Oxygen nonstoichiometry and thermodynamic characterization of Zr doped ceria in the 1573–1773 K temperature range†

M. Takacs, J. R. Scheffe*‡ and A. Steinfeld

This work encompasses the thermodynamic characterization and critical evaluation of Zr4+ doped ceria, a promising redox material for the two-step solar thermochemical splitting of H2O and CO2 to H2 and CO. As a case study, we experimentally examine 5 mol% Zr4+ doped ceria and present oxygen nonstoichiometry measurements at elevated temperatures ranging from 1573 K to 1773 K and oxygen partial pressures ranging from 4.50 × 10⁻³ atm to 2.3 × 10⁻⁴ atm, yielding higher reduction extents compared to those of pure ceria under all conditions investigated, especially at the lower temperature range and at higher pO2. In contrast to pure ceria, a simple ideal solution model accounting for the formation of isolated oxygen vacancies and localized electrons accurately describes the defect chemistry. Thermodynamic properties are determined, namely: partial molar enthalpy, entropy, and Gibbs free energy. In general, partial molar enthalpy and entropy values of Zr4+ doped ceria are lower. The equilibrium hydrogen yields are subsequently extracted as a function of the redox conditions for dopant concentrations as high as 20%. Although reduction extents increase greatly with dopant concentration, the oxidation of Zr4+ doped ceria is thermodynamically less favorable compared to pure ceria. This leads to substantially larger temperature swings between reduction and oxidation steps, ultimately resulting in lower theoretical solar energy conversion efficiencies compared to ceria under most conditions. In effect, these results point to the importance of considering oxidation thermodynamics in addition to reduction when screening potential redox materials.

Introduction

Solar-driven thermochemical redox cycles utilizing nonstoichiometric metal oxides are capable of splitting H2O and CO2 to produce H2 and CO (syngas), the precursors to the catalytic synthesis of conventional liquid fuels.1,2 Ceria (CeO2) is currently considered a state-of-the-art material because it displays rapid oxidation and reduction kinetics and is morphologically stable over a range of temperatures and reduction extents.3 The two-step thermochemical cycle using CeO2 as reactive intermediate is represented by:

Reduction at Tred:

\[ \text{CeO}_2 = \text{CeO}_{2-\delta} + \frac{\delta}{2} \text{O}_2 \] (1)

Oxidation at Tox:

\[ \text{CeO}_{2-\delta} + x \text{H}_2 \text{O} + \beta \text{CO}_2 = \text{CeO}_2 + x \text{H}_2 + \beta \text{CO} \] (2)

where \( x + \beta = \delta \). In the endothermic first step, eqn (1), ceria is reduced typically under an atmosphere of low oxygen partial pressure (pO2) at elevated temperatures, generally Tred > 1573 K, where the process heat is delivered by concentrated solar energy. In an exothermic second step, eqn (2), the reduced ceria is re-oxidized with H2O or CO2 at lower temperatures, generally Tox < 1573 K, to produce H2 or CO. The oxygen nonstoichiometry (\( \delta \)) achieved during reduction depends strongly on Tred and pO2 in the system4,5 and is directly related to the maximum amount of H2/CO capable of being produced per mole ceria in the second step. As ceria is not consumed within the process, the net reactions are H2O = H2 + 1/2O2 and CO2 = CO + 1/2O2. In contrast to direct thermolysis, two-step redox cycles bypass the separation of fuel and O2 at high temperatures. Contrary to photochemical processes, solar thermochemical processes utilize the entire solar spectrum and thus offer a thermodynamically favorable path towards fuel production.

Since the reduction extent of ceria is generally lower than those obtained by other appropriate redox materials (e.g. ferrite, ...
Experimental section

