (lower heating value, LHV), respectively.

FY 2011 Accomplishments

- Previously demonstrated that <5 nm thin ferrite films can be synthesized by atomic layer deposition (ALD) and provide for significant opportunities to reduce diffusional resistances and promote radiation-driven heat transfer; both potentially providing for rapid redox cycling. Since this material is not currently commercially available, determine the most reasonable market value (i.e. suggested retail price per kilogram of material) in order to finalize the H₂A process economic analysis.
- Improved the design and materials of construction of a multi-tube absorbing fixed-bed cavity reactor/receiver that provides for efficient internal heat recuperation and the potential for rapid cycling; mitigates erosion and complications associated with transporting solids.
- Finalized the process design/H₂A economic evaluation indicating that ALD of ferrite materials on 100 m²/g supports cycling every 5 to 1 minutes will have H₂A projected costs of less than \$6/kg and \$3/kg in 2015 and 2025, respectively [1].
- Cycling studies in a thermogravimetric analyzer as well as on-sun cycling studies are currently in progress to demonstrate the thin film's robustness and lack of deactivation over time.



Introduction

The direct thermolysis to split water by reaction 1 requires materials operating at $T > 3,500^\circ\text{C}$ as well as methods to separate the H_2 and O_2 gases at high temperature [2]. This seemingly impossible task can be overcome by implementing a two-step thermochemical water splitting cycle in which a ferrite spinel material (MFe_2O_4 ; $\text{M}=\text{Co}, \text{Ni}$) can be thermally reduced using concentrated sunlight to release O_2 as shown in reaction 2. The reduced ferrite is then subsequently oxidized (reaction 3) with steam producing H_2 [3-5] recovering the original spinel structure in the process. Reactions 2 and 3 combine to form a complete redox cycle with reactants and products equal to reaction 1.

1. $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
2. $\text{MFe}_2\text{O}_4 \rightarrow \text{MeO} (\text{Fe}^{2+} + \text{Fe}^{3+} + \text{M}^{2+}) + \frac{1}{2} \text{O}_2$
3. $\text{MeO} (\text{Fe}^{2+} + \text{Fe}^{3+} + \text{M}^{2+}) + \text{H}_2\text{O} \rightarrow \text{MFe}_2\text{O}_4 + \text{H}_2$

The reduction step of this cycle occurs at $1,450^\circ\text{C}$ while the oxidation step occurs at $1,000^\circ\text{C}$; with significantly lower operating temperatures this cycle is much more efficient and desirable than direct thermolysis.

Approach

The primary scientific barrier to successful implementation of a solar-thermal water splitting process

is access to a robust active material for efficiently and rapidly carrying out redox cycles producing H_2 . Further, the key engineering barrier to successful implementation is demonstration of a large scale solar reactor concept that allows for rapid redox cycling taking advantage of highly active thin film materials while providing for highly efficient usage of delivered solar energy. The key scientific challenges to successfully overcoming the primary scientific barrier are:

- Identify/synthesize high surface area active materials with favorable transport properties.
- Identify/demonstrate suitable interfacial substrate materials to facilitate rapid redox cycling.
- Combine the active/substrate materials into a characteristic volume sample and demonstrate robust cycling to split water, particularly if able to operate the reduction in air.

High surface area active ferrite materials ($\text{M}_x\text{Fe}_{3-x}\text{O}_4$; $\text{M}=\text{Co}, \text{Ni}$) were synthesized using ALD to deposit nanometer thick films onto nanosized particles [6-9]. Nanoparticle substrates were placed in fluidized bed reactors and coated (Figure 1) with Fe_2O_3 , CoO , and NiO thin films using self-limiting surface chemistry via metallocene $[(\text{C}_5\text{H}_5)_2\text{M}; \text{M}=\text{Fe}, \text{Co}, \text{Ni}]$ and O_2 precursors. The approach recommended is to design the nanometer thick ferrite films and to deposit them on high surface area support materials.

