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## **Strategic Partnerships Final LDRD Report: Nanocomposite Materials for Efficient Solar Hydrogen Production**

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# **Strategic Partnerships Final LDRD Report: Nanocomposite Materials for Efficient Solar Hydrogen Production**

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## **Abstract**

This “campus executive” project sought to advance solar thermochemical technology for producing the chemical fuels. The project advanced the common interest of Sandia National Laboratories and the University of Arizona in creating a sustainable and viable alternative to fossil fuels. The focus of this effort was in developing new methods for creating unique monolithic composite structures and characterizing their performance in thermochemical production of hydrogen from water. The development and processing of the materials was undertaken in the Materials Science and Engineering Department at the University of Arizona; Sandia National Laboratories performed the thermochemical characterization. Ferrite/yttria-stabilized zirconia composite monoliths were fabricated and shown to have exceptionally high utilization of the ferrite for splitting CO<sub>2</sub> to obtain CO (a process analogous to splitting H<sub>2</sub>O to obtain H<sub>2</sub>).



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## 1.0 Project Purpose

Solar energy is the most abundant sustainable energy option and hence is of interest not only as a source of electric power, but also as a source of transportation fuels. A practical route for the conversion of solar energy to chemical energy in the form of hydrogen would be a transformative advance. This “campus executive” project sought to advance technology for achieving this transformation and to build on the common interest of Sandia National Laboratories and the University of Arizona in creating a sustainable and viable alternative to fossil fuels. The focus of this effort was in developing new methods for creating unique monolithic composite structures and characterizing their performance in thermochemical production of chemical fuels. The development and processing of the materials was undertaken in the Materials Science and Engineering Department at The University of Arizona; Sandia National Laboratories performed the thermochemical characterization. The development of sustainable energy technologies helps to strengthen our nation’s long term energy independence and national security, and as such this work aligned with DOE goals in the areas of Defense, Energy, Science and Environment.

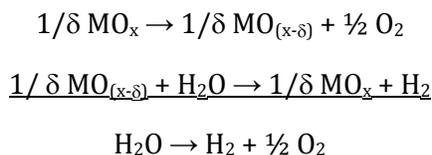
## 2.0 Context and Background

Solar insolation is a very attractive persistent energy source as it is by far the largest exploitable renewable resource. However, utilizing solar energy to power the transportation requires the solar energy to be captured and stored, e.g. in the form of a chemical fuel such as hydrogen. Hydrogen can be produced via the solar-driven electrolysis of water. Reasonable estimates for the average annual efficiency of solar electrolysis ranges from 11% to 18% for PV and Dish Stirling systems respectively. [1]. The primary factor limiting solar-to-chemical efficiency is the conversion of sunlight to electricity. Thermochemical approaches avoid the solar to electric conversion altogether. Sandia National Laboratories has been developing the field of metal oxide thermochemistry for many years; a summary of recent work and publications can be found in [2]. Briefly, water splitting thermochemical cycles couple two or more chemical reactions that sum to the desired reaction, and then perform these reactions in a cyclic manner, recycling all the reactants and products other than H<sub>2</sub>O, H<sub>2</sub>, and O<sub>2</sub>. Concentrating solar power (CSP) provides efficient utilization of solar energy and access to the very high temperatures (ca. 1500 °C) necessary to drive the known metal oxide-based cycles.

The basic chemistry is summarized below using a hypothetical metal oxide working material (MO<sub>x</sub>) as an example. Thermodynamics requires that the two chemical reactions of the cycle be carried

- 
1. Nathan P. Siegel, James E. Miller, Ivan Ermanoski, Richard B. Diver, and Ellen B. Stechel “Factors Affecting the Efficiency of Solar-Driven Metal Oxide Thermochemical Cycles” submitted for review (2012).
  2. James E. Miller, Mark D. Allendorf, Andrea Ambrosini, Ken S. Chen, Eric N. Coker, Daniel E. Dedrick, Richard B. Diver, Roy E. Hogan, Ivan Ermanoski, Terry A. Johnson, Gary L. Kellogg, Anthony H. McDaniel, Nathan P. Siegel, Chad L. Staiger, and Ellen B. Stechel “Final Report - Reimagining Liquid Transportation Fuels: Sunshine to Petrol” SAND2012-0307, January 2012.

out at different temperatures: the endothermic thermal reduction of the metal oxide at a high temperature, and the exothermic H<sub>2</sub>-producing oxidation step at a lower temperature. It is necessary therefore to cycle the temperature of the oxide as well as the gaseous environment.



