

## II.F.3 Solar-Thermal Atomic Layer Deposition Ferrite-Based Water Splitting Cycles

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Contract Number: DE-FC36-05GO15044

Project Start Date: March 31, 2005  
Project End Date: September 30, 2010

### Objectives

- Use H2A analysis to provide guidance for conceptual process design that is cost-effective.
- Conceptualize a scalable central solar reactor/receiver per H2A guidance on economics.
- Develop/demonstrate suitable materials for robust redox/thermochemical cycling.
- Develop an overall plan to take the technology to the point of demonstration in five years.

### Technical Barriers

This project addresses the following technical barriers from the 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 for solar-driven thermochemical conversion are summarized in Table 1. The projected thermal efficiency for the developed process is 54.6% based on lower heating value (LHV), thus exceeding the >35% requirement for the 2025 case. For a solar-to-receiver annual average efficiency of 40.2%, the overall solar-to-H<sub>2</sub> efficiency is estimated at 21.9% (LHV). Furthermore, the \$6/kg H<sub>2</sub> plant gate cost for the Central 100,000 kg H<sub>2</sub>/day facility 2015 case should be easily achieved for the \$126.50/m<sup>2</sup> installed heliostat cost. The \$3/kg H<sub>2</sub> plant gate cost for 2025 for a \$90/m<sup>2</sup> installed heliostat field may be achievable (details below).

**TABLE 1.** Progress towards Meeting Technical Targets for Solar-Driven High-Temperature Thermochemical Hydrogen Production

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

gge – gasoline gallon equivalent

### Accomplishments

- Discovered that a ferrite/alumina-based materials system provides for a hercynite intermediate that can be thermally reduced between 1,200 and 1,450°C without high temperature sintering/deactivation issues.
- 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.
- Designed 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.
- Carried out process design/economic evaluation indicating that ALD of ferrite materials on 100 m<sup>2</sup>/g supports cycling every 5 minutes will meet the DOE cost targets in 2015 and most likely in 2025 as well.

- Developed a 5-year plan to develop materials, build a prototype device for testing and design a demonstration facility.



## Introduction

The direct thermolysis to split water ( $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$ ) requires materials operating at  $T > 3,500^\circ\text{C}$  and methods to separate the  $\text{H}_2$  and  $\text{O}_2$  gases at high temperature [1]. This seemingly impossible task can be overcome by implementing a two-step thermochemical water splitting cycle in which a ferrite spinel material ( $\text{MFe}_2\text{O}_4$ ;  $\text{M}=\text{Co}, \text{Ni}$ ) can be thermally reduced using concentrated sunlight to release  $\text{O}_2$  and the reduced ferrite then subsequently oxidized (redox cycle) with steam producing  $\text{H}_2$  [2-4], recovering the original spinel structure in the process. It has recently been demonstrated at the University of Colorado that thin film cobalt ferrites can be deposited by ALD onto high surface area alumina ( $\text{Al}_2\text{O}_3$ ) supports and that a redox cycle through a hercynite ( $\text{FeAl}_2\text{O}_4$ ) pathway (Reduction:  $\text{MFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 + \text{solar energy} \rightarrow \text{MAl}_2\text{O}_4 + 2\text{FeAl}_2\text{O}_4 + 0.5 \text{O}_2$ ; Oxidation:  $\text{MAl}_2\text{O}_4 + 2\text{FeAl}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{MFe}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 + \text{H}_2$ ) can be cycled repeatedly and at lower temperatures than the conventional ferrite materials [5].

## 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  $\text{H}_2$ . 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:

- (1) Identify/synthesize high surface area active materials with favorable transport properties.
- (2) Identify/demonstrate suitable interfacial substrate materials to facilitate rapid redox cycling.
- (3) 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  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ , and  $\text{NiO}$  thin films using self-limiting surface chemistry