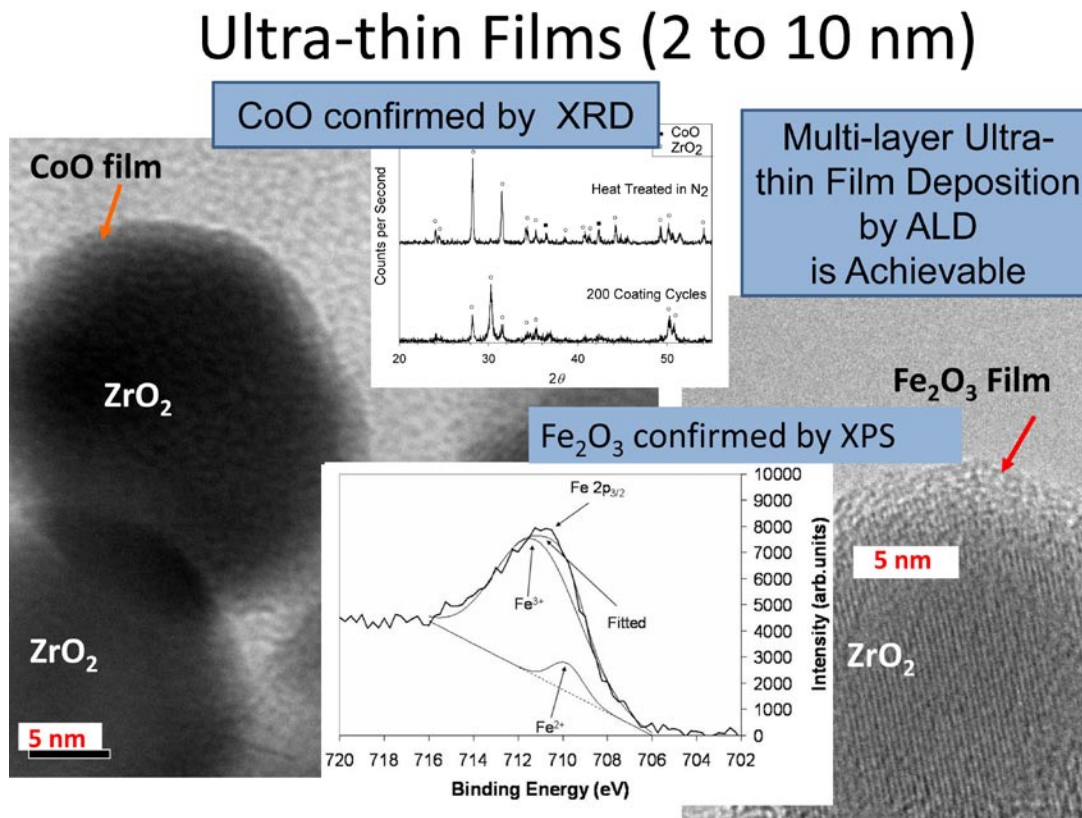


FIGURE 1. Thin Film Deposition of Ferrite Materials

Results

For this study, a 5-nm thick nickel ferrite film coated onto a 100 m²/g high surface area ZrO₂ support was considered; resulting in 0.67 moles ZrO₂ for every mole of NiFe₂O₄. Using the FACTSage™ thermodynamic database, it was determined that the amount of solar heat input required for this process is minimized when the solar reduction reaction occurs at 1,450°C and the oxidation reaction occurs at 1,000°C.

The conceptualized thermochemical redox receiver/solar reactor is shown in Figure 2. The reactor consists of a cavity-receiver, i.e. a well-insulated enclosure with a small opening – the aperture – for the access of concentrated solar radiation. The receiver will contain an even number of closed-end SiC tubes. Each tube will contain a 2nd open end SiC tube with a porous SiC plug at the base. Active high surface area and porous nickel ferrite material will be packed in the annular region between the two tubes allowing for efficient heat and mass transfer and, consequently, fast overall kinetics. The inner tube will be packed with media providing surface area for improved heat transfer to drive the vaporization of water to steam. At a given instant, half of the tubes will be operated in the reduction mode at T_R while the remaining half will be operated in the oxidation mode at T_O. When the reactions reach completion, the operational modes will be switched.

