

## II.F.3 Solar-Thermal Hydrogen Production Using a Metal-Oxide Based Thermochemical Water Splitting Cycle

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### Objectives

- Research and develop a cost-effective  $Mn_2O_3/MnO$  and ferrite-based ( $M_xFe_yO_4$ ) solar-thermal thermochemical cycle through theoretical and experimental investigations.
- Develop a process flow diagram and carry out an economic analysis of the best process option.

### Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure 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

Solar-Driven High-Temperature Thermochemical Hydrogen Production:

This project is conducting fundamental studies of metal oxide-based thermochemical cycles. Insights gained from these studies will be applied toward solar-driven high-temperature hydrogen production that meets the following DOE cost targets:

- 2012: \$6/gge  $H_2$
- 2017: \$3/gge  $H_2$

### Accomplishments

- Fabricated a high surface area  $CoFe_2O_4$  metal ferrite spinel using atomic layer deposition (ALD).
- Demonstrated water splitting capability with multiple cycles.



### Introduction

The most benign and renewable method for obtaining hydrogen is by using sunlight to split water. Splitting water directly with solar-thermal energy is not practical since the temperature required in order to obtain high conversion is above 4,000 K. Another huge challenge is the requirement to separate gaseous hydrogen from oxygen at these temperatures. Multi-step thermochemical cycles which split water through a series of two or more chemical reactions provide an opportunity for carrying out the high step in the process at more modest temperatures of less than 2,000 K. In addition, they remove oxygen and hydrogen in separate steps, thus avoiding the recombination issues. The  $Mn_2O_3/MnO$  and ferrite cycles allow lower operating temperatures than other thermochemical cycles and are of particular interest.

### Approach

An alternative ferrite cycle in which the ferrite ( $CoFe_2O_4$ ) is deposited on a porous  $Al_2O_3$  support (30  $m^2/g$ ) via ALD has been developed. Rather than a traditional cycle, in which the ferrite is deposited on an inert support or is unsupported, the ferrite reacts with  $Al_2O_3$  during thermal reduction to form hercynite ( $FeAl_2O_4$ ). This is advantageous because the reaction between the ferrite and  $Al_2O_3$  is favored at lower temperatures than the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  on an inert support. Subsequent water oxidation is then achievable at 1,000°C, similar to other ferrite cycles [1,2]. This redox cycle is shown in the two step reaction:



## Results

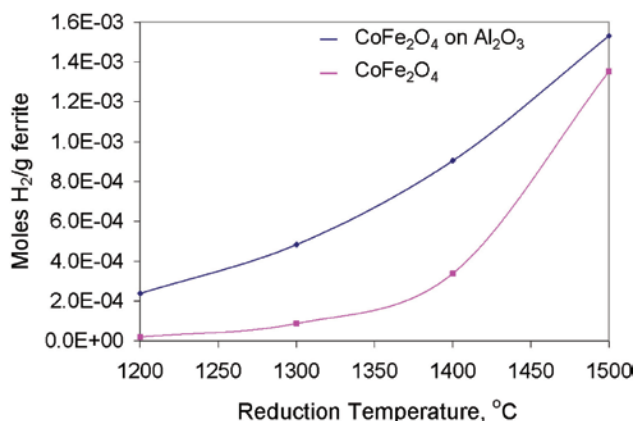
### Thermodynamic Analysis

Thermodynamic modeling was performed using the thermodynamic software package FactSage. Recent advances by Allendorf et. al. have contributed to a greater understanding of ferrite thermodynamics, and the methods used in their paper were utilized in our analysis [3]. Thermodynamically, reduction of a ferrite on an  $\text{Al}_2\text{O}_3$  support is favored at lower temperatures than on an inert support. Reduction is predicted to reach a maximum at 1,300°C for cobalt ferrite on alumina, whereas is expected to reach completion at 1,500°C for unsupported cobalt ferrite. Additionally, iron (II,III) oxide on alumina is reduced at 1,450°C but unsupported iron (II,III) oxide is not reduced fully at temperatures even greater than 1,600°C.