Synthesis technique and sample characterization

5 mol% Zr$^{4+}$ doped CeO$_2$ (CZO$_5$) powder was synthesized by sol–gel method as described by Scheff et al.$^8$ Briefly, Ce(NO$_3$)$_3$·6H$_2$O (Aldrich, catalog number 238538), Zr(NO$_3$)$_4$·6.3H$_2$O (Aldrich, catalog number 243493) and dry citric acid (Merck, catalog number 818707) in aqueous solution were used to carry out the synthesis. The ratio of the metal cations to the citric acid was 1 : 1.5. CeO$_2$ powder was purchased from a commercial distributor (Aldrich, catalog number 211575). CeO$_2$ and CZO$_5$ powders were uniaxially cold-pressed at 5 tons and sintered at 1873 K under air atmosphere for 5 hours into ~1250 mg dense cylindrical pellets. The approximate dimensions after sintering were 7 mm diameter and 5 mm height. The CZO$_5$ dopant concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS) analysis and was 4.5 mol%. Powder X-ray diffraction (XRD) was performed in the Bragg Brentano geometry using Cu K$_\alpha$ radiation (Philips, PANalytical/X’Pert MPD/DY636, $\lambda$ = 1.5406 Å, 20 = 10–100°, 0.01 s$^{-1}$ scan rate, 45 kV/20 mA output). Scanning electron microscopy (SEM) of the dense pellets were conducted on a TM-1000 Microscope (Hitachi, 15 kV accelerating voltage). XRD patterns and SEM images are shown in ESL.$^9$

Experimental measurements

Oxygen nonstoichiometry ($\delta$) was measured using a thermogravimetric analyzer (TGA, Setaram Setsys Evolution). Samples were suspended to the scale with a custom-made platinum hook to ensure good exposure to the purge gas and eliminate gas diffusion limitations. Special care was taken to ensure that reduction and oxidation reactions were not limited by gaseous mass transfer but by solid-state diffusion and/or surface reactions. The $p_{O_2}$ of the surrounding gas atmosphere was controlled by mixing Ar (Messer, Argon 4.6) with an O$_2$–Ar mixture (Messer, 0.5% O$_2$ 5.0 in Ar 5.0). Gases were mixed with electronic mass fl ow controllers (Brooks, Model 5850TR, accuracy ±1%) with a constant total flow rate of 200 ml min$^{-1}$. The gas species and concentrations at the outlet were monitored by mass spectrometry (Pfeiffer Vacuum, OmniStar GSD 320). Temperature was varied between 1573 K and 1773 K and $p_{O_2}$ between 4.50 × 10$^{-3}$ atm and 2.3 × 10$^{-4}$ atm. In all measurements, the sample mass ($m_s$) was equilibrated at a constant temperature and $p_{O_2}$. Following each equilibrium measurement, the $p_{O_2}$ was rapidly changed by adapting the O$_2$–Ar gas mixture, resulting in a temporal weight change of the sample due to evolving or uptake of oxygen until a new equilibrium was reached. To correct for buoyancy, blank runs were performed with Al$_2$O$_3$ sintered pellets of same dimensions. An additional correction was applied for a small amount of sample sublimation (<0.04 wt%) observed above 1723 K.

Oxygen nonstoichiometry

An exemplary experiment showing the dynamics of the reduction (decreasing $p_{O_2}$) and oxidation (increasing $p_{O_2}$) of CZO$_5$ and CeO$_2$ at 1573 K and 1773 K is shown in Fig. 1(a). Initially, their
weights were stabilized at a constant $p_{O_2}$, followed by a rapid $p_{O_2}$ decrease to initiate reduction. After stabilization at the new $m_s$, $p_{O_2}$ is increased back to its initial value to commence oxidation. At 1573 K, the reduction and oxidation of CZO_5 are noticeably slower than those of CeO_2. However, at 1773 K, the kinetic rates are similar for both materials. If surface reactions are assumed not to be limiting – a reasonable assumption at these length scales – this would imply that the activation energy for ambipolar diffusion is higher in the case of CZO_5.

Fig. 1(b) shows the mass change in wt% of CeO_2 and CZO_5 as a function of time for $T = 1673$ K for a broader range of $p_{O_2}$ and Fig. 1(c) shows all the reduction and oxidation runs over all temperatures and $p_{O_2}$. Samples were heated to 5 different set point temperatures followed by isothermal reduction and oxidation by stepwise changing $p_{O_2}$. As seen, CZO_5 releases more oxygen than CeO_2 under all measurement conditions. The much slower oxidation of CZO_5 at 1073 K agrees well with the observation that its activation energy for ambipolar diffusion is higher than CeO_2 (cf. Fig. 1(a) and discussion above). A total sublimated mass of 0.40 mg and 0.32 mg at 1773 K was observed for CeO_2 and CZO_5, respectively.