The thermochemical process of splitting of carbon dioxide to obtain carbon monoxide is entirely analogous, and more convenient to carry out in a laboratory setting. In addition, if one splits both water and carbon dioxide, the H<sub>2</sub> and CO products can be blended to form syngas, a precursor to synthetic hydrocarbon fuels.

The efficiency, and therefore the viability, of a metal oxide thermochemical cycle is heavily tied to the utilization of the material i.e. the extent to which the material reacts ( $\delta$  in the example above), and the effective utilization of the available thermal energy [1]. The utilization (reaction extent) of monolithic materials is a function of reaction kinetics and the transport of both mass (gas phase and solid phase), and thermal energy. The mass transfer is in turn a function of the monolith chemistry and geometry and the gas flows. In this work, novel approaches were developed and applied to produce ‘honeycomb-type’ monoliths of various channel dimensions. These open structures allow deep light penetration (direct exposure to solar flux – promote rapid heating), unimpeded gas flow, and high surface to volume ratios to promote the surface reaction and minimize mass transfer limitations with the bulk of the solid. The monoliths were composites of iron oxides with yttria-stabilized zirconia (YSZ) with varying Y concentrations. The monoliths were compared under similar operating conditions to elucidate important factors in overall thermochemical performance.

### 3.0 Project Accomplishments

The results of the project are extensively documented in a thesis and journal publication (see section 4.0). Therefore only a brief summary of the accomplishments is provided here.



Figure 1. Green monolith (left) showing ferrite/YSZ/polymer shells (red) and carbon/polymer cores (black) and finished product after calcination at 1400 °C (right).

A polymer co-extrusion process was developed for fabricating monolithic structures consisting of an Fe oxide/YSZ composite (final composition approximately 25% ferrite by weight). The

extrusion process yields a rod shaped piece with a carbon/polymer core with a ceramic/polymer shell. These individual rods were pressed to form larger groupings. The final ceramic honeycomb is obtained by burning out the carbon and sintering. An example of the green substrate and the final sintered part are shown in Figure 1 above.

Monolithic substrates with varying cell sizes were fabricated via the co-extrusion technique. These materials were then evaluated for the thermochemical splitting of  $\text{CO}_2$  to  $\text{CO}$  and  $\text{O}_2$  using techniques similar to those described previously [3]. The effect of  $\text{Y}_2\text{O}_3$  concentration in the YSZ (3% versus the standard 8%) was also evaluated for monoliths of similar geometry. Figure 2 illustrates some of the monoliths geometries that were compared, while Figure 3 shows a typical example of a  $\text{CO}$  yield curve from a monolith held in flowing  $\text{CO}_2$  at  $1100^\circ\text{C}$  after previous 1 hour reduction at  $1470^\circ\text{C}$  in flowing inert gas.



Figure 2. Examples of monoliths of varying cell size evaluated in this project.

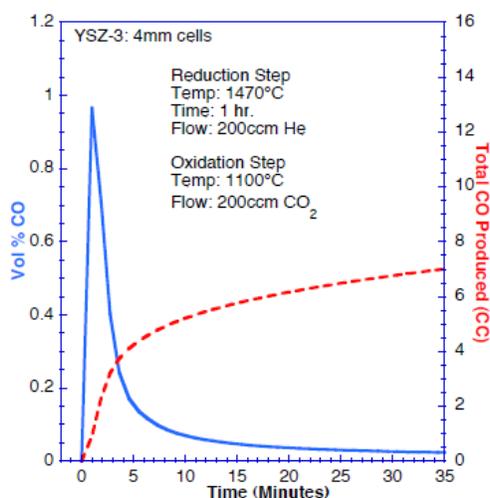


Figure 3. Typical  $\text{CO}$  yield curve obtained with composite monoliths.

The results showed that the utilization of the iron in the monoliths was quite high for all cell sizes, in some cases  $> 60\%$ , provided the  $\text{CO}_2$  gas flow rate was above some minimum value. This is larger than is typically at Sandia observed for materials with ferrite concentrations in this range. Figure 4

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3. J.E. Miller, M.D. Allendorf, R.B. Diver, L.R. Evans, N.P. Siegel, and J.N. Stuecker "Metal Oxide Composites and Structures for Ultra-High Temperature Solar Thermochemical Cycles" *Journal of Materials Science* 43 (2008) 4714 DOI: 10.1007/s10853-007-2354-7.

shows an example of data collected for three different monoliths at varying flow rates and temperatures. Data at the lowest flows where conversion plummets is not shown. At lower flow rates, the reaction rate was apparently limited by gas transport or local equilibrium considerations. The higher yttria content appeared to provide a significant advantage over the lower concentration (Figure 5).