The process flow diagram is shown in Figure 3; 32°C water is pumped into the reduction tubes of the solar reactor at 12 psig. The water pumps are centrifugal cast iron and require a total of 135 kWhr/day electricity. The reduction tubes operate at a reduced pressure of 380 torr reached via vacuum pumps. The vacuum pumps remove oxygen being produced to prevent recombination with reduced ferrites. The flowrate of oxygen through each of three single-stage large cast iron pumps is 52,160 ft³/min requiring a total

of 55,310 kWhr/yr electricity. The oxidation tubes of the solar reactor operate near atmospheric pressure producing hydrogen that must be compressed to 300 psig before entering the plant gate. The three stage compression system with intercoolers has a compression factor of 2.85 and the intercoolers have a 2 psig pressure drop. This system requires a total of 52,848 kWhr/yr electricity and is designed for four compressors with only three operating at any time. Six 223 meter tall towers are required to produce 100,000 kg H₂/day. With one solar reactor per tower the total solar input is 2,332 GWhr/yr. Each receiver has three heliostat fields with 65 acres of land per field and 2.09E6 m² of heliostats. The heliostat field requires 1.22 GWhr/yr of parasitic electricity. This field and process design results in a thermal efficiency of 55.5% and a solar to thermal efficiency of 22.3%.

An H2A analysis was completed using varying redox cycle times of 1, 5, and 15 minutes [1]. Reducing cycle times reduces the amount of ferrite required to produce 100,000 kg H₂/day, which also reduces the number of SiC reaction tubes required thus decreasing the size and cost of each solar reactor. Ferrites can be produced for the cost of materials plus a reasonable retail markup. The cost of NiFe₂O₄ precursors are approximately \$225/kg of ferrite produced. Three retail markups were considered in this study: 20, 35, and 50%. The capital cost breakdown can be seen in Figure 4 and the resulting H₂ selling prices in Figure 5. With projected costs of \$6/kg in 2015 and \$3/kg in 2025, Figure 5 shows that with 10 minute cycles or less in 2015 the projection is achievable. However, in 2025 the projection is only achievable with cycles times of 1 minute or less. To date we have achieved cycles less than 15 minutes experimentally. With process improvements to not only the ferrite materials, but also the reactor and solar field 1 minute cycles can be reached by 2025. Lastly, Figure 5 shows that the resulting H₂ selling price is not sensitive to the purchase price of nickel ferrites.

