Contents lists available at ScienceDirect

Open Ceramics

journal homepage: www.sciencedirect.com/journal/open-ceramics

Oxidation kinetics of La and Yb incorporated Zr-doped ceria for solar thermochemical fuel production in the context of dopant ionic radius and valence

Kangjae Lee^{a,*}, Nicole Knoblauch^b, Christos Agrafiotis^a, Mathias Pein^{a,c}, Martin Roeb^a, Christian Sattler^{a,c}

^a Institute of Future Fuels, DLR-German Aerospace Center, 51147, Cologne, Germany

^b Institute of Materials Research, DLR-German Aerospace Center, 51147, Cologne, Germany

^c Faculty of Mechanical Science and Engineering, Institute of Power Engineering, Solar Fuel Production, TU Dresden, 01062, Dresden, Germany

ARTICLE INFO

Keywords: Doped ceria Thermochemical redox cycling Thermogravimetric analysis Oxidation kinetics Ionic radii valence

ABSTRACT

The influence of ionic radii and valence of dopants in Ce_{0.9}La_xYb_yZr_{0.1-x-y}O_{2- δ} (x = 0, 0.05, 0.1, y = 0, 0.05, 0.1) on the oxidation kinetics were investigated by thermogravimetric analysis in synthetic air and were compared to undoped ceria. Samples co-doped with Zr–La and Zr–Yb exhibited moderate oxidation kinetics that were slower than undoped ceria, but much faster than 10mol% Zr-doped ceria. The extrinsic oxygen vacancy induced by the trivalent dopants improves the kinetics at oxidation temperatures below 700 °C, where the diffusion, and not the surface exchange reaction is the limiting factor. A smaller ionic radius of the substituent (i.e. $r(Yb^{3+}) < r(La^{3+})$) in the co-doped ceria tends to facilitate lower activation energy resulting in slightly faster oxidation kinetics at temperatures below 700 °C. In contrast, additional extrinsic vacancies are rather obstructive at high temperatures (i.e. T > 700 °C) due to a change of rate limiting mechanism from bulk oxygen diffusion to surface exchange reaction. Overall, the valence of the dopant rather than the ionic radius seems to determine the oxidation kinetics primarily, and additional La or Yb doping on Zr-doped ceria is appealing especially when the applications are focused on low temperature reactions.

1. Introduction

Among the various approaches for renewable hydrogen production, redox oxide-based water-splitting (WS) thermochemical cycles have attracted significant interest since they are the only ones among their counterparts that are directly adaptable to carbon dioxide splitting (CDS) and/or combined CO_2/H_2O splitting for CO or synthesis gas (syngas) production, respectively. Combined with the commercially practiced conversion of syngas to liquid fuels e.g. via the Fischer-Tropsch (FT) technology, these cycles can essentially culminate to the synthesis of carbon-neutral, liquid hydrocarbons from purely renewable and virtually inexhaustible resources: solar energy, water and (waste) carbon dioxide [1]. These cycles operate as per the reactions (1) and (2) below, written for the case of ceria, where high-temperature thermal reduction of the oxide's oxidized state is followed by oxidation of its reduced state via steam and/or carbon dioxide. The indexes $\delta_{\rm red}$ and $\delta_{\rm ox}$ refer to the oxygen nonstoichiometry during reduction and oxidation,

respectively (that can also be written with a single δ , the reduction extent assuming that this is fully replenished during oxidation). Indeed, ceria has been considered as a state-of-the-art redox material in these thermochemical applications for syngas production (e.g. WS, CDS, combined CO₂/H₂O splitting, chemical looping dry reforming of methane, etc.) [2–6], because of its favorable thermodynamic and kinetic properties as well as its chemical and physical stability under extreme redox conditions (i.e. high temperatures and very low oxygen partial pressures) [7–9].

$$\operatorname{CeO}_{2-\delta_{\mathrm{ox}}} \rightarrow \operatorname{CeO}_{2-\delta_{\mathrm{red}}} + (\delta_{\mathrm{red}} - \delta_{\mathrm{ox}})/2O_2$$
 (g) (1)

$$CeO_{2-\delta_{red}} + (\delta_{red} - \delta_{ox})H_2O/CO_2 \quad (g) \rightarrow CeO_{2-\delta_{ox}} + (\delta_{red} - \delta_{ox})H_2/CO \quad (g)$$
(2)

These thermochemical redox cycles are already materialized in demonstration scale with solar-irradiated ceria shaped in reticulated porous ceramic (RPCs) structures also known as ceramic foams [3,4].

