SAND2011-3183C

HIGH TEMPERATURE SPLITTING OF WATER AND CARBON DIOXIDE USING COMPLEX OXIDES AS A ROUTE TO SOLAR FUELS

Anthony H. McDaniel[1], *Jonathan R. Scheffe*[3], *Victoria J. Aston*[4], *Darwin Arifin*[4], *Eric N. Coker*[2], *James E. Miller*[2], *Mark D. Allendorf*[1], *and Alan W. Weimer*[4]

[1]Sandia National Laboratories, Livermore, CA 94551, USA
[2]Sandia National Laboratories, Albuquerque, NM 87185, USA
[3]Institute of Energy Technology, ETH Zurich, Switzerland
[4]Chemical Engineering Department, University of Colorado, Boulder CO 80309, USA

Introduction

High temperature, thermochemical-based approaches to splitting water and carbon dioxide are attractive options for storing solar energy in the form of chemical fuels. A two-step, non-volatile metal oxide cycle, driven by concentrated solar energy as shown in figure 1, has the potential to be highly efficient because it can overcome the inherent limitations of photosynthesis and sidestep the solar-to-electric conversion losses suffered by electrolytic pathways.[1-3] Sandia National Laboratories has embarked on a program to develop an industrial-scale solar fuel production process entitled "Sunshine to Petrol" (S2P). The goal of S2P is to directly harness highly-concentrated thermal energy from the sun, and produce synthesis gas in a continuous manner with high solar-to-fuel conversion efficiency.

Although a large number of material systems have been considered for performing the reduction/oxidation chemistry, it is still far from clear which of these will lead to the highest overall efficiency. Research at Sandia has demonstrated that no clear answer to this question can be obtained apart from a reactor concept, since factors such as radiative heat transfer and loss, thermal recuperation, reaction cycle time, and material chemistry play critical roles. Furthermore, a solar-driven reactor will operate continuously for thousands of hours without requiring service. Therefore, any reactive materials used in such a process must demonstrate an acceptable level of chemical activity and mechanical durability.

A variety of novel reactive structures formulated from ceria, zirconia, and iron oxides have been prepared using conventional ceramic processing methods such as tape casting, as well as unconventional methods such as aerogels or thin films applied to substrates via atomic layer deposition (ALD). The kinetics of chemical and thermal reduction, and water or carbon dioxide splitting reactions, were measured to determine rate-controlling phenomena for prototypical structures. The discussion will focus on differences observed between various reactive structures having the same chemical composition, as well as those comprised of different metal oxides.

Experimental

Samples of metal oxides were prepared either free-standing as aerogels or powders, as thin films deposited by ALD on high surface area m-ZrO_2 or cerium oxide supports, or via impregnation on zirconium oxide supports. Preparation of aerogels followed the methods described by Gash et al. using epoxides mixed with ethanolic Fe or Ni salt solutions.[4] The ALD thin films were deposited using organometallic precursors ferrocene and cobaltocene.[5] Impregnated samples were synthesized by conventional means from nitrate salt solutions. Reactive structures were prepared from pure powders or felts using tape casting, hot pressing, and infiltration methods where appropriate.

A variety of analytical techniques, such as X-ray diffraction, SEM, TEM, and Raman spectroscopy, were used to characterize the morphology and composition of the as-prepared and redox-cycled samples. Reactive structures were reduced and oxidized in a stagnation flow reactor (SFR) shown in figure 2. The reactor consists of a stainless steel gas-handling manifold, ceramic reactor core, high temperature furnace, 500 W continuous-wave NIR diode laser, and modulated effusive beam mass spectrometer. The reactor is configured to allow inlet gases flowing downward toward the round-bottom, closed end of an alumina tube to impinge on a zirconia flat creating a stagnation plane that can be describe by an ideal 1-D flow field (see figure 2 inset). It is important to note that the SFR operates in a flow regime where velocity and thermal gradients are independent of tube radius such that materials sitting on the zirconia flat experience a uniform gas composition and transport is dominated by diffusion.

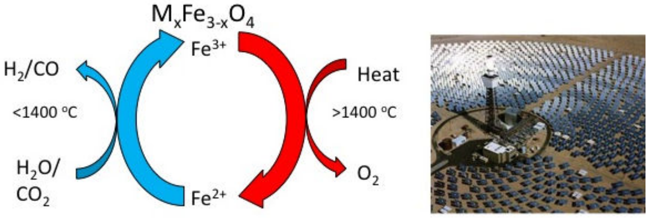

Figure 1. Schematic of a two-step thermochemical cycle using a metal-substituted ferrite ($M_xFe_{3-x}O_4$) as the reactive material. Heating the ferrite to high temperature is accomplished using concentrated solar energy. The reduced material is exposed to either CO_2 or H_2O to produce fuel in the form of CO or H_2.

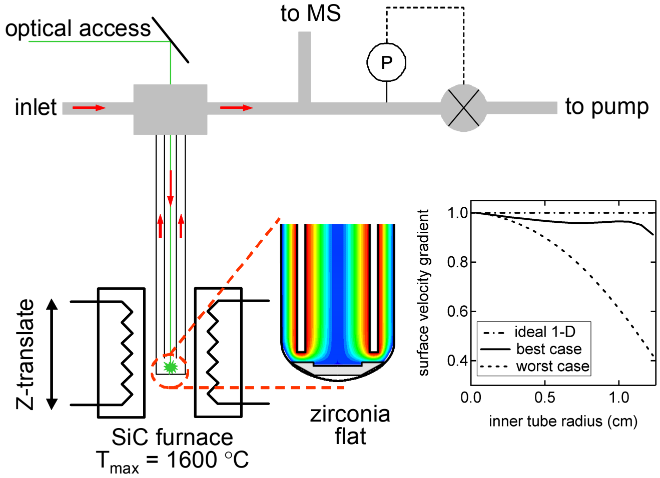

Figure 2. Schematic of the stagnation flow reaction (SFR). Transport gradients are independent of inner tube radius out to 1.0 cm.