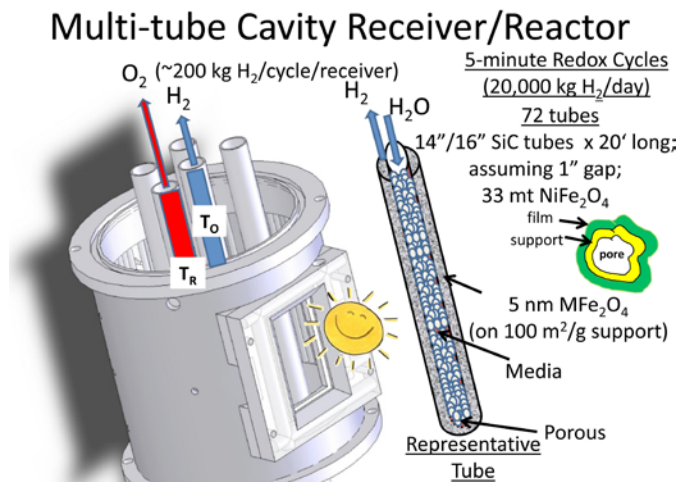


FIGURE 2. Schematic of Solar Reactor/Receiver

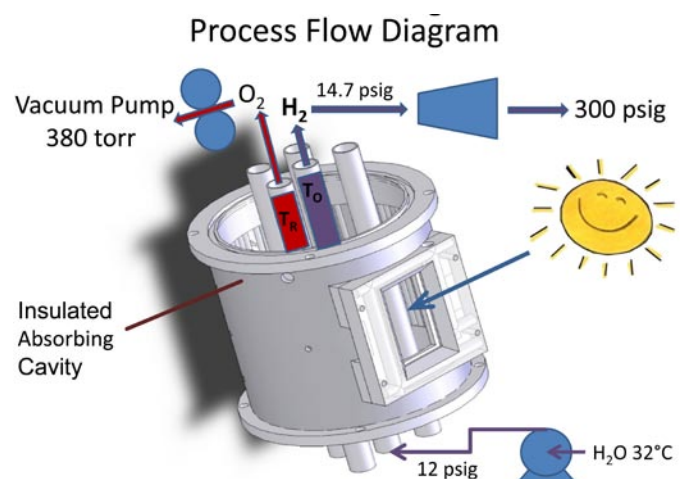


FIGURE 3. Process Flow Diagram

Capital Cost Breakdown

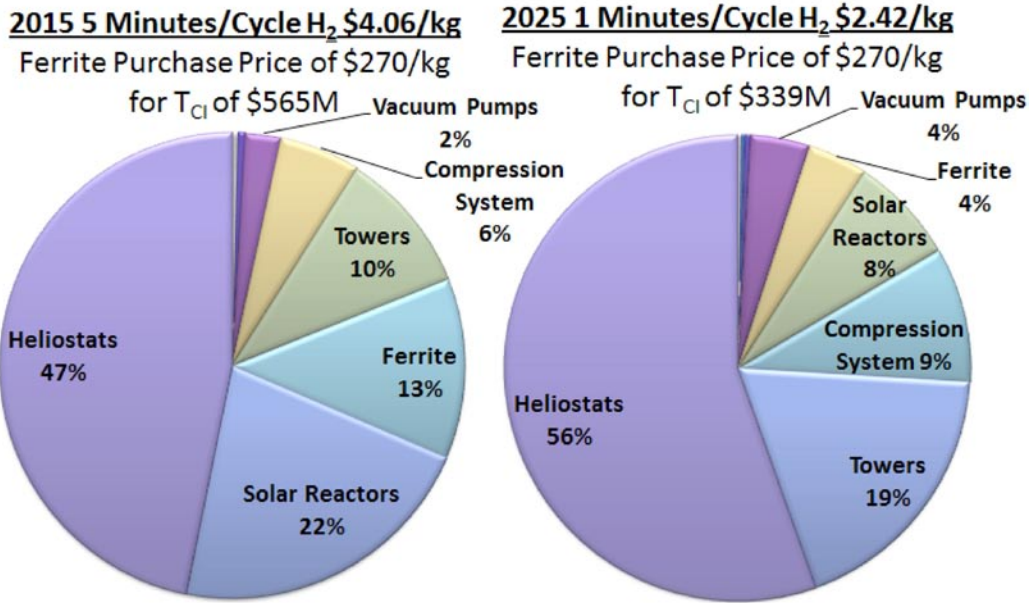


FIGURE 4. Capital Cost Breakdown

H₂ Selling Price for 20, 35, & 50% Ferrite Purchase Price Markup

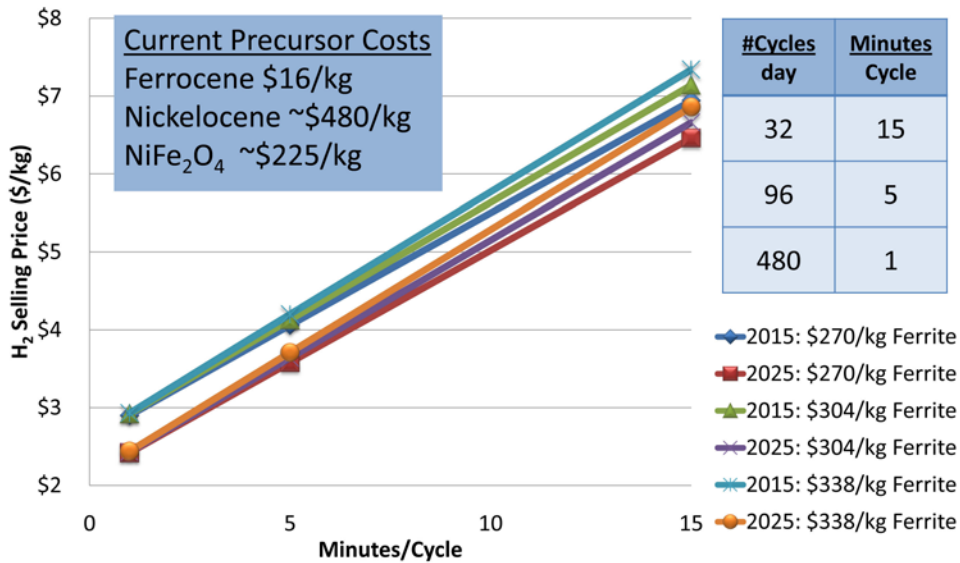


FIGURE 5. H2A Results of H₂ Selling Prices

Conclusions and Future Directions

- ALD materials remain active for up to 30 water spitting cycles with no sign of deactivation after initial aggregation.
- ALD thin films are ~100X more active than conventionally produced bulk ferrites; the challenge is holding them together.
- Ferrite process is anticipated to meet H2A cost projections of less than 6/kg and \$3/kg for 2015 and 2025, respectively, if performance metrics are met [1].
- Future work will focus exclusively on the “hercynite” cycle which has been shown to be more stable than conventional ferrites and to operate over a lower temperature range (upper temperature limit ~1,300°C).

Special Recognitions & Awards

1. 2010 AIChE Excellence in Process Development Research Award.
2. 2010 Dean’s Award for Outstanding Research (College of Engineering and Applied Science).

FY 2011 Peer-Reviewed Publications

1. Kreider, P.B., H.H. Funke, K. Cuche, M. Schmidt, A. Steinfeld and A.W. Weimer, “Manganese Oxide Based Thermochemical Hydrogen Production Cycle,” *International Journal of Hydrogen Energy*, **36**, 7028-7037 (2011).