* Corresponding author. *E-mail address:* Kangjae.Lee@dlr.de (K. Lee).

https://doi.org/10.1016/j.oceram.2022.100269

Received 28 March 2022; Received in revised form 13 May 2022; Accepted 16 May 2022 Available online 18 May 2022





^{2666-5395/© 2022} The Authors. Published by Elsevier Ltd on behalf of European Ceramic Society. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

However, the reduction extent δ achieved, even under high reduction temperatures, is relatively low. Doping ceria provides a pathway towards improving the reduction extent or reducing the reduction temperature. Specifically, Zr^{4+} is a strong candidate as a dopant and (Ce, Zr) solid solutions are substantially more reducible than ceria as a result of its lower reduction enthalpy, thus providing a better syngas productivity than pure ceria [10–13]. For example, the reduction extent of 10 mol% Zr-doped ceria was approximately double that of ceria when reduced at 1500 °C and at partial pressure of oxygen (p_{O2}) = 10⁻⁴ atm [10]. However, Zr-doped ceria suffers from slow oxidation kinetics that leads to lower syngas productivity depending on oxidation conditions [10, 11]. Thus, it is crucial to significantly improve the oxidation kinetics for Zr-doped ceria to be a viable candidate for thermochemical redox cycling and to eventually replace ceria.

Incorporation of additional dopants into Zr-doped ceria has been studied to enhance thermodynamic and kinetic properties, especially oxidation kinetics. It is reported that the introduction of trivalent cations leads to the formation of extrinsic oxygen vacancies [14,15], which contribute to the increase in oxygen ion conductivity in the crystal lattice of ceria [8,16]. Several trivalent dopants such as La^{3+} or Sm^{3+} combined with Zr^{4+} have been reported to provide a moderate reduction capability than Zr-doped ceria [17,18]. An extensive description of the various dopants tested within this context, can be found in a recent review [19]. However, there is only limited characterization for the ternary-doped ceria available from literature, and the influences of ionic radii or valence of the dopants on oxidation kinetics have not been systematically investigated yet.

In the present work, La³⁺ and Yb³⁺ were incorporated into Zr-doped ceria in quantities resulting in the favorable 10 mol% total dopant concentration reported above, to elucidate the influence of ionic radii and valence of the trivalent and tetravalent dopants on oxidation kinetics under synthetic air investigated via thermogravimetric analysis (TGA). It should be noted that oxidation with air is, in general, substantially faster than CO2/H2O splitting that apparently involves an additional energy required for the CO₂/H₂O dissociation ($\Delta H_{CO2} = 286$ kJ/mol, $\Delta H_{\rm H2O} = 283$ kJ/mol, where $\Delta H_{\rm CO2}$ and $\Delta H_{\rm H2O}$ refer to the reaction enthalpies of CO2 and H2O dissociation, respectively) [20]. On the other hand, the mechanism of solid-state diffusion of oxygen ions for the oxidation with air, in principle, remains the same with those of CO₂/H₂O splitting. Thus, synthetic air was selected as an oxidant that provides a faster overall oxidation kinetics but the same mechanism of oxygen diffusion within the bulk to that of practical applications (e.g. CO₂/H₂O splitting), so that the kinetic analysis focused more on bulk diffusion of oxygen ions is possible. Specific dopant concentrations were carefully chosen so that the effective averaged ionic radius of 10 mol% Zr-La co-doped ceria is the same as that of 10 mol% Yb-doped ceria. Various oxidation temperatures between 1000 °C and 400 °C were considered to inspect any changes in kinetic behavior depending on materials, with a hypothesis that diffusion is a rate-limiting factor at low temperatures, and surface exchange at high temperatures. Activation energy was also calculated based on Arrhenius-type plots during oxidation to provide more information on kinetic limitations.