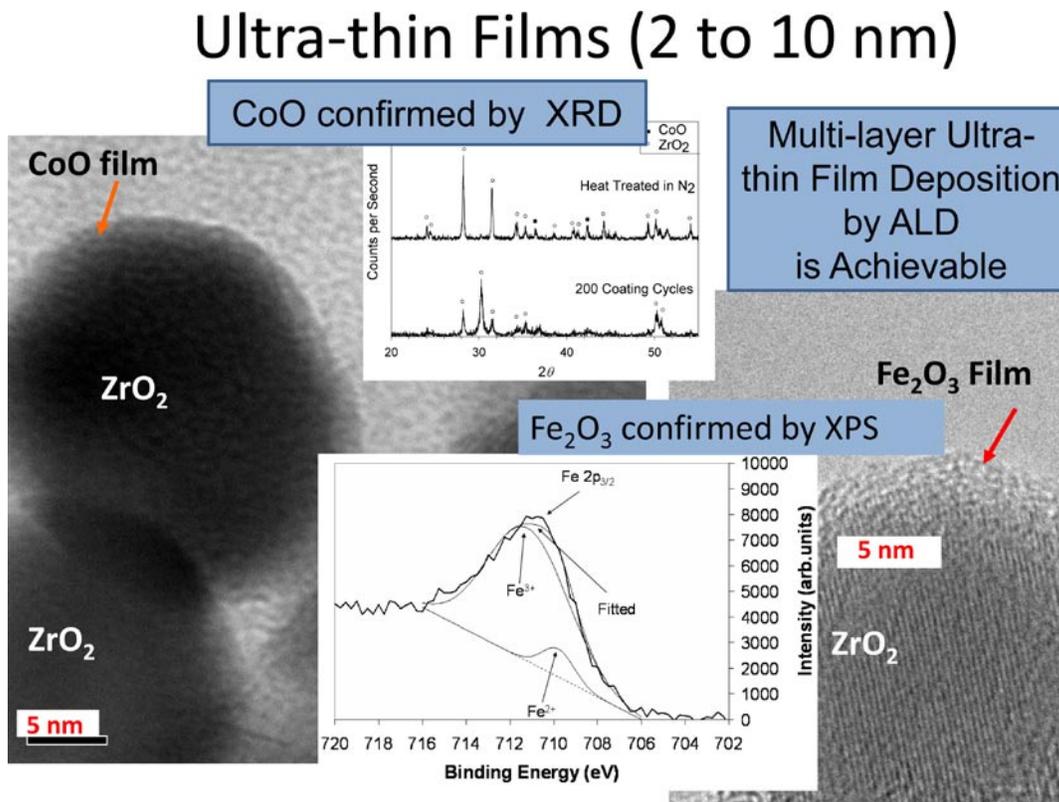


FIGURE 1. Thin Film Deposition of Ferrite Materials

via metallocene  $[(C_5H_5)_2M; M = Fe, Co, Ni]$  and  $O_2$  precursors. The approach recommended is to design the nm thick ferrite films and to deposit them on high surface area ( $100 \text{ m}^2/\text{g}$ ) support materials.

## Results

Unlike the conventional cobalt ferrite process that requires  $T > 1,200^\circ\text{C}$  to release  $O_2$  and is then plagued by a deactivating liquid solution “slag” phase at  $\sim 1,525^\circ\text{C}$ , the “spinel/hercynite” cycle requires reduction temperatures of only  $T > 900^\circ\text{C}$  and does not have a “slag” phase present for  $T < 1,600^\circ\text{C}$ . Furthermore, nano-thick  $MFe_2O_4$  films deposited by ALD mitigate both the typical M/steam diffusional resistances and the slow conduction heat transfer that plague bulk ferrite materials. Instead, the ALD thin films provide for an opportunity to drive the redox cycle quickly using fast solar radiation heat transfer and fast mass transfer. As shown in Figure 2, the thin film “spinel/hercynite” cycle can produce significant quantities of  $H_2$  for reduction temperatures as low as  $1,200^\circ\text{C}$ , while the conventional ferrite cycle requires a reduction temperature of at least  $1,450^\circ\text{C}$  (within  $75^\circ\text{C}$  of the “slag” liquid solution phase) in order to produce sufficient  $H_2$ . Likewise, oxidation can be carried out for  $T > 1,200^\circ\text{C}$ , providing an opportunity to drive a thermochemical cycle in which redox  $\Delta T < 300^\circ\text{C}$ ,

thus, simplifying the recuperation of heat during redox steps. These phenomena are predicted by free energy minimization thermodynamics calculations as well [5].