Oxygen nonstoichiometry is calculated according to:

$$\delta = \frac{\Delta m_s}{M_O}$$

where $\Delta m_s$ is the relative weight loss at equilibrium, $M_s$ is the molar mass of the sample and $M_O$ the molar mass of O. Measured $\delta$ versus $p_{O_2}$ of CeO_2 and CZO_5 for all temperatures investigated are shown in Fig. 2(a) and (b), respectively. Open symbols show $\delta$ measurements of this work whereas literature data are shown by closed symbols (Panlener et al.) and crossed symbols (Iwasaki et al.18). Lines indicate defect models used to describe $\delta$, presented in the following section. As seen, $\delta$ of CZO_5 is higher over the whole measurement range investigated compared to CeO_2. Improvement in oxygen release is highest at low $T_{red}$ and high $p_{O_2}$. For example, at $T = 1623$ K and $p_{O_2} = 4.50 \times 10^{-3}$ atm, the improvement is almost 90% per mole of oxide ($\delta = 0.010$ for CZO_5 and $\delta = 0.0055$ for CeO_2) and around 27% at $T = 1773$ K and $p_{O_2} = 2.3 \times 10^{-4}$ atm ($\delta = 0.042$ for CZO_5 and $\delta = 0.033$ for CeO_2). Nonstoichiometry of CZO_5 at 1573 K is not shown because the sample weight did not equilibrate completely within the allotted time due to slower kinetics. $\delta$ values of pure CeO_2 measured in this work are slightly higher than the values reported in literature, especially towards higher $p_{O_2}$. The reason for the discrepancy is not clear but may be related to sample impurities and sublimation. Panlener et al.4 performed oxygen nonstoichiometry measurements based on thermogravimetric analysis over a broad range of $p_{O_2}$ from 0.01 atm to $10^{-23}$ atm between 873 K and 1773 K while Iwasaki et al.18 performed measurements only at temperatures up to 1573 K.

**Defect model**

Defect models were used to describe the chemical equilibria of both CeO_2 and CZO_5. For small reduction extents (as small as $\delta = 0.01$ for pure ceria and higher with dopant type and dopant concentration) the reduction of ceria and doped ceria can be described in Kröger-Vink notation as:

$$2\text{Ce}_x^+ + \text{O}_2^0 \rightarrow 2\text{Ce}_x^{0+} + \frac{1}{2}\text{O}_2$$

where oxygen atoms on oxygen lattice sites ($O_2^0$) and cerium on cerium lattice sites ($Ce_2O_x$) are in equilibrium with gaseous oxygen, doubly ionized oxygen vacancies ($V_{O}^{2+}$) and electrons localized on cerium lattice sites ($Ce_x^{0+}$). Assuming there are no
cluster formations between the various defects, $\delta$ can be described by:\textsuperscript{10,20}

$$\delta = \text{constant} \cdot p_{O_2}^{-1/6} \quad T = \text{const.}$$  \hspace{1cm} (5)

which implies a slope of $-1/6$ when plotting $\log \delta$ versus $\log p_{O_2}$.

For larger deviations from stoichiometry, the formation of oxygen vacancy–polaron associations $(\text{Ce}_{\text{Ce}}^\bullet \text{V}_{\text{O}}^\bullet \text{Ce}_{\text{Ce}}^\bullet)^x$ should be accounted for, and is described as:

$$2\text{Ce}_{\text{Ce}}^\bullet + \text{V}_{\text{O}}^\bullet = (\text{Ce}_{\text{Ce}}^\bullet \text{V}_{\text{O}}^\bullet \text{Ce}_{\text{Ce}}^\bullet)^x$$  \hspace{1cm} (6)

Assuming all defects form associations according to eqn (6),

$$\delta = \text{constant} \cdot p_{O_2}^{-1/2} \quad T = \text{const.}$$  \hspace{1cm} (7)