2. Experimental methods

Materials in this research were synthesized as a powder using a Pechini sol-gel method. Synthesized powders were pelletized using a hydraulic press (PerkinElmer, 25×10^4 N) and a 15-mm pellet die, and then sintered in a box furnace (Nabertherm, HTC) at 1650 °C for 2 h for a better homogeneity and high density to minimize the effect of porosity on solid-state diffusion of oxygen ions that is a key factor to determine oxidation kinetics. Final dimension of pellets was in 12.35 \pm 0.85 mm and 1.96 \pm 0.12 mm for diameter and thickness, respectively. Mass of pellets was 1478.65 \pm 9.91 mg.

X-ray Diffraction (XRD) was performed in a diffractometer (Bruker,

HT-XRD D8 Advance A25) with Cu-K α configuration for 2 θ between 20° and 80°. Energy Dispersive X-ray Spectroscopy (EDS) was performed in a scanning electron microscope (Carl Zeiss, Ultra 55 FEG) to confirm the actual composition of elements for the synthesized samples. Table 1 summarizes the nominal and actual composition obtained by EDS as well as corresponding abbreviation for all doped ceria samples.

A thermogravimetric analyzer (Netzsch, STA 449 F3 Jupiter) was utilized to characterize the oxidation state of materials during chemical oxidation by precisely measuring changes of the sample mass. Total flow rate of the gas mixture was kept at 100 standard cubic centimeter per minute (sccm) with a total pressure of 1 bar, where pure Ar (purity of 99.999%) was delivered during all ramping and reduction steps, and a mixture of 80 sccm synthetic air (80% N2, 20% O2) balanced with 20 sccm Ar as a protective gas required for the TGA measurement was delivered for a chemical oxidation that took place 5 min after the oxidation temperature was reached. All heating and cooling rates were set at 20 °C/min and at 40 °C/min, respectively. Temperature was initially ramped to 800 °C and was maintained for an hour to ensure that the sample was fully oxidized prior to every experiment for consistency. Temperature was then ramped to 1400 °C and maintained for 2 h for reduction. Oxidation was initialized after cooling down to the target oxidation temperature, which was maintained for an hour prior to the following reduction. Thermochemical redox cycling was repeated for all oxidation temperatures (i.e. 1200, 1000, 900, 800, 700, 600, 500, and 400 °C). Exemplary TGA raw data with changes in mass of ceria and corresponding temperature profile is shown in Fig. 1.

3. Results and discussion

Material characterization was performed via XRD and EDS to ensure that the synthesis led successfully to single-phase products. XRD patterns of all doped ceria compositions after heat treatment at 1650 °C are shown in Fig. 2, which exhibit sharp peaks confirming homogeneous distribution of elements. All samples investigated were in cubic fluorite crystal structure and no other phase was observed. Actual compositions in Table 1 were calculated based on EDS results and were very close to nominal composition with a slight deviation of lanthanum contents for CLO10 and CZLO55 samples.

Lattice constants determined by the Rietveld method based on the XRD patterns of Fig. 2 are shown in Table 2. Changes in lattice constants are attributed to lattice expansion or contraction of the cubic fluorite structure by the substitution of dopant cations with an effective ionic radius larger (La^{3+} , Yb^{3+}) or smaller (Zr^{4+}) than that of Ce^{4+} (97 pm). Accordingly, the highest and the lowest lattice constants were achieved with La^{3+} and Zr^{4+} doping, respectively. In the case of ternary mixed oxides (i.e. CZYO55 and CZLO55), lattice constants closely correspond to the calculations based on the averaged ionic radii shown in Table 2. Thus, the measured lattice constant of CZLO55 is approximately as high as that of CYO10, where the slight deviation is possibly because the actual composition of the sample is slightly different from the nominal composition as shown in Table 1. It should be noted that a partial reduction may take place depending on the material at very high temperatures above 1500 °C, which can lead to a crystal lattice expansion [21.22].