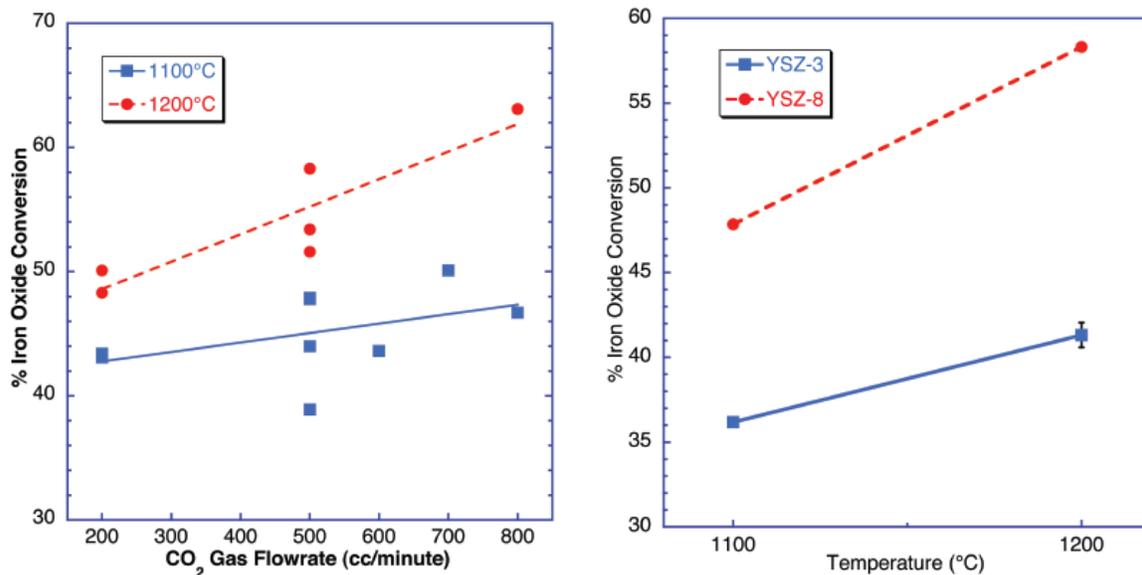


Figure 4. (Left) Ferrite utilization over several monoliths as a function of gas flow rate and temperature.

Figure 5. (Right) Effect of yttria content on iron utilization over substrates with similar geometries.

Overall the approach taken here led to materials with intriguing properties, particular in regards to ferrite utilization. Additional characterization to determine the long term physical and chemical stability of these materials and in particular the evolution of the ferrite utilization over time should be of interest.

## 4.0 Summary of Metrics

**Graduate student supported:** Luke S. Walker, University of Arizona, Erica Corral, advisor

**Master of Science Thesis:** "Effect of Y<sub>2</sub>O<sub>3</sub> Content and Surface Area on Renewable Fuel Production in Zirconia-Based Thermochemical Carbon Monoxide Generation Materials" (L.S. Walker, September 2010).

**Conference Presentations:**

L.S. Walker, J.E. Miller, N.P. Siegel, and E.L. Corral, "Zirconia based ceramic honeycombs for solar-based thermochemical generation of renewable fuels," Symposium on Clean Energy: Fuel Cells,

Batteries, Renewables - Materials, Processing, and Manufacturing, Materials Science & Technology Meeting and Exposition, Houston, TX, October 18-21, 2010.

L.S. Walker, J.E. Miller, N.P. Siegel, and E.L. Corral, "Zirconia based ceramic honeycombs for the production of synthesis gas by thermochemical decomposition of CO<sub>2</sub> and H<sub>2</sub>O at elevated temperatures," Symposium on Porous Ceramics, 34th International Conference on Advanced Ceramics and Composites, Daytona Beach, FL, January 24-28, 2011.

***Journal Publication:***

L.S. Walker, J.E. Miller, G.E. Hilmas, L.R. Evans, and E.L. Corral "Coextrusion of Zirconia-Iron Oxide Honeycomb Substrates for Solar-Based Thermochemical Generation of Carbon Monoxide for Renewable Fuels" ENERGY & FUELS, 26(1), pp. 712-721 (2012) DOI:10.1021/ef201346g.

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