As seen in the case of CeO$_2$ (Fig. 2(a)), the slope of $\log \delta$ vs. $\log p_{O_2}$ best describing the data is close to $-1/5$, indicating that eqn (5) cannot adequately describe its defect equilibria, in agreement with previous investigations.\textsuperscript{4,16,19,21,22} A slope of $-1/5$ indicates that a combination of both defect models (eqn (4) and (6)) is needed to accurately describe ceria’s defect chemistry, as evidenced by Otake et al.\textsuperscript{19} who showed that the isolated defect model is only valid for very low nonstoichiometries ($\delta < 0.01$). A slope of $-1/6$, on the other hand adequately describes the data of CZO$_5$ over the entire measurement range. This is consistent with observations of 3+ valence dopants such as Sm$^{3+}$,\textsuperscript{22,23} Gd$^{3+}$,\textsuperscript{22,24,25} and Y$^{3+}$\textsuperscript{19} but in such cases much higher concentrations are required to describe the measurement data with only a single defect model. For example, when doping ceria with 10 mol% Y$^{3+}$, a single isolated defect model can only describe the data up to $\delta \approx 0.02$, whereas in the case of 20 mol% it is valid until $\delta \approx 0.03$. Here, with only 5 mol% Zr$^{4+}$ a single model appears to adequately describe $\delta$ at least until $\delta \approx 0.04$.

The nonstoichiometry as a function of $T$ and $p_{O_2}$ may be modelled by fitting appropriate equilibrium constants from eqn (4) and (6) to the experimental data. To do so, the following site and charge relations for 4+ valence dopants and pure ceria\textsuperscript{19} are needed:

$$[\text{Ce}_{\text{Ce}}^\circ] = 1 - 2\delta - X$$  \hspace{1cm} (8)

$$[O_{\text{O}}^\circ] = 2 - \delta$$  \hspace{1cm} (9)

$$2[\text{V}_{\text{O}}^\bullet] = [\text{Ce}_{\text{Ce}}^\circ]$$  \hspace{1cm} (10)

$$2\delta = [\text{Ce}_{\text{Ce}}^\circ] + 2[\text{Ce}_{\text{Ce}}^\circ \text{V}_{\text{O}}^\bullet \text{Ce}_{\text{Ce}}^\circ]^x$$  \hspace{1cm} (11)

where $X = 0.045$ is the dopant concentration of Zr$^{4+}$ in the case of CZO$_5$. Thus, the equilibrium constants $K_1$ for eqn (4) and $K_2$ for eqn (6) are given by:

$$K_1 = \frac{[\text{Ce}_{\text{Ce}}^\circ]^2 [\text{V}_{\text{O}}^\bullet]^{1/2} p_{O_2}^{1/2}}{[\text{Ce}_{\text{Ce}}^\circ]^2 [O_{\text{O}}^\circ]^{1/2}} = \frac{4 [\text{V}_{\text{O}}^\bullet] p_{O_2}^{1/2}}{(1 - 2\delta - X)^2 (2 - \delta)}$$  \hspace{1cm} (12)

$$K_2 = \frac{[\text{Ce}_{\text{Ce}}^\circ]^2 [\text{V}_{\text{O}}^\bullet]^x}{[\text{Ce}_{\text{Ce}}^\circ]^2 [\text{V}_{\text{O}}^\bullet]^x} = \frac{\delta - [\text{V}_{\text{O}}^\bullet]}{4 [\text{V}_{\text{O}}^\bullet]^3}$$  \hspace{1cm} (13)

$K_1$ and $K_2$ can be determined through a least square minimization of eqn (12) and (13) with the experimental nonstoichiometry data. Results are summarized in Fig. 3(a) and (b) for CeO$_2$ and CZO$_5$, respectively. As expected, $K_1$ for CZO$_5$ is higher compared to that for CeO$_2$ because of its higher reduction extent. Additionally, the slope for CeO$_2$ is higher than that for CZO$_5$, indicating that its reduction enthalpy (at least at low $\delta$ where the reaction is dominated by $K_1$) is higher and consistent with Kuhn et al.\textsuperscript{10} $K_2$ for CeO$_2$ is decreasing with increasing temperature meaning defect interactions become less predominant at higher temperatures. $K_2$ for CZO$_5$ does not show a meaningful trend and values are much smaller than for CeO$_2$, because defect associations are probably not significant under the conditions investigated. In fact, in the case of CZO$_5$ at 1573 K, the best fit of $K_2$ is of orders of magnitude below the fits at higher temperatures. These findings directly support the conclusions drawn from Fig. 2, namely that a single isolated defect
model appears to adequately describe the defect chemistry of CZO_5, whereas electron-vacancy associations should be additionally taken into account in the case of CeO_2. By fitting $K_1$ and $K_2$ over all experimental data, indicated by the lines in Fig. 2(a) and (b), it can be seen that the agreement is very good. When including both defect models, the RMS deviations of the fitted log $P_{O_2}$ (cf. Fig. 2) are 0.013 and 0.005 in the case of CeO_2 and CZO_5, respectively. Both deviations are less than the uncertainty in the $P_{O_2}$ setting, equal to 0.017. Considering only the isolated defect model (eqn (4)) the RMS deviations are 0.094 for CeO_2 and 0.038 for CZO_5. This reflects that defect associations are more important in the case of CeO_2 than in the case of CZO_5. The improvement in the RMS deviation for CZO_5 when including electron-vacancy associations may rather be a result of having an additional fitting parameter than having a more adequate physical model (cf. trend of $K_2$ for CZO_5 in Fig. 3(b)).