Fig. 3a shows the isothermal oxidation of undoped ceria with δ = 0.012 in terms of temporal changes in non-stoichiometry, oxidized at

Table 1
Nominal and actual compositions and abbreviation of all samples.

Abbreviation	Nominal Composition	Actual Composition	
CYO10 CLO10 CZO10 CZYO55 CZLO55	$\begin{array}{c} Ce_{0.9}Yb_{0.1}O_{1.95} \\ Ce_{0.9}La_{0.1}O_{1.95} \\ Ce_{0.9}Zr_{0.1}O_2 \\ Ce_{0.9}Zr_{0.0547}Yb_{0.0453}O_{1.97735} \\ Ce_{0.9}Zr_{0.0547}La_{0.0453}O_{1.97735} \end{array}$	$\begin{array}{c} Ce_{0.9}Yb_{0.1}O_{1.95} \\ Ce_{0.91}La_{0.09}O_{1.96} \\ Ce_{0.9}Zr_{0.1}O_2 \\ Ce_{0.9}Zr_{0.05}Yb_{0.05}O_{1.975} \\ Ce_{0.9}Zr_{0.06}La_{0.04}O_{1.98} \end{array}$	



Fig. 1. Changes in mass of ceria and corresponding temperature profile during the thermogravimetric analysis (reduced at 1400 °C under Ar and oxidized at 1200 – 400 °C under 80 mol% synthetic air balanced by 20 mol% Ar).



Fig. 2. XRD patterns of all doped ceria samples after heat treatment at 1650 °C.

Table 2

Lattice constants of all doped ceria calculated by the Rietveld method based on the XRD patterns, and corresponding averaged dopant ionic radii for Z = 8 based on the values of Shannon (doi: 10.1107/S0567739476001551).

Samples	Lattice Constant [Å]	Averaged Dopant Ionic Radii [pm]
CYO10	5.40810	98.5
CLO10	5.44915	116.0
CZO10	5.38926	84.0
CZYO55	5.39469	90.6
CZLO55	5.41152	98.5

400 – 1200 °C under 80% synthetic air balanced with Ar. Oxidation at higher temperatures is faster than that at lower temperatures as expected, although oxidation kinetics of ceria is generally very rapid [23]. Fig. 3b compares the isothermal oxidation at 800 °C among all ceria-based materials investigated, which indicates the influence of the individual doping ions. Doping Yb³⁺ and La³⁺ on ceria in this work indeed shows faster re-oxidation kinetics comparable to undoped ceria. The size of the doping ion does not seem to have a specific effect on the re-oxidation kinetics, but rather additional oxygen vacancies appear to





Fig. 3. Isothermal oxidation of a) ceria oxidized at 400 - 1200 °C, and b) all samples oxidized at 800 °C. All samples were reduced at 1400 °C under Ar atmosphere.

play a more significant role. The re-oxidation of CZO10 is the slowest among all investigated materials, but as shown in the figure, can be significantly improved by the addition of the specific trivalent cations.

Further kinetic analysis was performed with the exponential decay fit as shown in the following equation to determine the characteristic relaxation time constant during oxidation for each material:

$$\delta = \delta_{\rm red} + A \cdot \exp\left(-\frac{t - t_0}{\tau}\right) \tag{3}$$

where δ is the transient oxygen nonstoichiometry, δ_{red} is the oxygen nonstoichiometry when reduced at thermodynamic equilibrium, A is a fitted constant, and τ is the characteristic relaxation time constant. The magnitude of τ approaches 50%, 36.8%, 13.5% and about 5% (i.e. the system is relaxed to approximately 95%) of the full oxidation after the time t = ln(2) $\tau \sim 0.69\tau$ (half-life), t = τ , t = 2τ , and t = 3τ , respectively. The corresponding relaxation times for all materials investigated are shown in Fig. 4. Undoped ceria exhibits the fastest oxidation kinetics followed by CYO10 and CLO10, whereas CZO10 exhibits the slowest kinetics under the investigated oxidation temperature range. The relaxation time for CYO10 and CLO10 deviates from undoped ceria and from each other at temperatures below 700 °C, where the influence of