The subsequent hydrolysis reaction at 1,000°C for alumina supported cobalt ferrite is expected to produce more  $\text{H}_2$  per gram of unsupported ferrite at lower reduction temperatures, as shown in Figure 1. Unsupported cobalt ferrite does not produce a significant quantity of  $\text{H}_2$  until about 1,400°C, and begins to increase rapidly afterwards. However, supported cobalt ferrite produces nearly as much  $\text{H}_2$  at 1,200°C as unsupported cobalt ferrite at 1,400°C. Nearly three times as much  $\text{H}_2$  is expected to be evolved for alumina supported ferrite at a reduction temperature of 1,200°C.

### Experimental Results

$\text{CoFe}_2\text{O}_4$  on  $\text{Al}_2\text{O}_3$  (60% by mass, 30  $\text{m}^2/\text{g}$ ) was reduced at temperatures between 1,200°C and 1,500°C in



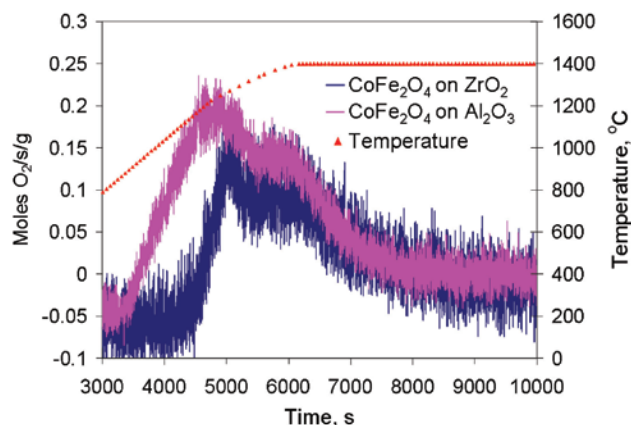
**FIGURE 1.**  $\text{H}_2$  Evolution Profiles as a Function of Temperature for  $\text{CoFe}_2\text{O}_4$  on  $\text{Al}_2\text{O}_3$  and  $\text{CoFe}_2\text{O}_4$

a high temperature horizontal furnace. A powder X-ray diffractometer (XRD,  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5406\text{\AA}$ ) was then used to measure the crystallinity changes of the sample. Only peaks representative of  $\text{Al}_2\text{O}_3$  are present for uncoated alumina substrates. However, once coated with  $\text{CoFe}_2\text{O}_4$ , the alumina peaks are reduced and mostly only peaks due to  $\text{CoFe}_2\text{O}_4$  are present. Only alumina's strongest peak, at 26.65 degrees, is apparent. At 1,200°C, peaks representative of  $\text{FeAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  are present, and as the temperature is increased peaks due to  $\text{FeAl}_2\text{O}_4$  become more pronounced and alumina peaks are diminished. This is likely due to the fact that the sample is reduced further at higher temperatures, resulting in an increased concentration of  $\text{FeAl}_2\text{O}_4$ .

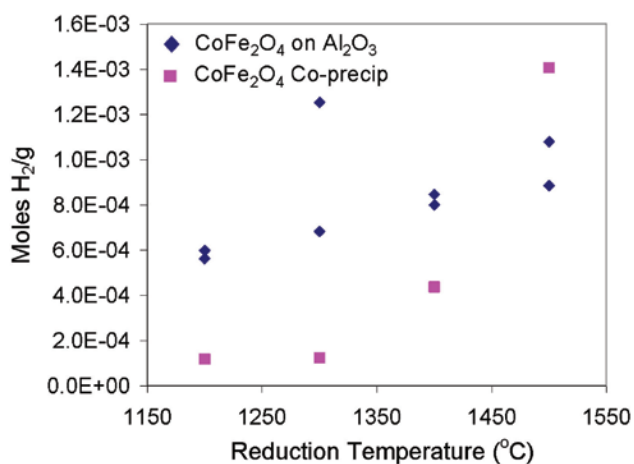
A comparison between  $\text{O}_2$  evolution during the reduction of  $\text{CoFe}_2\text{O}_4$  on  $\text{Al}_2\text{O}_3$  (60% by mass) and on  $\text{ZrO}_2$  (33% by mass) is shown in Figure 2. Oxygen begins to evolve slightly after the temperature reaches 800°C for  $\text{CoFe}_2\text{O}_4$  on alumina, which agrees well with thermodynamic modeling discussed above. By 1,200°C, the reaction rate has reached a maximum, and  $\text{O}_2$  subsequently decreases. This is in contrast to  $\text{CoFe}_2\text{O}_4$  on zirconia, in which the oxygen begins to evolve once the temperature reaches 1,150°C.

