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Reticulated porous ceria undergoing thermochemical reduction with high-flux irradiation

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ABSTRACT

A numerical and experimental analysis is performed on the solar-driven thermochemical reduction of ceria as part of a H_2O/CO_2-splitting redox cycle. A transient heat and mass transfer model is developed to simulate reticulated porous ceramic (RPC) foam-type structures, made of ceria, exposed to concentrated solar radiation. The RPC features dual-scale porosity in the mm-range and μm-range within its struts for enhanced transport. The numerical model solves the volume-averaged conservation equations for the porous fluid and solid domains using the effective transport properties for conductive, convective and radiative heat transfer. These in turn are determined by direct pore-level simulations and Monte-Carlo ray tracing on the exact 3D digital geometry of the RPC obtained from tomography scans. Experimental validation is accomplished in terms of temporal temperature and oxygen concentration measurements for RPC samples directly irradiated in a high-flux solar simulator with a peak flux of 1200 suns and heated to up to 1940 K. Effective volumetric absorption of solar radiation was obtained for moderate optically thick structures, leading to a more uniform temperature distribution and a higher specific oxygen yield. The effect of changing structural parameters such as mean pore diameter and porosity is investigated.

1. Introduction

Solar-driven thermochemical cycles for splitting H_2O and CO_2 comprise an endothermic step for the reduction of a metal oxide using concentrated sunlight followed by an exothermic step for the oxidation of the reduced metal oxide with H_2O and CO_2 to form the basic components of syngas, H_2 and CO [1]. Syngas can then be further processed to conventional liquid hydrocarbon fuels (e.g. kerosene, diesel) via Fischer-Tropsch synthesis or other gas-to-liquid technologies. Ceria-based oxides have emerged as highly attractive redox materials [2–14] because of their relatively high oxygen exchange capacities [15–19], fast oxygen-ion transport [20–22] and high oxidation rates [23–27]. The redox reactions with pure ceria are represented by:

$$\text{High}-\text{temperature reduction}: CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2}O_2 \quad (1)$$

$$\text{Low}-\text{temperature oxidation with } H_2O: \\ CeO_{2-\delta} + \delta H_2O \rightarrow CeO_2 + \delta H_2 \quad (2a)$$

$$\text{Low}-\text{temperature oxidation with } CO_2: \\ CeO_{2-\delta} + \delta CO_2 \rightarrow CeO_2 + \delta CO \quad (2b)$$

where the non-stoichiometry δ denotes the reduction extent.

In a previous paper [14], we proposed the use of reticulated porous ceramic (RPC) foam-type structures having dual-scale porosity: mm-size pores with struts containing micron-size pores. The mm-size pores enable volumetric absorption of concentrated solar radiation [28] and thus effective heat transfer during the reduction step, while the micron-size pores within the struts offer increased specific surface area leading to enhanced reaction kinetics during the oxidation step. The thermochemical redox cycle is performed under a temperature/pressure-swing operational mode; thus, the cyclic process is inherently of transient nature and the reduction step, Eq. (1), proceeds as the RPC is heated to the desired upper temperature. It was experimentally shown that these ceria RPC structures with dual-scale porosity remain morphologically stable over 227 consecutive redox cycles in a solar reactor [14]. A representative 3D rendering of a computer tomography (CT) scan of a RPC sample is shown in Fig. 1, along with the scanning electron micrograph (SEM) of the strut's cross section.

Optimization of the RPC structure demands the development of numerical simulation models for heat and mass transfer [13,29,30].