Fig. 4. Relaxation time vs. oxidation temperature for all samples. Solid and dashed lines are drawn to guide eyes.

solid-state diffusion of oxygen ions within the bulk is greater than that of the surface exchange reaction. In general, chemical diffusion is more active at higher reaction temperature, which is indicated by the increased chemical diffusion coefficient [8,24,25]. It is reported that the change in chemical diffusion coefficient is substantially larger at temperatures lower than 800 °C [19], which is in part similar to the observation shown in this research. Therefore, the doping elements and their influence on oxygen ion diffusion within the bulk are of an increased importance, especially in the diffusion dominated temperature regime shown above. In this temperature range, the size of the dopant ion, in addition to the valence, is also a decisive factor to determine the oxidation kinetics. CZO10 has a relaxation time substantially longer than any other material investigated, and the temperature dependence also appears noticeably stronger even at high temperatures. Additional Yb³⁺ and La³⁺ doping on Zr-doped ceria significantly improved the oxidation kinetics, and the relaxation times became very close to that of the undoped ceria at higher temperatures. In determining the kinetics of the ceria-based redox reaction, especially at different temperature regimes, it is essential to look at the chemical equilibrium between the gas phase and the solid closely. At the chemical equilibrium, various individual processes can be decisive, and therefore, the following processes must be considered [26]:

- a) Transport of oxygen, water or carbon dioxide within the gas phase
- b) Rate of chemical reaction at the phase boundary (solid gas)
- c) Diffusion of oxygen inside the solid

The driving force of bulk diffusion is the gradient of oxygen vacancy concentration [27], which causes electrons to move simultaneously in the opposite direction to maintain electrical neutrality. High oxygen permeability is thus possible if the exchange of oxygen within the gas phase and at the gas-solid interface, as well as the diffusion within the bulk are rapid. The slowest partial reaction among the aforementioned reactions (e.g. surface exchange reaction in the case of rapid diffusion) becomes a rate limiting factor of the overall reaction. Since diffusion has activation energy different from that of the surface exchange reaction, the rate-limiting mechanism in determining activation energy can change depending on the reaction temperature even if the physical dimension and composition remain constant [19,28,29].

The results are also reflected in an Arrhenius plot in Fig. 5. The observed changes in the slope of the Arrhenius plot indicate that

Fig. 5. Arrhenius plot during oxidation $(\ln 1/\tau \text{ vs. } 10^3/T)$ for all samples. Solid and dashed lines are drawn to guide eyes.

diffusion is the dominant limiting factor at lower temperatures (i.e. T <700 °C), while the surface exchange reactions remains dominant at higher temperatures (i.e. T > 700 °C). This also explains the greater influence of extrinsic vacancies at lower temperatures that induces improved oxygen diffusion. Table 3 summarizes the calculated activation energy of the two different temperature regimes (i.e. $T \ge 700$ °C and T < 700 °C) for all samples. While the difference in activation energy between each temperature regime is rather small for the undoped ceria, CYO10 and CLO10, with a slight increase in the case of CYO10, it becomes very significant for CZO10. Oxygen diffusion is considerably disturbed in the low temperature regime by Zr^{4+} ions, and thus, it can be assumed that the mobility of the intrinsic vacancies is significantly limited by narrowing the possible positions in the crystal lattice with, for example, a pyrochlore-like cluster. Additional extrinsic vacancies via Yb³⁺ and La³⁺ co-doping on Zr-doped ceria positively affect the oxygen diffusion (compare the activation energies at T < 700 °C). At this low temperature, smaller cations (i.e. Yb^{3+}) with lower lattice constants demonstrate slightly faster kinetic behavior than larger ones (i.e. La^{3+}) with larger lattice constants, when incorporated into Zr-doped ceria. The trend is reversed at higher temperatures where CZO10 has a very low activation energy, while additional trivalent cations increase the activation energy. It is important to note that despite the fact that the averaged ionic radii and lattice constants of CYO10 and CZLO55 are closer than any other sample in this work, the kinetic behaviors of CYO10 and CZLO55 are, however, rather similar to those of CLO10 and CZYO55, respectively. Thus, the dopants valence, rather than the ionic radius, proves to have a bigger impact on kinetic behavior, especially at this low temperature regime. Furthermore, the additional extrinsic vacancies, implicated by La and Yb ions doped on Zr-doped ceria, are rather obstructive for the surface exchange reaction.