A conceptualized prototype thermochemical redox receiver/reactor is shown in Figure 3. 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. Because of multiple inner reflections, the cavity-receiver is able to capture efficiently incoming concentrated solar energy. To some extent, the aperture size may be reduced with the help of non-imaging secondary concentrators, e.g. compound parabolic concentrators, placed at the receiver’s aperture in tandem with the primary concentrating system.

The cavity-receiver will contain an even number of closed-end SiC tubes. Each tube will contain a second open end SiC tube with a porous SiC plug at the base. Active high surface area and porous ferrite material,  $M_xFe_{3-x}O_4$ , in the form of catalyst honeycomb support, foams, reticulate material, etc. for the redox reactions will be packed in the annular region between the two tubes to allow for efficient heat and mass transfer and, consequently, fast overall kinetics. The active material will be deposited on a high surface area supporting alumina ( $Al_2O_3$ ) substrate material in which the substrate takes part in the redox reaction (e.g.  $FeAl_2O_4$ , hercynite).

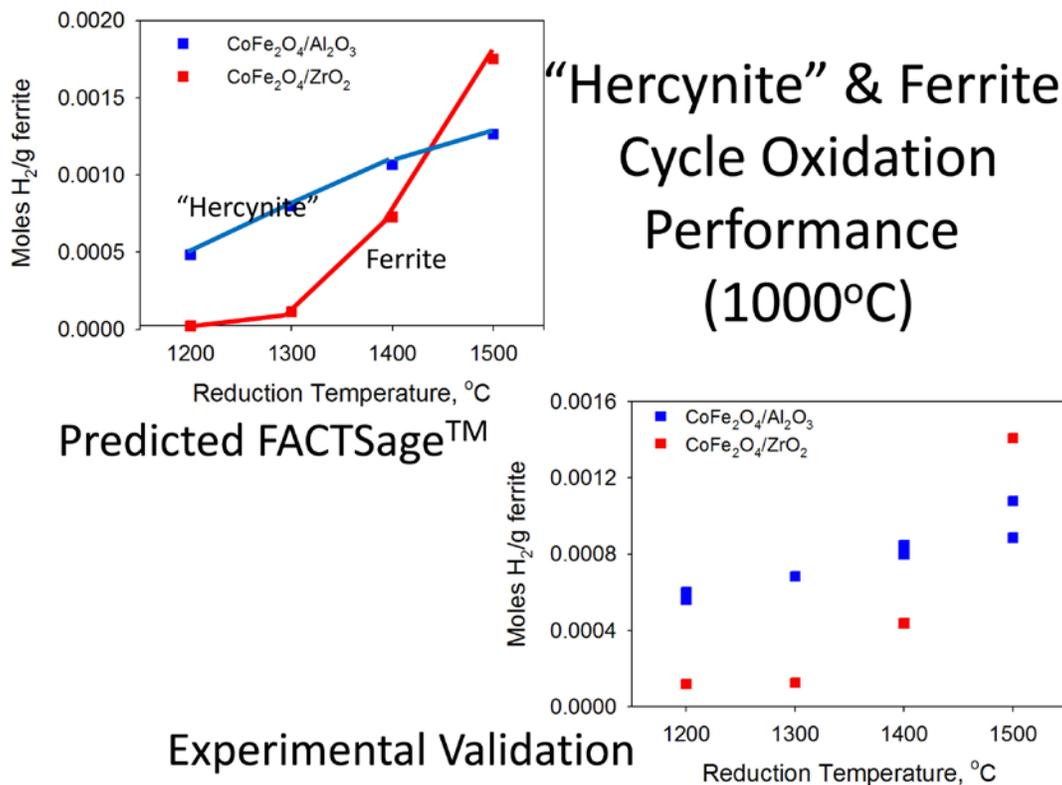


FIGURE 2. “Hercynite” Cycle Compared to Standard Ferrite Cycle Performance – Theory and Experiment

