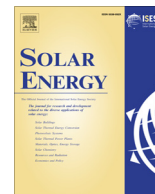




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Advances and trends in redox materials for solar thermochemical fuel production

Richard J. Carrillo, Jonathan R. Scheffe*

Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611-6250, United States

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ABSTRACT

Solar thermochemical (STC) redox cycles have made substantial advances in recent years, in large part due to the utilization of nonstoichiometric ceria over other iron oxide and zinc oxide based materials that undergo crystallographic or solid-to-gas phase changes. These changes render their utilization in a cyclic nature to be challenging because of the ever-changing physical properties over time and difficulty in preventing reverse reactions when cooling, for example $\text{Zn(g)} + 0.5\text{O}_2\text{(g)} \rightarrow \text{ZnO(s)}$. However, such phase changes also have the distinct benefit of being accompanied by large changes in entropy which is typically favorable from a thermodynamic perspective. As a result, the theoretical solar-to-fuel energy conversion efficiencies of ceria-based cycles are usually predicted to be lower than their volatile and nonvolatile stoichiometric counterparts; however, in actuality their measured performance is superior. For this technology to become commercially viable, there is a need to develop new materials that can outperform ceria in terms of solar-to-fuel energy conversion efficiency and operate at more benign conditions. This has been a large focus in the thermochemical community over the last 5–6 years and, to date, most of the effort has been centered on reducing the relatively high operating temperatures that are required while maintaining ceria's desirable characteristics such as favorable oxidation thermodynamics, rapid reaction kinetics, and crystallographic stability. This effort resulted in many perovskite related materials that operate several hundred degrees lower (e.g. 1473 K). Unfortunately, however, their entropy change is usually lower than that of ceria and the results are consistently a compromise in the thermodynamic driving force for oxidation that results in less efficient materials overall. This work focuses on the thermodynamic, experimental, and computational aspects related to the discovery and characterization of new and better performing redox materials and the attributes necessary of them in order to drive the next generation of efficient STC redox materials.

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1. Introduction

Solar energy, an ubiquitous and essentially unlimited resource, offers the ability to generate electricity via solar photovoltaics (PV) (Parida et al., 2011), supply the process heat needed to drive a heat engine (e.g. Rankine cycle) (Steinfeld, 2005), provide hot water for domestic heating applications (Duffie and Beckman, 1980), or any number of other thermally demanding applications. The major caveats with all of these methods are related to the sun's intermittency and, therefore, they should be integrated with storage technologies, e.g. batteries (Cook et al., 2010) or thermal storage (Kreith and Kreider, 1978), if they are to be used on demand. The conversion of incident sunlight directly to chemical fuels such as

molecular hydrogen or fuel precursors like synthesis gas (syngas) offers the potential to efficiently store solar energy, transport it, and utilize it on demand (Graves et al., 2011). Given that the current transportation infrastructure is largely based on the use of liquid hydrocarbon fuels, efficient conversion of concentrated solar energy into fungible fuels provides a pathway to begin the transition away from fossil fuels and towards renewable fuel sources. There are a variety of methods to convert sunlight to fuels through the dissociation of H_2O and/or CO_2 , and most of them are low temperature photon-driven approaches that take advantage of a portion of the sun's solar spectrum that has sufficient energy drive the process of interest; the remainder of the spectrum is not capable of being utilized (Lewis, 2016; McKone et al., 2013). This work will focus on thermochemical approaches that utilize concentrated sunlight as a thermal input to drive the dissociation of H_2O and CO_2 . In such an approach, the entire solar spectrum is

* Corresponding author.

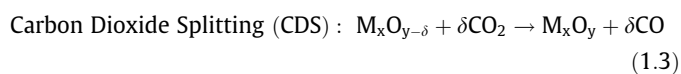
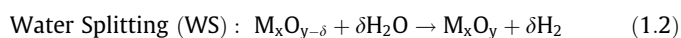
E-mail address: jscheffe@ufl.edu (J.R. Scheffe).

absorbed thermally and, therefore, provides a thermodynamically attractive pathway to solar fuel production (Steinfeld and Palumbo, 2001). A variety of mature three-dimensional concentrating technologies such as parabolic dishes or heliostat fields (Duffie and Beckman, 1980; Steinfeld and Palumbo, 2001) may be utilized to focus the sun's radiant energy enough (e.g. 1000–10000 suns, where 1 sun is equivalent to 1 kW m^{-2}) to drive a number of STC processes at elevated temperatures, usually in the range of 873–2273 K (Chueh and Haile, 2009; Furler et al., 2014; Muhich et al., 2013; Steinfeld, 2002; Tamaura et al., 1995).

One promising method of STC fuel production is the two-step metal-oxide based thermochemical redox cycle. The first step is described by a high-temperature endothermic reaction in which a metal oxide (M_xO_y) is reduced upon heating with concentrated solar energy, see Eq. (1.1).



In a lower temperature step, the reduced metal-oxide is oxidized with H_2O to produce H_2 (water splitting, Eq. (1.2)) or with CO_2 to produce CO (carbon dioxide splitting, Eq. (1.3)) (Furler et al., 2014; Steinfeld, 2005).