Based on computational investigations, Yang et al.\textsuperscript{26} concluded that an oxygen vacancy is most likely created close to a Zr\textsuperscript{4+}-dopant which might serve as nucleation center for vacancy clustering. Based on these results, Kuhn et al.\textsuperscript{10} proposed that the considerably smaller Zr\textsuperscript{4+}, compared with Ce\textsuperscript{4+}, prefers a 7-fold coordination (instead of 8-fold) with oxygen which can be achieved if an oxygen vacancy is created next to the smaller Zr\textsuperscript{4+} cation. Therefore, (Ce\textsuperscript{4+}O\textsuperscript{2-})\textsuperscript{7+} instead of (Ce\textsuperscript{4+}O\textsuperscript{2-}O\textsuperscript{2-}Ce\textsuperscript{4+})\textsuperscript{5+} associations were also tested, but this did not improve the isolated defect model within the $\delta$-range investigated.

**Thermodynamic properties**

Thermodynamic properties, namely partial molar enthalpy ($\Delta h_{O_2}$), partial molar entropy ($\Delta s_{O_2}$) and partial molar Gibbs free energy ($\Delta g_{O_2}$), defined per mole of monoatomic oxygen, can be determined as a function of $\delta$, temperature and $P_{O_2}$ according to eqn (14) and (15).

$$\Delta g_{O_2} = \frac{1}{2}RT \ln P_{O_2} \quad (14)$$

$$\Delta g_{O_2} = \Delta h_{O_2} - T\Delta s_{O_2} \quad (15)$$

By combining eqn (14) and (15) it is clear that $\Delta h_{O_2}$ and $\Delta s_{O_2}$ as a function of $\delta$ can both be solved by determining the slope and intercept of $\ln P_{O_2}$ versus $1/T$ for a constant $\delta$, as shown in eqn (16).

$$\frac{1}{2} \ln P_{O_2} = \frac{\Delta h_{O_2}}{RT} - \frac{\Delta s_{O_2}}{R} \mid_{\delta=\text{const.}} \quad (16)$$

Constant $\delta$ values are obtained by interpolating our defect models within the temperature range investigated (1573 K to 1773 K) and a slightly extrapolated $P_{O_2}$ range (±20% of the measured $-\log P_{O_2}$ range). Results of $\Delta h_{O_2}$ and $\Delta s_{O_2}$ versus $\delta$ are shown in Fig. 4 and 5, respectively, for CeO_2 (open squares) and CZO_5 (open triangles) measurements from this work. For reference we have included CeO_2 data of Panlener et al.,\textsuperscript{4} Campserveux et al.,\textsuperscript{17} Bevan et al.,\textsuperscript{5} and Sørensen.\textsuperscript{16} Additionally, measurements of CZO_5 by Kuhn et al.\textsuperscript{10} and Hao et al.\textsuperscript{12} are indicated by closed and crossed triangles, respectively. Measurements of 20 mol% Zr\textsuperscript{4+} doped CeO_2 (CZO_20) by Kuhn et al.\textsuperscript{10} and Hao et al.\textsuperscript{12} are indicated by closed circles and crossed circles, respectively. In general, it can be observed that $\Delta h_{O_2}$ increases with increasing dopant concentration. This is expected due to the ease with which Zr\textsuperscript{4+} doped ceria reduces compared to pure ceria.

