



## Solar thermochemical CO<sub>2</sub> splitting using cork-templated ceria ecoceramics

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### ABSTRACT

This work addresses the solar-driven thermochemical production of CO and O<sub>2</sub> from two-step CO<sub>2</sub>-splitting cycles, using both ceria granules prepared from cork templates (CG) and ceria foams from polyurethane templates (CF). These materials were cycled in a high-temperature indirectly-irradiated solar tubular reactor using a temperature-swing process. Samples were typically reduced at 1400 °C using concentrated solar power as a heating source and subsequently oxidised with CO<sub>2</sub> between 1000–1200 °C. On average, CO production yields for CG were two times higher than for CF, indicating that the morphology of this three-dimensionally ordered macroporous (3-DOM) CeO<sub>2</sub> improves the reaction kinetics. Their performance stability was demonstrated by conducting 11 cycles under solar irradiation conditions. Slightly increasing the reduction temperature strongly enhanced the reduction extent, and thus the CO production yield (reaching about 0.2 mmol g<sup>-1</sup> after reduction at 1450 °C in inert gas), while decreasing the oxidation temperature mainly improved the CO production rate (up to 1.43 μmol s<sup>-1</sup> g<sup>-1</sup> at 1000 °C). Characterisation of the 3-DOM structure, by means of XRD and SEM, provided insights into the reactivity behaviour of the developed materials. The pre-sintered ceria granules retained their structure after cycling. The fact that the mean cell size of CG is smaller (at least one order of magnitude) than that of CF suggests that its exposed surfaces enhanced reaction rates by a factor of two. Moreover, the maximum fuel production rate of CG was roughly three times greater than that reported previously for a ceria reticulated porous foam with dual-scale porosity.

## 1. Introduction

The conversion of sunlight directly to chemical fuels such as synthesis gas (or syngas – primarily a CO/H<sub>2</sub> mixture), hydrogen alone, or further to liquid fuels, offers the potential to efficiently store solar energy, transport it and utilise it on demand [1–3]. Thus, the generation of renewable solar fuels, derived from the sun, water and carbon dioxide and based on existing concentrated solar power (CSP) technology, is gaining considerable attention. The impact of solar fuels would be of utmost importance to ensure a sustainable energy future. Several methods for producing solar fuels, such as electrochemical, thermochemical and photochemical processes have been developed [4]. The use of solar radiation to drive a two-step thermochemical cycle based on redox materials benefits from the favourable thermodynamics arising from high temperature operation, the entire solar spectrum utilisation, the avoidance of the costly solar-to-electric conversion (used in electrolytic processes), and the elimination of CO/O<sub>2</sub> or H<sub>2</sub>/O<sub>2</sub> gas

separation. The latter is regarded as a tricky problem for one-step splitting methods [5]. Comprehensive literature reviews on solar thermochemical processes have been carried out [6–11]. Basically, two distinct types of metal oxides are being considered for the splitting of H<sub>2</sub>O and/or CO<sub>2</sub>: the volatile oxide cycles (ZnO/Zn or SnO<sub>2</sub>/SnO) and the non-volatile oxide cycles such as Fe<sub>3</sub>O<sub>4</sub>/FeO or CeO<sub>2</sub>/CeO<sub>2-δ</sub>. This study is focused on the cerium oxide redox pair.

On paper, the two-step cyclic process appears reasonably simple: concentrated solar radiation (a focused beam of sunlight) heats the metal oxide up to 1400 °C or more, driving its endothermic reduction and releasing oxygen. The reduced oxide is then cooled to 1000 °C or below (temperature-swing cycle), while a flow of steam and/or carbon dioxide re-oxidizes it, liberating hydrogen or carbon monoxide. Making such technology practical and cost-effective, however, poses noteworthy engineering challenges.

One of the most critical aspects is solar-to-fuel energy conversion efficiency, which in turn depends upon the redox material and the solar

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thermochemical reactor design [12–14].