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6. Francis, T.M., P.R. Lichty, and A.W. Weimer, “Manganese Oxide Dissociation Kinetics for the Mn₂O₃ Thermochemical Water-splitting Cycle. Part II: CFD Model,” *Chemical Engineering Science*, **65**, 4397-4410 (2010).

7. Francis, T.M., P.B. Kreider, P.R. Lichty, and A.W. Weimer, “An Investigation of a Fluidized Bed Solid Feeder for an Aerosol Flow Reactor,” *Powder Technology*, **199**, 70-76 (2010).

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4. Kodama, T., Y. Kondoh, R. Yamamoto, H. Andou, and N. Satou, “Thermochemical hydrogen production by a redox system of ZrO₂-supported Co(II)-ferrite,” *Solar Energy* Vol. 78, No. 5, 2005, pp. 623-631.
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6. Ferguson, J.D., A.W. Weimer, and S.M. George, “Atomic layer deposition of ultrathin and conformal Al₂O₃ films on BN particles,” *Thin Solid Films* Vol. 371, No. 1-2, 2000, pp. 95-104.
7. George, S.M., “Atomic Layer Deposition: An Overview,” *Chemical Reviews* Vol. 110, No. 1, 2010, pp. 111-131.
8. Hakim, L.F., J.H. Blackson, and A.W. Weimer, “Modification of interparticle forces for nanoparticles using atomic layer deposition,” *Chemical Engineering Science* Vol. 62, No. 22, 2007, pp. 6199-6211.
9. King, D.M., J.A. Spencer, X. Liang, L.F. Hakim, and A.W. Weimer, “Atomic layer deposition on particles using a fluidized bed reactor with in situ mass spectrometry,” *Surface & Coatings Technology* Vol. 201, No. 22-23, 2007, pp. 9163-9171.