Table 3

Activation energy of oxidation for all samples at two different temperature regimes ($T \ge 700$ °C and T < 700 °C). Adjusted R² refers to the proximity of the linear fit to calculate the activation energy.

	Materials	$E_{\rm a}$ at $T \ge 700~^{\circ}{ m C}$ [kJ/mol]	Adjusted R ²	$E_{\rm a}$ at $T < 700~^\circ{ m C}$ [kJ/mol]	Adjusted R ²
	CeO ₂ CYO10 CLO10 CZO10 CZYO55 CZLO55	9.44 16.79 19.62 21.54 43.87 42.28	0.9967 0.9934 0.9912 0.9636 0.996 0.9986	6.21 36.22 19.12 99.39 18.91 22.52	0.9838 0.9963 0.9904 0.8365 0.9667 0.9915

4. Conclusions

The analysis of the oxidation kinetics of various doped ceria compositions have shown that, overall, oxidation of undoped ceria, as well as those of CYO10 and CLO10, were much faster than CZO10 at all oxidation temperatures as expected. Addition of Yb³⁺ and La³⁺ to Zrdoped ceria significantly enhanced oxidation kinetics through the formation of extrinsic vacancies. Calculated activation energies further support that slow diffusion of oxygen ions in Zr-doped ceria at low temperatures is improved with additional doping of either Yb^{3+} or La^{3+} . There is a slight improvement in oxidation kinetics in using a smaller cation (i.e. $r(Yb^{3+}) < r(La^{3+})$) with a lower lattice constant as a codoping element, indicated by the lower activation energy at temperatures below 700 °C. However, it is the dopants valence, rather than the ionic radius, that has a bigger role in determining the kinetic behavior, at a low temperature regime. On the other hand, it is noteworthy that further extrinsic vacancies hinder the surface exchange reaction, resulting in higher activation energy at high temperatures. That makes La and Yb appealing candidates for co-doping Zr-doped ceria utilized in applications at considerably low oxidation temperatures. While the findings of this work call for further investigation on the underlying mechanism inducing the changes in the oxidation kinetics behavior of the analyzed compositions, it showcases the importance of the dopant choice when it comes to oxidation kinetics, especially at lower oxidation temperatures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG, Grant No. 1367/5-1).