### Multi-tube Cavity Receiver/Reactor

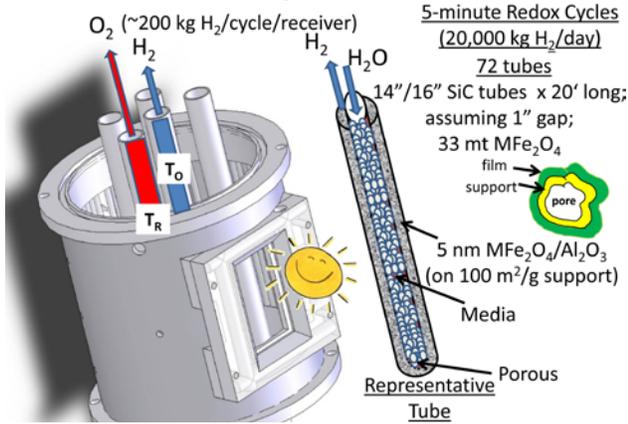


FIGURE 3. Schematic of Solar Reactor/Receiver

The inner tube will be packed with media providing surface area for improved heat transfer to drive the vaporization of water to steam.

The redox cycle will be effected at temperatures  $T_R$  for the reduction step and  $T_O$  for the oxidation step ( $T_R > T_O$ ). 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 temperatures  $T_R$  and  $T_O$  will be controlled by the endothermicity of the reaction during

the reduction step and by the flow of H<sub>2</sub>O during the oxidation step, respectively. Arrangement of the tubes inside of the cavity-receiver is a key aspect and will be such that they are arranged symmetrically in such a manner as to achieve the desired temperatures ( $T_R$  or  $T_O$ ) under thermal equilibrium. Concentrated solar radiation entering the cavity-receiver and radiation emitted by the hot tubes undergoes absorption and multiple reflections. The net thermal energy absorbed by the tubes is transferred to the reaction site by combined conduction, convection, and radiation heat transfer. *With such an arrangement, the sensible heat of the solids components during the switching of modes is transferred among tubes and kept inside the cavity, achieving high internal recuperation of heat.* The sensible heat of the hot gaseous streams exiting the cavity-receiver will be recovered via heat exchangers and used to generate steam and preheat the cold gaseous streams to the operating temperatures.

Process/heliostat field design considerations coupled with H2A analysis indicated that 100,000 kg H<sub>2</sub>/yr can be produced using five towers (250 m tall each) on a total of 237 acres of land. Each receiver provides for 250 MW<sub>thermal</sub> power. A net solar concentration of 4,000 suns is delivered to the receiver with a 40.2% annual average efficiency. This combined with the 54.6% LHV thermal efficiency provides for an overall solar-to-H<sub>2</sub> efficiency of 21.9%. A total of 2,376 GWhr annually drives the process. In order to achieve the 2015 H2A cost target of \$6/kg H<sub>2</sub>, ferrite must be produced for <\$2,600/kg (Figure 4).