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Nomenclature

Symbols

A_{domain}	area of the volume-averaged domain [m^2]
A_{sf}	fluid-solid interfacial area relevant for the convective transport [m^{-1}]
$c_{p,(.)}$	heat capacity [$J\ kg^{-1}\ K^{-1}$]
$d_{m,(.)}$	mean pore diameter [m]
D_{ArO2}	binary gas diffusion coefficient [$m^2\ s^{-1}$]
F_D	Dupuit-Forchheimer coefficient [m^{-1}]
h_{sf}	interfacial heat transfer coefficient [$W\ m^{-2}\ K^{-1}$]
$H_{(.)}$	Enthalpy [$J\ kg^{-1}$]
HV_{CO}	heating value of CO [$J\ kg^{-1}$]
ΔH_{O2}	reaction enthalpy [$kJ\ mol^{-1}$]
I	intensity of radiative flux [$W\ m^{-2}\ sr^{-1}$]
I_b	blackbody radiation intensity [$W\ m^{-2} sr^{-1}$]
I_{solar}	flux of incident solar radiation [$W\ m^{-2}$]
k_{eff}	effective thermal conductivity [$W\ m^{-1}\ K^{-1}$]
$k_{(.)}$	thermal conductivity [$W\ m^{-1}\ K^{-1}$]
K	permeability [m^2]
L	length of domain [m]
m_{O2}	oxygen mass [kg]
M	molar mass [$kg\ mol^{-1}$]
n_{ppi}	number of pores per inch [–]
$\mathbf{n}$	normal vector [–]
p	pressure [Pa]
Δp	pressure drop [Pa]
p_{O2}	oxygen partial pressure [Pa]
q''_{out}	radiative heat flux leaving the solid domain [$W\ m^{-2}$]
Q_{CO}	Combustion heat of CO [J]
Q_{solar}	cumulative energy of the incident solar radiation [J]
$\mathbf{r}$	position vector
r	total hemispherical reflectance of ceria [–]
r_{O2}	oxygen evolution rate [$kg\ s^{-1}$]
s	path length of a ray [m]
$\mathbf{s}$	direction vector
$\mathbf{s'}$	scattering direction vector
S_{MD}	momentum source for porous media [$kg\ m^{-2}\ s^{-2}$]
$S_{radiative}$	source term for the radiative net flux [$W\ m^{-3}$]
$S_{reradiation}$	source term for the reradiated flux [$W\ m^{-3}$]
S_{solar}	source term for the absorbed high-flux irradiation [$W\ m^{-3}$]
t	time [s]
$T_{(.)}$	temperature [K]
u_D	superficial velocity [$m\ s^{-1}$]
$\mathbf{u}$	velocity vector
V_{cell}	cell volume [m^3]
Y_{O2}	oxygen concentration [–]

Greek symbols

$\alpha_{(.)}$	absorption coefficient [m^{-1}]
β	effective extinction coefficient of RPC [m^{-1}]
δ	nonstoichiometry [–]
$\varepsilon_{(.)}$	porosity [–]
ε_{emit}	total hemispherical emittance of ceria [–]
η	solar-to-fuel energy conversion efficiency [%]
$\mu_{(.)}$	dynamic viscosity [Pa s]
μ_s	cosine of the scattering angle [–]
$\rho_{(.)}$	density [$kg\ m^{-3}$]
σ	scattering coefficient [m^{-1}]
σ_S	Stefan-Boltzmann constant [$W\ m^{-2}\ K^{-4}$]
Φ	scattering phase function [–]
Ω'	solid angle [rad]

Dimensionless numbers

Nu	Nusselt number [–]
Pr	Prandtl number [–]
Re	Reynolds number [–]

Operator

<. >	superficial average

Subscripts

amb	ambient conditions
Ar	argon
CeO_2	ceria
f	fluid phase
O_2	oxygen
RPC-dual	morphological property of RPC with porous struts (dual-scale porosity)
RPC-single	morphological property of RPC with non-porous struts
s	solid phase
strut	morphological property of the porous strut

Abbreviations

CFD	computational fluid dynamics
CT	computed tomography
DPLS	direct pore level simulation
ETH	Swiss Federal Institute of Technology in Zurich
FV	finite volume
HFSS	high flux solar simulator
MC	Monte Carlo
ppi	pores per inch
RPC	reticulated porous ceramic

The effective transport properties can be determined by applying direct pore-level simulations (DPLS) on the exact 3D digital representation of the RPC, including the μm-size pores of the struts, obtained by high-resolution synchrotron CT [31–37]. Since the numerical solution of the governing unsteady Navier-Stokes equations at the pore scale is computational expensive, the volume-averaging theory for porous media is applied for the fluid and solid domains [38–42] by incorporating the effective transport properties determined by DPLS. In this paper, we follow this methodology to develop a heat and mass transfer model of the ceria RPC with dual-scale porosity and investigate its transient behaviour during the reduction step. The model is validated with experimental data obtained from temporal measurements of temperature and reduction extents on RPC samples exposed to high-flux irradiation. To guide the optimization of the RPC structure, virtual samples with a wide range of porosities and mean pore diameters are numerically engineered based on the CT scan of a real RPC sample and their performance is studied by applying the heat and mass transfer model.

2. Experimental methods

Ceria RPC samples with dual-scale porosities were manufactured of cylindrical shape, 30 mm-diameter and 15 mm-height, following the recipe described previously [14]. Two mm-size porosities were selected: 10 and 35 pores per inch (ppi) foams with a corresponding porosity of 0.825 and 0.867, respectively, and mean pore diameter of 2.3 and 0.7 mm, respectively. The strut porosity was 0.26 with a mean pore diameter of 10 μm [37].

The experimental setup is schematically shown in Fig. 2. Experimentation was carried out at ETH's High-Flux Solar Simulator (HFSS) [43], which comprises an array of high-pressure Xenon arcs,