Materials were chemically reduced using mixtures of H_2, CO, and CO_2. Thermal reduction was achieved by either ramping the furnace temperature to 1450 ºC at a rate of 0.17 ºC/s, or by exposure to a high flux (1000 – 3000 sun equivalent) of NIR radiation, which can achieve heating rates in excess of 100 ºC/s. Reduction by laser heating is more representative of thermal stresses experienced by reactive structures in the actual application. Reduced materials were subsequently oxidized under mixtures of H_2O or CO_2 not exceeding 50 mol% in He at a total pressure of 75 torr. Product gas composition exiting the SFR was measured by mass spectrometry at a rate of ~ 1 Hz.

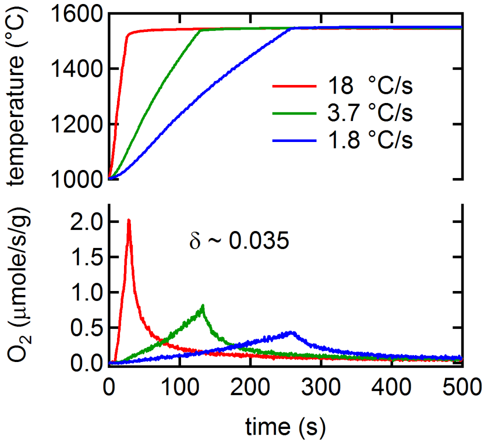

Figure 3. Rate of oxygen production measured in the SFR during thermal reduction of $CeO_{2-\delta}$ at three heating rates.

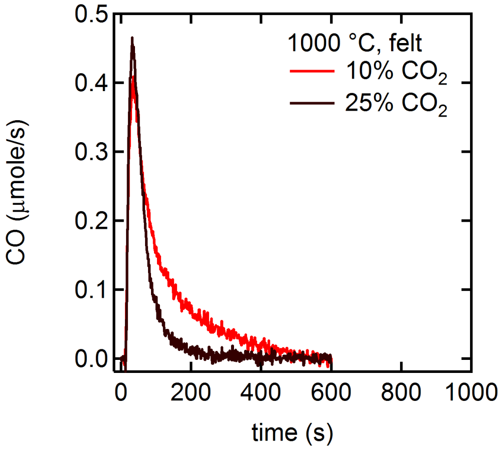

Figure 4. Rate of carbon monoxide production measured in the SFR during oxidation of $CeO_{2-\delta}$ at two oxidant mole fractions.

Discussion

Figures 3 and 4 are representative of the kinetic data collected during thermal reduction and oxidation, respectively. Here commercial felts made of cerium oxide are reduced by exposure to NIR radiation at various heating rates to a maximum temperature of 1550 ºC (figure 3). Ceria ($CeO_{2-\delta}$) is a non-stoichiometric oxide that is a prime candidate for solar-fuel applications because it resists sintering and maintains a single-phased structure for oxygen deficiencies below $\delta = 0.15$. Figure 4 shows representative kinetic behavior for re-oxidation by CO_2, which produces CO. Ceria reduction is a very facile process that does not appear to be limited by diffusion of oxygen ion vacancies in the solid or the availability of reactive sites for oxygen recombination at the surface. Re-oxidation by CO_2, on the other hand, is limited by surface-mediated processes.

For high surface area ALD ferrite (γ-Fe_2O_3) and cobalt ferrite ($Co_{0.85}Fe_{2.15}O_4$) thin films, materials that are also of great interest to solar-fuel applications, we have observed peak H_2 production rates that are 38-100 times greater than ZrO_2-supported iron oxides at oxidation temperatures much lower than those reported in the literature.[5] Regardless of material chemistry, in order to optimize the solar-to-chemical conversion efficiency it is imperative that the rates of oxidation and reduction are matched to the solar flux. Our observations indicate that this may be accomplished through creative use of reactive structures.

Advances in synthesizing, characterizing, and understanding the dynamic behavior of these materials will be discussed. Differences in reactivity for various structures and material chemistries will be framed within the context of solid-state kinetic theory, which is used to identify rate-controlling processing by way of Master Plot analysis. Overall, our research indicates that, although substantial engineering problems must still be solved, a pilot-scale process operating at greater than 20% efficiency is achievable.

Acknowledgement. This work was supported by the Laboratory Directed Research and Development Sunshine to Petrol program at Sandia National Laboratories and the U.S. Department of Energy Fuel Cell Technologies Program via the Solar Thermochemical Hydrogen (STCH) directive. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

References

(1) Kodama, T.; Gokon, N. *Chem. Rev.* **2007**, *107*, 4048-4077.
(2) Diver, R. B.; Miller, J. E.; Allendorf, M. D.; Siegel, N. P.; Hogan, R. E. *J. Sol. Energy Eng.* **2008**, *130*, 041001.
(3) Chueh, W. C.; Falter, C.; Abbott, M.; Scipio, D.; Furler, P.; Haile, S. M.; Steinfeld, A. *Science* **2010**, *330*, 1797-1801.
(4) Gash, A. E.; Satcher,, J. H.; Simpson, R. L. *Chem. Mater.* **2003**, *15*, 3268-3275.
(5) Scheffe, J. R.; Allendorf, M. D.; Coker, E. N.; Jacobs, B. W.; McDaniel, A. H.; Weimer, A. W. *Chem. Mater.* **2011**, 110330070752057.