The H_2 or CO produced may be used directly to generate power through combustion or electrochemical oxidation. Additionally, the mixture of the two, syngas, may be further processed to fungible liquid hydrocarbon fuels such as kerosene, diesel, and gasoline via catalytic processes such as Fischer-Tropsch (FT) synthesis (Marxer et al., 2015). Since the metal-oxide is recycled back to the first step, the net reactions resulting from the thermochemical process are simply the splitting of H_2O ($\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2$) and/or CO_2 ($\text{CO}_2 \rightarrow \text{CO} + 0.5\text{O}_2$). The oxygen exchange capacity of the redox cycle, δ , is directly proportional to the maximum amount of fuel that may be produced during the oxidation step and the energy conversion efficiency for the cycle (Scheffe and Steinfeld, 2014). Compared to direct thermal dissociation (thermolysis) of H_2O or CO_2 , the two-step metal-oxide based thermochemical redox cycle allows for significantly reduced operating temperatures (e.g. typical reduction temperatures range from 1673 to 1873 K) and eliminates the risk of explosive recombination of products by producing oxygen and the desired fuel in separate steps (Miller et al., 2014b; Nakamura, 1977).

Siegel et al. (2013) suggested that, when evaluated in comparison to H_2 production via photovoltaics coupled with electrolysis, STC technologies need to achieve an annual average solar-to-fuel efficiency of at least 20% to be economically competitive. To date, the largest reported average solar-to-fuel energy conversion efficiency for STC CDS is 5.25% by Marxer et al. (2017) using ceria (CeO_2) as the metal-oxide. CeO_2 is currently considered to be the state-of-the-art redox material because of its favorable oxidation thermodynamics, rapid reaction kinetics, and morphological stability (Ackermann et al., 2014; Chueh and Haile, 2010; Panlener et al., 1975; Siegel et al., 2013). Despite its high regard, the fuel production efficiency achievable with CeO_2 and the practicality of its use are limited by the extremely high temperatures required for the thermal reduction step; higher operating temperatures imply larger energy penalties due to heat losses, place constraints on the materials of construction of the thermochemical reactor, and result in extreme solar concentrator demands (Furler et al., 2012b).

To address the abovementioned limitations on the efficiency and operability, recent experimental and computational efforts

have focused on the discovery of new redox materials that operate at more moderate temperatures than CeO_2 while still retaining the thermodynamic favorability, fast reaction rates, and high physical and chemical stability. The discussion herein will focus on reviewing the performance of solar redox materials in two-step thermochemical cycles studied within the past 5–6 years in terms of their oxygen exchange capacity, thermodynamic properties, reaction kinetics, and morphological and chemical stability in relation to their viability for efficient STC WS and/or CDS.

2. Advancements in solar redox materials

2.1. Background

There exist three distinct classes of metal-oxide redox pairs: (1) volatile stoichiometric, (2) nonvolatile stoichiometric, and (3) nonstoichiometric. In a volatile redox cycle, the temperature required for reduction is greater than the vaporization temperature of the metal-oxide, thereby causing it to undergo a solid-to-gas phase transition (e.g. $\text{M}_x\text{O}_y (\text{s}) \rightarrow x\text{M} (\text{g}) + 0.5y\text{O}_2$) (Steinfeld, 2002). Some volatile redox pairs include ZnO/Zn (Steinfeld, 2002) and SnO_2/SnO (Abanades et al., 2008). The practicality of large-scale implementation of volatile redox cycles is largely limited by the need for rapid quenching of the gas phase products (Alxneit, 2008). In nonvolatile stoichiometric and nonstoichiometric cycles, the redox intermediate remains in the solid phase throughout the reduction step (Scheffe and Steinfeld, 2014). Nonvolatile stoichiometric reactions involve a change in crystal structure and the reduction of the cation to form solid compounds (e.g. $\text{M}_3\text{O}_4 \rightarrow 3\text{MO} + 0.5\text{O}_2$) (Chueh and Haile, 2010; Nakamura, 1977; Scheffe and Steinfeld, 2014). Examples of nonvolatile stoichiometric redox pairs include $\text{Fe}_3\text{O}_4/\text{FeO}$ (Charvin et al., 2007; Gokon et al., 2008; Nakamura, 1977), ferrite systems in which transition metal cations (e.g. $\text{Co}^{3+/2+}$ and Ni^{2+}) are substituted for $\text{Fe}^{3+/2+}$ in Fe_3O_4 (Allendorf et al., 2008; Kodama et al., 2005; Scheffe et al., 2011, 2013b), and hercynite systems wherein reduction of Fe_3O_4 or ferrites is performed in the presence of Al_2O_3 (Muhich et al., 2013; Scheffe et al., 2010). Stoichiometric reactions have a greater oxygen exchange capacity compared to that of nonstoichiometric reactions; however, as shown in iron oxide cycles, they typically exhibit poor stability (i.e. the reduction temperatures required for thermodynamic favorability exceed the melting point of the reduction product, FeO) and slower reaction kinetics (Chueh and Haile, 2010; Scheffe and Steinfeld, 2014). ZrO_2 and yttria-stabilized zirconia (YSZ) have been used as supports or thermally stable solvents to address problems regarding physical stability, but this leads to an extra sensible heating energy penalty and the efficiency suffers as a result (Coker et al., 2011; Gokon et al., 2009; Kodama et al., 2005, 2006). From a thermodynamic perspective, large changes in entropy during oxygen exchange are desirable, as the entropy has a strong impact on the thermodynamic favorability and the temperature swing between reduction and oxidation. The solid-to-gas and crystallographic phase changes that occur during cyclic operation with the volatile and nonvolatile stoichiometric redox pairs, respectively, are associated with larger changes in entropy than those of nonstoichiometric oxygen exchange. Nonstoichiometric reactions with metal-oxides such as CeO_2 and LaMnO_3 perovskites involve the partial reduction of the bulk metal-oxide, while maintaining the crystallographic structure (e.g. $\text{MO}_2 \rightarrow \text{MO}_{2-\delta} + 0.5\delta\text{O}_2$) (Panlener et al., 1975; Scheffe and Steinfeld, 2014). Similar to ferrite systems, doping schemes have been employed with CeO_2 and different perovskites to tune the thermodynamic parameters and redox performance.

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