

# The morphological stability and fuel production of commercial fibrous ceria particles for solar thermochemical redox cycling



Adam C. Gladen, Jane H. Davidson\*

Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States

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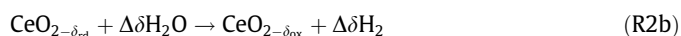
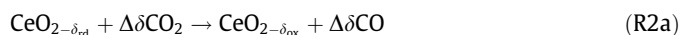
## ABSTRACT

Implementation of the solar thermochemical ceria redox cycle to split water and carbon dioxide depends in part on the morphological stability of a porous ceria substrate and the ability to acquire porous substrate in high volume. Here we evaluate the evolution of morphology and fuel production of ceria particles formed of fibers in a commercially relevant manufacturing process. The particles are evaluated over 1000 CO<sub>2</sub>-splitting cycles (56 h) at 1773 K followed by sixteen temperature-swing cycles (5.7 h) with oxidation at 1073 K. New particles are 78% porous with a specific surface area of 0.14 m<sup>2</sup> g<sup>-1</sup> and a grain size of 3.7 μm. During isothermal cycling, the morphology stabilized after 500 cycles (28 h) to 73% porosity, a surface face 0.08 m<sup>2</sup> g<sup>-1</sup> and a grain size of 8 μm. The stabilized particles retained 89% of the peak cycle average rate of CO production. During temperature-swing cycling, the specific surface area decreased to 0.06 m<sup>2</sup> g<sup>-1</sup>. The mass-produced fibrous structures have adequately stable morphologies to produce fuel production performance similar to less scalable (lab-scale) ceria structures of similar pre-cycling surface area.

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## 1. Introduction

Spitting water and carbon dioxide via solar thermochemical, metal oxide redox cycles provides long-term storage of solar energy as hydrogen and synthesis gas, which can be used to produce electricity or converted to liquid hydrocarbon fuel. The non-stoichiometric cerium dioxide (ceria) cycle is an attractive approach because oxygen diffuses rapidly through the lattice (Chueh and Haile, 2010; Eyring, 1991), and there are no irreversible phase transitions between the fully oxidized and partially reduced states for non-stoichiometry less than 0.2 (Ackermann et al., 2014; Millot and Mierry, 1985). The cycle is represented by reactions (R1) and (R2a)/(R2b) for splitting CO<sub>2</sub> and H<sub>2</sub>O respectively.



Concentrated solar energy provides the process heat to drive the endothermic reduction step (R1). The change in nonstoichiometry between reduction and oxidation,  $\Delta\delta = \delta_{\text{rd}} - \delta_{\text{ox}}$ , represents the amount of fuel produced per mole of ceria.

The cycle can be operated isothermally or via a temperature-swing with oxidation hundreds of degrees cooler than reduction. The isothermal cycle has the same thermodynamic limitations as direct thermolysis of CO<sub>2</sub> or H<sub>2</sub>O, but with the benefit of separating the product gases into two streams. As demonstrated through implementation of a prototype reactor, isothermal cycling reduces thermal stresses on ceramic components, and facilitates continuous fuel production and effective heat recovery (Chandran and Davidson, 2016; Hathaway et al., 2016, 2015). On the other hand, solar-to-fuel efficiency is higher for a temperature-swing cycle (Brendelberger et al., 2015; Bulfin et al., 2015; Ermanoski et al., 2014; Jarrett et al., 2016; Krenzke and Davidson, 2015). Based on chemical thermodynamics (Panlener et al., 1975), reduction temperatures of 1673 K and preferably higher are required for meaningful fuel production per kg of ceria.

With such high reduction temperatures, a consideration for successful implementation of the cycle is the morphological stability of the ceria substrate. Porous structures featuring high surface area are desired to speed the rate of oxidation (Chueh and Haile, 2010; Venstrom et al., 2012), limit pressure drop (Bader et al., 2015; Venstrom et al., 2014), and enhance heat and mass transfer

\* Corresponding author.

E-mail address: [jhd@umn.edu](mailto:jhd@umn.edu) (J.H. Davidson).

## Nomenclature

$b_{i,\text{ref}}$	mass spectrometer calibration constants	$X_i$	mole fraction of species 'i'
$C_{i,\text{ref}}$	mass spectrometer signal for species 'i', A	$\Delta\delta$	change in non-stoichiometry, –
$T_{\text{ox}}$	oxidation temperature, K	$\tau_{\text{ox}}$	oxidation half cycle time, s
$T_{\text{rd}}$	reduction temperature, K	$\tau_{\text{purge}}$	purge time, s
$\dot{V}_{\text{ox}}^v$	oxidizer mass specific, volumetric flow rate, $\text{mL s}^{-1} \text{g}^{-1}$	$\tau_{\text{rd}}$	reduction half cycle time, s
$\dot{V}_{\text{rd}}^v$	reduction gas mass specific, volumetric flow rate, $\text{mL s}^{-1} \text{g}^{-1}$		
$\dot{V}_{\text{ref}}$	reference (Argon) volumetric flow rate, $\text{mL s}^{-1}$		

(Bader et al., 2015; Furler et al., 2014; Venstrom et al., 2014). However, the higher surface area ceria materials ( $10\text{--}100 \text{ m}^2 \text{ g}^{-1}$ ) evaluated for this application (e.g., a three-dimensionally ordered macro-porous (3DOM) structure (Rudisill et al., 2013; Venstrom et al., 2012), a decomposition synthesized structure with a disordered, mesoporous morphology (Venstrom et al., 2012), and a wood-templated structure (Malonzo et al., 2014)) undergo densification and a corresponding significant loss of surface area below the target reduction temperature.