References

- R. Schäppi, D. Rutz, F. Dähler, A. Muroyama, P. Haueter, J. Lilliestam, A. Patt, P. Furler, A. Steinfeld, Drop-in fuels from sunlight and air, Nature 601 (7891) (2022) 63–68, https://doi.org/10.1038/s41586-021-04174-y.
- [2] K. Lee, D.C. McCord, R.J. Carrillo, B. Guyll, J.R. Scheffe, Improved performance and efficiency of lanthanum-strontium-manganese perovskites undergoing isothermal redox cycling under controlled ph(2)o/ph(2), Energy Fuels 34 (12) (2020) 16918–16926, https://doi.org/10.1021/acs.energyfuels.0c02872.
- [3] P. Furler, J. Scheffe, D. Marxer, M. Gorbar, A. Bonk, U. Vogt, A. Steinfeld, Thermochemical co2 splitting via redox cycling of ceria reticulated foam structures with dual-scale porosities, Phys. Chem. Chem. Phys. 16 (22) (2014) 10503–10511, https://doi.org/10.1039/c4cp01172d.
- [4] D. Marxer, P. Furler, M. Takacs, A. Steinfeld, Solar thermochemical splitting of co2 into separate streams of co and o-2 with high selectivity, stability, conversion, and efficiency, Energy Environ. Sci. 10 (5) (2017) 1142–1149, https://doi.org/ 10.1039/c6ee03776c.
- [5] P. Furler, J. Scheffe, A. Steinfeld, Syngas production by simultaneous splitting of h2o and co2 via ceria redox reactions in a high-temperature solar reactor, Energy Environ. Sci. 5 (3) (2012) 6098–6103, https://doi.org/10.1039/c1ee02620h.
- [6] K. J. Warren, R. J. Carrillo, B. Greek, C. M. Hill, J. R. Scheffe, Solar reactor demonstration of efficient and selective syngas production via chemical-looping dry reforming of methane over ceria, Energy Technol. 8 (6). doi:10.1002/ ente.202000053.