Towards higher $\delta$, the $\Delta h_{O_2}$ values are in good agreement with literature data of CeO_2\textsuperscript{4,5,16,17} and CZO_5:10,12 However, at lower $\delta$, they deviate. The same trend can be observed for $\Delta s_{O_2}$.
Deviations can be attributed primarily to different measurement temperatures and to a lesser extent to differences in nonstoichiometry measurements. For example, the literature data shown in Fig. 4 and 5 were calculated based on measurements below 1573 K or as an average of measurements at higher (>1573 K) and lower temperatures (<1573 K), whereas values of this work are based on measurements only above 1573 K. Although it is often assumed that \( \Delta h_{\text{ox}} \) and \( \Delta s_{\text{ox}} \) are independent of temperature, this simplifying assumption is not always valid. For example, a temperature dependence of \( \Delta h_{\text{ox}} \) is observed for the case of CeO\(_2\) where two reactions dictate the defect chemistry. The degree of dependence varies in accordance with the magnitude of \( K_2 \) in regards to \( K_1 \). Sørensen has shown that the slope of \( \Delta G_{\text{ox}} \) vs. \( T \) (see eqn (15)) is constant at \( T < 1623 \) K and \( \delta < 0.08 \), but decreases at higher temperatures due to the formation of sub-phases. The more negative \( \Delta h_{\text{ox}} \) values at low \( \delta \) from this work are in agreement with Sørensen. Deviations in the measurements of CZO\(_5\) can be additionally attributed to differences in Zr\(^{4+}\) dopant concentrations. For example, in this work the dopant concentration is 4.5 mol\% compared to 5.2 mol\% in the work of Hao et al.

The reduction of nonstoichiometric ceria is represented by:

\[
\frac{1}{\delta_{\text{red}} - \delta_{\text{ox}}} \Delta G_{\text{red}} = \frac{1}{\delta_{\text{red}} - \delta_{\text{ox}}} \Delta G_{\text{ox}} = \Delta G_{\text{ox},\text{red}} + \frac{1}{2} \Delta G_{\text{H}_2\text{O}}
\]  

The standard Gibbs free energy change of eqn (17), \( \Delta G_{\text{red}} \), can be calculated by integrating \( \Delta G_{\text{ox}} \) over the range of \( \delta \):

\[
\Delta G_{\text{red}} = \int_{\delta_{\text{ox}}}^{\delta_{\text{red}}} \Delta G_{\text{ox}} d\delta
\]

where \( \delta_{\text{ox}} \) is the nonstoichiometry before reduction and \( \delta_{\text{red}} \) is the nonstoichiometry after reduction. \( \Delta G_{\text{red}} \) as a function of temperature for the reduction of CeO\(_2\), CZO\(_5\), and CZO\(_{20}\) from \( \delta_{\text{ox}} = 0 \) to \( \delta_{\text{red}} = 0.1 \) (solid lines) and \( \delta_{\text{ox}} = 0 \) to \( \delta_{\text{red}} = 0.05 \) (dashed lines). At lower temperatures, where \( \Delta G_{\text{red}} > 0 \), reduction would only proceed if additional work is performed to the system, e.g. lowering \( p_{\text{O}_2} \) by vacuum pumping or flushing with inert gas. Therefore, this implies that at lower temperatures (<2000 K), CZO\(_{20}\) can be reduced more easily compared to CZO\(_5\) and CeO\(_2\), which is related to its less negative \( \Delta h_{\text{ox}} \) and consistent with experimental observations. For all materials, a higher \( \Delta G_{\text{red}} \) for \( \delta_{\text{red}} = 0.1 \) compared to \( \delta_{\text{red}} = 0.05 \) is related to the increasing \( \Delta s_{\text{ox}} \) with increasing \( \delta \) (cf. Fig. 5).

The oxidation of nonstoichiometric ceria and doped ceria with H\(_2\)O is described by:

\[
\frac{1}{\delta_{\text{red}} - \delta_{\text{ox}}} \Delta G_{\text{red}} = \frac{1}{\delta_{\text{red}} - \delta_{\text{ox}}} \Delta G_{\text{ox}}(\text{H}_2\text{O}) + \frac{1}{2} \Delta G_{\text{H}_2\text{O}}
\]

Fig. 5: Partial molar entropy of CeO\(_2\) (open squares) and CZO\(_5\) (open triangles) as a function of \( \delta \) and a comparison to literature data of CeO\(_2\) (Panlener et al.\(^4\) closed squares, Bevan et al.\(^5\) half closed squares, Sørensen.\(^6\) closed squares, Kuhn et al.\(^10\) closed triangles, Hao et al.\(^12\) crossed triangles) and CZO\(_{20}\) (Kuhn et al.\(^10\) closed circles, Hao et al.\(^12\) crossed circles).