Among the several redox material candidates, there is as yet no clear winner because of the stringent performance requirements [15–21], namely favourable thermodynamics, fast kinetics and microstructural stability [22]. In recent years, several researchers have looked at ceria (CeO<sub>2</sub>) redox materials, since they display high oxygen ion mobility and fast fuel production kinetics compared to ferrite-based and other non-volatile metal oxides [23,24]. The two step CO<sub>2</sub> or H<sub>2</sub>O splitting cycle based on oxygen-deficient ceria encompasses (1) the solar thermal reduction (endothermic) that proceeds via the formation of oxygen vacancies and the release of gaseous O<sub>2</sub>, resulting in the subsequent change in ceria stoichiometry ( $\delta$  in CeO<sub>2- $\delta$</sub> ), and (2) the oxidation (ideally non-solar) that proceeds with CO<sub>2</sub> and/or H<sub>2</sub>O when decreasing the operating temperature, thereby releasing CO and/or H<sub>2</sub> and re-incorporating oxygen into the lattice. The non-stoichiometry  $\delta$  determines the fuel production yield and it is a function of temperature and oxygen partial pressure. Ceria can accommodate relatively large oxygen non-stoichiometries due to high capabilities in oxygen storage and mobility while the crystallographic fluorite structure remains stable [25]. As with most of the nonstoichiometric oxides, its thermochemical properties are directly influenced by the type and concentration of point defects [26]. To find the best performing materials, novel compositions are being developed combining constituents with morphologies promoting reaction efficiency. For instance, the limited reduction capacity of ceria can be improved through doping with other metals, such as Zr, in order to increase oxygen mobility by creating oxygen vacancies [27–31]. On the other hand, both the efficiency and the cycling rates in the solar reactor were found to be limited by thermal losses associated with the poor conductive and radiative heat transfer across the ceria structures [32,33]. Several morphologies with  $\mu\text{m}$ -size (such as macroporous materials, 3-DOM and felts) and mm-size (such as honeycomb monoliths and foams) porous structures have been examined [34–37]. However, if these structures are coated with metal oxides, they can undergo side reactions with the support, spallation and deactivation [38].

Another approach is to use naturally occurring and sustainable materials, such as wood (or wood wastes) and cork, as a template to create biomimetic/biomorphic ceramics, known as environmentally conscious ceramics, i.e. ecoceramics [39,40]. Of particular interest is the innovative work by Pullar et al. in creating cork-templated biomorphic ecoceramics of ferrites and ceria [41–43]. Cork is especially interesting as it has a very porous 3-DOM (three-dimensionally ordered macroporous) microstructure, consisting of elongated hexagonal cells  $\sim 20\ \mu\text{m}$  diameter and 40–50  $\mu\text{m}$  long [44]. The walls of these cells are only around 1  $\mu\text{m}$  in thickness, resulting in an extremely porous, lightweight and regular microstructure, with up to 200 million cells per cm<sup>3</sup> [45].

Cork is the bark of a Mediterranean evergreen oak tree (*Quercus suber* L.), and Portugal supplies around 50% of the world's cork [46]. The cork layer is regenerated after each extraction from the tree every 9–13 years, and absorbs the equivalent amount of CO<sub>2</sub> which may be released from the cork during processing, with cork forests sequestering up to 5.7 T CO<sub>2</sub>/ha/yr [44].

Eastern white pine was used as a template to produce ceria ecoceramics by Malonzo et al. [40]. The pine wood has elongated rectangular pores around 20  $\mu\text{m}$  diameter with 10  $\mu\text{m}$  wide cell walls, but when converted to an ecoceramic a large amount of the wood template was lost, resulting in a fragile material with cells of 20  $\mu\text{m}$  diameter but with cell walls only 1  $\mu\text{m}$  thick. Upon oxidation with CO<sub>2</sub> at 800 °C, this pine wood-templated CeO<sub>2</sub> reduced at 1400 °C then achieved CO production rates about 4 times higher than nonporous CeO<sub>2</sub> [40]. However, the cells were found to collapse with thermal cycling as grain growth caused the cell walls to fuse together, thereby reducing the active surface area. Furthermore, when the reduction temperature was raised to 1500 °C, CO production rates decreased by a factor of 7 compared to oxidation after reduction at 1400 °C (from 9 to 1.3 mL