Morphologies with surface areas of the order  $0.1 \text{ m}^2 \text{ g}^{-1}$ , including pore formed monoliths (Chueh and Haile, 2010; Chueh et al., 2010; Hao et al., 2013; Rhodes et al., 2015; Venstrom et al., 2014), reticulated porous ceramic (RPC) (Furler et al., 2014, 2012a), and electrospun fibers (Gibbons et al., 2014), are more stable at or above 1673 K but still lose surface area over time. The impact of surface area on fuel production depends on the rate limiting mechanism and the thermodynamic driving force. For this reason, direct comparison of the rate of fuel production among the prior studies of different morphologies is generally not meaningful due to wide variation of test conditions, notably temperatures, gas flow rates, oxidizer, and cycle duration.

In early work to produce porous ceria substrates for this application, Chueh et al. used a sacrificial pore former to fabricate pressed ceria monoliths with 65–80% porosity and specific surface area of  $0.1 \text{ m}^2 \text{ g}^{-1}$  (Chueh and Haile, 2010; Chueh et al., 2010). Over 416 h of redox cycling between 1773 K and 1073 K to split water,  $\text{H}_2$  production decreased 50% (Chueh and Haile, 2010). The decrease was attributed to an assumed loss of surface area based on a threefold increase in grain size. More recently, Rhodes et al. compared the CO production of a ceria monolith produced using a sacrificial graphite pore former to that of nano- and micron-diameter ceria powder (Rhodes et al., 2015). The results are consistent with the comparative studies of 3DOM (Rudisill et al., 2013; Venstrom et al., 2012) and wood-templated structures (Malonzo et al., 2014) with commercial ceria powder; higher surface area yields faster fuel production.

RPC morphologies have been considered (Furler et al., 2014, 2012a) due to the relatively high effective thermal conductivity and low pressure drop possible for high porosity and large pore size foams (e.g. 90% porosity; 10 pores per inch). RPCs manufactured utilizing the replication method have specific surface areas on the order of  $0.0001 \text{ m}^2 \text{ g}^{-1}$  (Furler et al., 2014). Furler et al. (2014) used pore formers to increase the accessible surface area in the struts of ceria RPC. Over 50 h of cycling between 1773 K and 1273 K, the surface area decreased from  $0.095$  to  $0.089 \text{ m}^2 \text{ g}^{-1}$ . After 120 h in air at 1773 K, the surface area was  $0.056 \text{ m}^2 \text{ g}^{-1}$ .

Ceria structures formed from fibers are potentially a lower cost option than templated materials and RPC and are available commercially. However, not all fibrous materials are stable. Ceria “felt” which is available commercially for use in used in molten carbonate fuel cells was evaluated in a solar thermochemical reactor. The felt had an initial surface area of  $\sim 6 \text{ m}^2 \text{ g}^{-1}$  (Furler et al., 2012a)

but densified substantially after  $\sim 8$  h with a reduction temperature of approximately 1800 K (Furler et al., 2012b). On the other hand, electrospun  $\text{Ce}_{0.975}\text{Zr}_{0.025}\text{O}_2$  fibers retained an open porous structure over 29 h of cycling between 1673 K and 1073 K even as the specific surface area decreased from  $0.6$  to  $0.34 \text{ m}^2 \text{ g}^{-1}$  (Gibbons et al., 2014). With reduction at 1773 K, sintering was more extensive and fuel production decreased despite more favorable thermodynamics.

The encouraging behavior of the electrospun fibers at 1673 K motivated the development and evaluation of mm-sized fibrous ceria particles for use in a fixed bed isothermal solar thermochemical reactor (Bader et al., 2015; Bala Chandran et al., 2015; Chandran and Davidson, 2016; Hathaway et al., 2016, 2015; Venstrom et al., 2015, 2014). The selection of the size and morphology of the particles was driven by the desire to minimize pressure drop and temperature gradients in a packed bed, and to ensure gas phase diffusion was not rate limiting (Bader et al., 2015; Venstrom et al., 2014, 2012). The other motivation was the need to acquire kilograms of material coupled along with the desire to identify a commercially relevant synthesis approach. The fibers were developed in conjunction with an industrial partner and were formed in a proprietary process using a precursor method in which organic textiles are converted into ceramic oxide textiles. The textile is milled to obtain bulk fibers. The 5 mm diameter, 5 mm long cylindrical particles produced from the fibers were fired in air at 1873 K to stabilize the morphology prior to cycling at 1773 K. The cost of the particles in kilogram quantities is high (on the order of 6000 US \$ per kg in 2016) because of the expense of development and the relatively high labor cost for a small production of 3 kg. However, the manufacturing process for the base material is similar to the process used to produce high temperature refractory insulation. Thus, larger scale structures, similar to those produced for refractory insulation, could be made and will be less expensive than the smaller mm-sized particles. Based on discussion with the supplier, it is reasonable to expect an order of magnitude cost reduction for the particles and even greater cost reduction for larger structures if the market for ceria fiber structures expands.

The durability of the fibrous particles was evaluated during isothermal  $\text{CO}_2$  splitting at 1773 K for 56 h followed by temperature-swing cycling at the same reduction temperature and oxidation at 1073 K for 6 h. To help delineate the effects of thermochemical cycling and temperature on the morphological changes, evolution of particle morphology was also evaluated in a flow of air at 1773 K.

## 2. Approach

### 2.1. Isothermal cycling

The evolution of surface area, particle porosity, grain size and the rates of  $\text{O}_2$  and CO production was monitored in eight experiments of increasing duration from 0.056 to 55.56 h, corresponding

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