Fig. 6: Gibbs free energy change versus temperature for the reduction of CeO\(_2\) (black), CZO\(_5\) (blue) and CZO\(_{20}\) (red) from \( \delta_{\text{ox}} = 0 \) to \( \delta_{\text{red}} = 0.1 \) (solid lines) and \( \delta_{\text{ox}} = 0 \) to \( \delta_{\text{red}} = 0.05 \) (dashed lines).
thermodynamically favorable only if additional work is added to the system.

By combining the reaction equilibrium constant of water dissociation ($K_W$)

$$K_W = \frac{n_{H_2}P_{O_2}^{1/2}}{[n_{H_2}O_i - n_{H_2}]}$$  \hspace{1cm} (20)

with eqn (14), equilibrium H$_2$ yields can be calculated according to:

$$\Delta g_{ox} (\delta_{ox} = \delta_{red} - n_{H_2}) = RT \ln \left[ \frac{K_W (n_{H_2}O_i - n_{H_2})}{n_{H_2}} \right]$$  \hspace{1cm} (21)

where $n_{H_2}$ is the molar amount of H$_2$ produced at equilibrium per mole oxide, and $n_{H_2}O_i$ is the initial molar amount of H$_2$O in the system per mole oxide. $n_{H_2}$ is obtained by iteratively solving eqn (21) and is shown in Fig. 8 versus temperature for CeO$_2$ (black), CZO$_5$ (blue), and CZO$_{20}$ (red). $n_{H_2}O_i$ is set equal to $\delta_{red}$ (solid lines) and $100 \times \delta_{red}$ (dashed lines), where $\delta_{red}$ is the nonstoichiometry achieved after reduction at $T_{red} = 1773$ K and $p_{O_2} = 2.3 \times 10^{-4}$ atm. The calculations reaffirm that the oxidation with H$_2$O becomes thermodynamically less favorable with increasing Zr$^{4+}$ dopant concentrations. For example, for $n_{H_2}O_i = \delta_{red}$, maximum $n_{H_2}$ is reached at $T \leq 900$ K for CeO$_2$, $T \leq 700$ K for CZO$_5$, and $T < 400$ K for CZO$_{20}$. If $n_{H_2}O_i$ is increased by a factor of hundred, these oxides can be oxidized at higher temperatures but at the expense of heating excess H$_2$O. In this case, maximum $n_{H_2}$ is obtained at as high as 1200 K for CeO$_2$, 1100 K for CZO$_5$, and 500 K for CZO$_{20}$. For CZO$_{20}$, $n_{H_2}$ is only shown up to 0.042 moles because $\Delta h_0$ and $\Delta g_{ox}$ are not available at $\delta \leq 0.03$. Because $\Delta h_0$ and $\Delta g_{ox}$ of CeO$_2$ and CZO$_5$ are not measured over the range $\delta = 0$ to 0.1, they are assumed to be constant for low $\delta$ and taken as the average from literature data $^{4,5,10,16,17}$ for high $\delta$.

Fig. 7  Gibbs free energy change versus temperature for the oxidation of CeO$_2$ (black), CZO$_5$ (blue), and CZO$_{20}$ (red) with H$_2$O from $\delta_{red} = 0.1$ to $\delta_{ox} = 0$ (solid lines) and $\delta_{red} = 0.05$ to $\delta_{ox} = 0$ (dashed lines).

Fig. 8  Molar amount of H$_2$ produced by oxidation of CeO$_2$ (black), CZO$_5$ (blue) and CZO$_{20}$ (red) with H$_2$O as a function of temperature assuming $n_{H_2}O_i = \delta_{red}$ (solid lines) and $100 \times \delta_{red}$ (dashed lines) where $\delta_{red}$ is the nonstoichiometry achieved after reduction at $T_{red} = 1773$ K and $p_{O_2} = 2.3 \times 10^{-4}$ atm ($\delta_{red} = 0.0328$ for CeO$_2$, $\delta_{red} = 0.0417$ for CZO$_5$, and $\delta_{red} = 0.0725$ for CZO$_{20}$).