min<sup>-1</sup> g<sup>-1</sup>). Cork naturally has similar dimensions to the ecoceramic created by Malonzo et al. [40] (20  $\mu\text{m}$  cells with 1  $\mu\text{m}$  walls), yet with a more regular 3-DOM structure, and hence would appear to be an ideal template material. To our knowledge, there are no data available on the performance of ceria-based ecoceramics developed from cork substrates. In addition, the performance evaluation of reactive ceria structures in solar reactors under real and temporally-variable solar irradiation conditions has not been addressed so far.

In the present study, we report on the synthesis and experimental assessment of a novel form of biomimetic material – an ecoceramic produced from a cork template with the unique, highly porous cellular microstructure of cork – made of pure CeO<sub>2</sub> for CO production in an indirectly irradiated tubular solar reactor via concentrated solar heating. For comparison purposes, ceria foams manufactured by the replication method were also evaluated.

## 2. Experimental

### 2.1. Preparation of materials

Two ceria-based materials synthesised at both the University of Aveiro and LNEG were investigated in the form of granules and foams.

For this purpose, cork-template based-ceria granules (hereafter denoted as CG) were synthesised following a procedure described elsewhere [42], in which cork granules (typically of a size of several millimetres) were heat treated in a nitrogen atmosphere at 900 °C for 30 min to form carbon templates. These were then infiltrated with cerium nitrate solution (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99%, Sigma Aldrich), dried overnight, and heated in air to 1600 °C for 30 min to remove the carbon, leaving a pure ceria ceramic while preserving the 3-DOM structure of cork.

Polymeric template ceria foams (hereafter called CF), of cylindrical shape (20 mm in diameter and 20 mm height), were manufactured by the replication method reported in detail elsewhere [47]. Briefly, an aqueous slurry with a solid content of 40 vol.% was prepared from cerium oxide powders (E. Merck, ref. 12446, Darmstadt, Germany, with an average particle size ( $d_{50}$ ) of 1  $\mu\text{m}$ , 99.9% purity and Fluka Chemica, ref. 22390, Buchs, Switzerland,  $d_{50} = 0.2\ \mu\text{m}$ , purity > 99%; 50 wt% of each) together with 0.8 wt% dispersant (Targon 1128, BK, Ladenburg, F.R. Germany). Additions of 1 wt. % sodium bentonite (MO34, Chemicer, Spain) and 1 wt. % kaolinite (supplied by Rauschert Portuguesa Ltd.) powders were made for structure stabilisation to prevent the collapse of the foam structure during polymer removal. They were mixed together for 12 h in an alumina ball mill jar (solids/ball ratio of 1:4). The resulting stock slurry was then used to impregnate an open-cell polyurethane (PU) foam (grade 20DB, manufactured by Flexipol – Espumas Sintéticas S.A., Portugal). The mean cell size of PU foam was determined to be  $\sim 700\ \mu\text{m}$  (36 ppi) by using image analysis and its density is 21 kg m<sup>-3</sup> [48]. After drying under controlled temperature and humidity conditions overnight, the samples were heated at 1 °C min<sup>-1</sup> to 500 °C for 1 h and subsequently sintered at 1450 °C for 30 min. The same foams were also prepared without any structure stabiliser additives for comparison purposes (hereafter referred to as CFBL; i.e. binder less).

### 2.2. Thermochemical activity testing

The activity of the synthesised materials was first investigated by thermogravimetric analysis performed in controlled atmospheres (TG, Setaram Setsys Evo 1750). About 150 mg of sample was placed in a platinum crucible hung inside the furnace chamber (the foam was preliminary crushed into small parts before being loaded in the crucible). The TG chamber was then evacuated to eliminate residual air and filled with argon gas flowing at 20 mL min<sup>-1</sup> (99.999% purity). The reduction step was carried out at 1400 °C (heating rate of 20 °C min<sup>-1</sup>), held for 45 min, and the mass change was registered

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