- [7] W. Chueh, S. Haile, Ceria as a thermochemical reaction medium for selectively generating syngas or methane from h2o and co2, ChemSusChem 2 (8) (2009) 735–739, https://doi.org/10.1002/cssc.200900138.
- [8] W. Chueh, S. Haile, A thermochemical study of ceria: exploiting an old material for new modes of energy conversion and co2 mitigation, Phil. Trans. Math. Phys. Eng. Sci. 368 (1923) (2010) 3269–3294, https://doi.org/10.1098/rsta.2010.0114.
- J. Scheffe, A. Steinfeld, Thermodynamic analysis of cerium-based oxides for solar thermochemical fuel production, Energy Fuels 26 (3) (2012) 1928–1936, https:// doi.org/10.1021/ef201875v.
- [10] J.R. Scheffe, R. Jacot, G.R. Patzke, A. Steinfeld, Synthesis, characterization, and thermochemical redox performance of hf4+, zr4+, and sc3+ doped ceria for splitting co2, J. Phys. Chem. C 117 (46) (2013) 24104–24114, https://doi.org/ 10.1021/jp4050572.
- [11] F. Call, M. Roeb, M. Schmücker, H. Bru, D. Curulla-Ferre, C. Sattler, R. Pitz-Paal, Thermogravimetric analysis of zirconia-doped ceria for thermochemical production of solar fuel, Am. J. Anal. Chem. (2013) 37–45, https://doi.org/ 10.4236/ajac.2013.410A1005, 04 (10).
- [12] Y. Hao, C.K. Yang, S.M. Haile, Ceria-zirconia solid solutions (ce1-xzrxo2-delta, x <= 0.2) for solar thermochemical water splitting: a thermodynamic study, Chem. Mater. 26 (20) (2014) 6073–6082, https://doi.org/10.1021/cm503131p.
- [13] M. Takacs, J. Scheffe, A. Steinfeld, Oxygen nonstoichiometry and thermodynamic characterization of zr doped ceria in the 1573-1773 k temperature range, Phys. Chem. Chem. Phys. 17 (12) (2015) 7813–7822, https://doi.org/10.1039/ c4cp04916k.
- [14] T. Kobayashi, S.R. Wang, M. Dokiya, H. Tagawa, T. Hashimoto, Oxygen nonstoichiometry of ce(1-y)sm(y)o(2-0.5y-x) (y = 0.1, 0.2), Solid State Ionics 126 (3-4) (1999) 349-357, https://doi.org/10.1016/S0167-2738(99)00259-3.
- [15] L.J. Gauckler, M. Godickemeier, D. Schneider, Nonstoichiometry and defect chemistry of ceria solid solutions, J. Electroceram. 1 (2) (1997) 165–172, https:// doi.org/10.1023/A:1009928817542.
- [16] S.R. Wang, T. Kobayashi, M. Dokiya, T. Hashimoto, Electrical and ionic conductivity of gd-doped ceria, J. Electrochem. Soc. 147 (10) (2000) 3606–3609, https://doi.org/10.1149/1.1393946.
- [17] F. Call, M. Roeb, M. Schmücker, C. Sattler, R. Pitz-Paal, Ceria doped with zirconium and lanthanide oxides to enhance solar thermochemical production of fuels, J. Phys. Chem. C 119 (13) (2015) 6929–6938, https://doi.org/10.1021/ jp508959y.
- [18] A. Le Gal, S. Abanades, N. Bion, T. Le Mercier, V. Harle, Reactivity of doped ceriabased mixed oxides for solar thermochemical hydrogen generation via two-step water-splitting cycles, Energy Fuels 27 (10) (2013) 6068–6078, https://doi.org/ 10.1021/ef4014373.
- [19] Y. J. Lu, L. Y. Zhu, C. Agrafiotis, J. Vieten, M. Roeb, C. Sattler, Solar fuels production: two-step thermochemical cycles with cerium-based oxides, Prog. Energy Combust. Sci. 75. doi:10.1016/j.pecs.2019.100785.
- [20] C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, Sustainable hydrocarbon fuels by recycling co2 and h20 with renewable or nuclear energy, Renew. Sustain. Energy Rev. 15 (1) (2011) 1–23, https://doi.org/10.1016/j.rser.2010.07.014.
- [21] N. Knoblauch, H. Simon, M. Schmücker, Chemically induced volume change of ceo2-delta and nonstoichiometric phases, Solid State Ionics 301 (2017) 43–52, https://doi.org/10.1016/j.ssi.2017.01.003.
- [22] S.R. Bishop, Chemical expansion of solid oxide fuel cell materials: a brief overview, Acta Mech. Sin. 29 (3) (2013) 312–317, https://doi.org/10.1007/s10409-013-0045-y.
- [23] S. Ackermann, L. Sauvin, R. Castiglioni, J. Rupp, J. Scheffe, A. Steinfeld, Kinetics of co2 reduction over nonstoichiometric ceria, J. Phys. Chem. C 119 (29) (2015) 16452–16461, https://doi.org/10.1021/acs.jpcc.5b03464.
- [24] M.A. Panhans, R.N. Blumenthal, A thermodynamic and electrical-conductivity study of nonstoichiometric cerium dioxide, Solid State Ionics 60 (4) (1993) 279–298, https://doi.org/10.1016/0167-2738(93)90006-0.
- [25] L.Y. Zhu, Y.J. Lu, S.H. Shen, Solar fuel production at high temperatures using ceria as a dense membrane, Energy 104 (2016) 53–63, https://doi.org/10.1016/j. energy.2016.03.108.
- [26] H. Dünwald, C. Wagner, Methodik der Messung von Diffusionsgeschwindigkeiten bei Lösungsvorgängen von Gasen in festen Phasen, Akad. Verl-Ges., 1934.
- [27] B. Bulfin, A.J. Lowe, K.A. Keogh, B.E. Murphy, O. Lübben, S.A. Krasnikov, I. V. Shvets, Analytical model of ceo2 oxidation and reduction, J. Phys. Chem. C 117 (46) (2013) 24129–24137, https://doi.org/10.1021/jp406578z.
- [28] R. Merkle, J. Maier, How is oxygen incorporated into oxides? a comprehensive kinetic study of a simple solid-state reaction with srtio3 as a model material, Angew. Chem. Int. Ed. 47 (21) (2008) 3874–3894, https://doi.org/10.1002/ anie.200700987.
- [29] N. Knoblauch, L. Dörrer, P. Fielitz, M. Schmücker, G. Borchardt, Surface controlled reduction kinetics of nominally undoped polycrystalline ceo2, Phys. Chem. Chem. Phys. 17 (8) (2015) 5849–5860, https://doi.org/10.1039/C4CP05742B.