Samples reduced at temperatures between 1,200°C and 1,500°C were oxidized at 1,000°C, and results are shown in Figure 3. The coprecipitated sample does not show any appreciable  $\text{H}_2$  evolution until the reduction temperature reaches 1,400°C, which agrees well with thermodynamic calculations discussed above. However, at 1,200°C for  $\text{CoFe}_2\text{O}_4$  on  $\text{Al}_2\text{O}_3$ , there is a substantial amount of  $\text{H}_2$  evolved, and it increases linearly with temperature. The amount of  $\text{H}_2$  evolved at this temperature is greater than the coprecipitated sample reduced at 1,400°C.

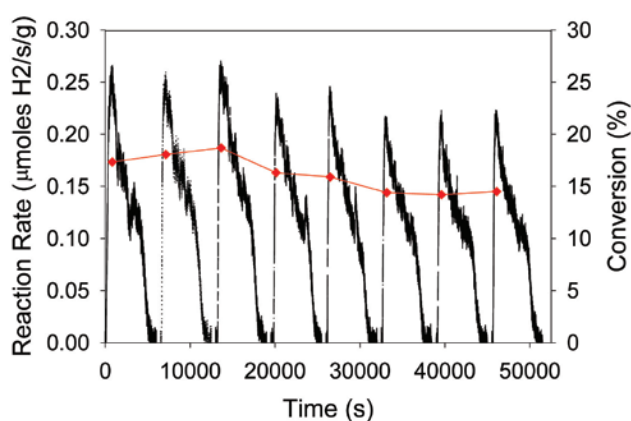
Finally, samples were cycled at 1,200°C reduction and 1,000°C oxidation in order to study their cyclical repeatability, and results are shown in Figure 4. The



**FIGURE 2.** Comparison of  $\text{O}_2$  Evolution Profiles during Reduction of  $\text{CoFe}_2\text{O}_4$  on  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$



**FIGURE 3.** Comparison of H<sub>2</sub> Evolution as a Function of Reduction Temperature



**FIGURE 4.** Eight Cycles Conducted at 1,200°C Reduction and 1,000°C Oxidation

conversion varies between 15% and 18%, and there is no obvious increasing or decreasing trend. However, a more detailed cycling study should be conducted to determine the samples lifetime over many more cycles in order to study its efficacy for this water splitting cycle.

## Conclusions and Future Directions

Significant theoretical/experimental progress has been made with the CoFe<sub>2</sub>O<sub>4</sub> “ferrite” cycle:

- Thin films were produced by ALD.
- Alumina was demonstrated to be a unique substrate that can take part in the reaction cycle.
- The cycle was experimentally demonstrated.

Future work:

- Additional cycle validation via further cycling.
- Gain better understanding of H<sub>2</sub> generation and reduction kinetics.

## FY 2009 Publications

1. Scheffe, J.R., A. Frances, D.M. King, X.H. Liang, B.A. Branch, A.S. Cavanagh, S.M. George, and A.W. Weimer, “Atomic Layer Deposition of Iron (III) Oxide on Zirconia Nanoparticles in a Fluidized Bed Reactor using Ferrocene and Oxygen,” *Thin Solid Films*, **517**, 1874-1879 (2009).

## References

1. T. Kodama, N. Gokon, R. Yamamoto, *Solar Energy* 82/1 (2008) 73.
2. Y. Tamaura, A. Steinfeld, P. Kuhn, K. Ehrensberger, *Energy* 20/4 (1995) 325.
3. M.D. Allendorf, *Energy & Fuels* 22/6 (2008) 4115.