## Capital Cost Breakdown

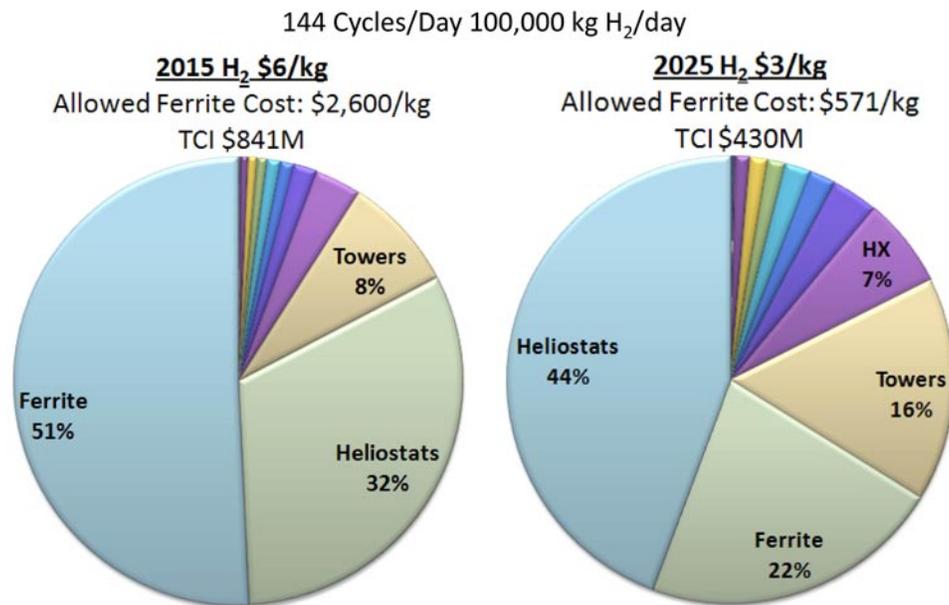


FIGURE 4. H2A Cost Analysis Results

To achieve the 2025 cost target of \$3/kg H<sub>2</sub>, ferrite must be produced for <\$571/kg. Since the current cost of ALD precursors is \$240/kg ferrite, cost targets appear reasonable, although 2025 is somewhat of a stretch. This design calls for redox cycling averaging 144 cycles/day.

### Conclusions and Future Directions

- ALD films are advantageous in terms of fast redox cycling.
- The “hercynite” cycle operates in the solar thermal sweet spot of 1,200 to 1,450°C where fast radiation heat transfer dominates, but where containment materials issues are mitigated; forgiving chemistry with no sintering/deactivating liquid solution phase.
- Future work should demonstrate redox cycling over thousands of cycles in order to validate materials robustness.

### FY 2010 Publications

1. Scheffe, J.R., J. Li, and A.W. Weimer, “A Spinel Ferrite/Hercynite Water-Splitting Redox Cycle,” *International Journal of Hydrogen Energy*, **35**, 3333-3340 (2010).
2. Martinek, J, M. Channel, A. Lewandowski and A.W. Weimer, “Considerations for the Design of Solar-thermal Chemical Processes,” *Journal of Solar Energy Engineering*, **132**, 031013 (2010).
3. Steinfeld, A. and A.W. Weimer, “Thermochemical Production of Fuels with Concentrated Solar Energy,” *Optics Express*, **18** (9), A100-A111 (2010).
4. Francis, T.M., P.R. Lichty, and A.W. Weimer, “Manganese Oxide Dissociation Kinetics for the Mn<sub>2</sub>O<sub>3</sub> Thermochemical Water-splitting Cycle. Part I: Experimental,” *Chemical Engineering Science*, **65**, 3709-3717 (2010).
5. Francis, T.M., P.R. Lichty, and A.W. Weimer, “Manganese Oxide Dissociation Kinetics for the Mn<sub>2</sub>O<sub>3</sub> Thermochemical Water-splitting Cycle. Part II: CFD Model,” *Chemical Engineering Science*, **65**, 4397-4410 (2010).
6. 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).

### References

1. Perkins, C., and A.W. Weimer, “Solar-Thermal Production of Renewable Hydrogen,” *AIChE Journal* Vol. 55, No. 2, 2009, pp. 286-293.
2. Kodama, T., N. Gokon, and R. Yamamoto, “Thermochemical two-step water splitting by ZrO<sub>2</sub>-supported Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> for solar hydrogen production,” *Solar Energy* Vol. 82, No. 1, 2008, pp. 73-79.
3. Kodama, T., Y. Kondoh, R. Yamamoto, H. Andou, and N. Satou, “Thermochemical hydrogen production by a redox system of ZrO<sub>2</sub>-supported Co(II)-ferrite,” *Solar Energy* Vol. 78, No. 5, 2005, pp. 623-631.
4. Kodama, T., Y. Nakamuro, and T. Mizuno, “A two-step thermochemical water splitting by iron-oxide on stabilized zirconia,” *Journal of Solar Energy Engineering-Transactions of the ASME* Vol. 128, No. 1, 2006, pp. 3-7.
5. Scheffe, J.R., J. Li, and A.W. Weimer, “A spinel ferrite/hercynite water-splitting redox cycle,” *International Journal of Hydrogen Energy* Vol. 35, 2010, pp. 3333-3340.
6. Ferguson, J.D., A.W. Weimer, and S.M. George, “Atomic layer deposition of ultrathin and conformal Al<sub>2</sub>O<sub>3</sub> 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.