### Efficiency analysis

The theoretical solar-to-fuel energy conversion efficiency ($\eta_{solar-to-fuel}$) for the case of hydrogen production is defined as:

$$\eta_{solar-to-fuel} = \frac{HHV_{H_2}n_{H_2}}{Q_{input,min}}$$  \hspace{1cm} (22)

where $HHV_{H_2} = 285.5$ kJ mol$^{-1}$ is the higher heating value of H$_2$. $Q_{input,min}$ is the minimum input of energy required to produce $n_{H_2}$ and comprises the solar process heat for driving the reduction, for heating the redox material from $T_{ox}$ to $T_{red}$, and for generating steam at $T_{red}$ as well as the equivalent minimum work to drive the reduction for the case of $\Delta h_{red} > 0$. Assuming no heat recuperation between the redox steps,

$$Q_{input,min} = \frac{1}{\eta_{absorption}} \left( \Delta h_{red} (\delta_{red} - \delta_{ox}) + \int_{T_{ox}}^{T_{red}} c_p dT + \Delta h_{H_2O}^{298K_T_{ox}} n_{H_2}O_i + \frac{\Delta g_{red}}{\eta_{Carnot}} (\delta_{red} - \delta_{ox}) \right)$$  \hspace{1cm} (23)

where $\Delta h_{red}$ is the enthalpy change of the reduction (eqn (17)),

$$\Delta h_{red} = \frac{\delta_{red} - \delta_{ox}}{\delta_{ax}}$$  \hspace{1cm} (24)

$\Delta h_{H_2O}^{298K_T_{ox}}$ is the thermal energy required to heat H$_2$O from ambient temperature to $T_{ox}$ (obtained from NIST-JANAF tables), $n_{H_2}O_i$ is the initial molar amount of H$_2$O determined by eqn (21), and $c_p$ is the specific heat capacity of pure ceria. $^{27}$ The excess H$_2$O needed is calculated for $n_{H_2}$ approaching $\delta_{red}$. Note that the maximum $\eta_{solar-to-fuel}$ may not be attained by completely re-oxidizing the material, as shown by Chueh et al. $^{28}$ and Furler et al.,$^{29}$ but an
overall optimization routine is outside the scope of this work. Due to the low dopant concentration of Zr⁴⁺, $c_p$ of CZO₀.₅ and CZO₂₀ are assumed to be identical to that of pure CeO₂. $\dot{Q}_{\text{input,min}}$ is assumed to be delivered by concentrated solar energy. The solar absorption efficiency ($\eta_{\text{absorption}}$) for a blackbody cavity-receiver is given by:

$$\eta_{\text{absorption}} = 1 - \frac{\sigma T_{\text{red}}^4}{C}$$

(25)

where $\sigma$ is the Stefan–Boltzmann constant, $I = 1 \text{ kW m}^{-2}$ the direct normal irradiation (DNI) and $C = 2000$ the solar flux concentration ratio. The fourth term in eqn (23) is the minimum work required to drive the reduction at conditions for which $\Delta g_{\text{red}} > 0$; when $\Delta g_{\text{red}} \leq 0$ this term is omitted. $\eta_{\text{Carnot}}$ is the efficiency of an ideal heat engine converting solar heat at $T_{\text{red}}$ to work.³⁰

A contour plot of $\eta_{\text{solar-to-fuel}}$ shown as a function of $\delta_{\text{red}}$ and $T_{\text{ox}}$ is shown in Fig. 9 for CeO₂ (a) and CZO₀.₅ (b) respectively. $P_{O_2} = 10^{-6} \text{ atm}$ is assumed for the efficiency calculations resulting in reduction temperatures of 1744 K for CeO₂ and 1741 K for CZO₀.₅ needed to reach $\delta_{\text{red}} = 0.1$ and 1564 K and 1510 K respectively to reach $\delta_{\text{red}} = 0.02$. It is shown that the maximum efficiency for CeO₂ is slightly higher compared to CZO₀.₅. $\eta_{\text{solar-to-fuel}}$ is slightly greater than 17% at $\delta_{\text{red}} = 0.1$ ($T_{\text{ox}} = 1050 \text{ K}$) for CeO₂ and slightly greater than 16% at $\delta_{\text{red}} = 0.1$ ($T_{\text{ox}} = 880 \text{ K}$) for CZO₀.₅. Simply stated, the energy savings during reduction of CZO₀.₅ cannot compensate the additional energy inputs due to the less favorable re-oxidation with H₂O (lower $T_{\text{ox}}$ and/or higher $n_{H_2O,i}$ compared to CeO₂). In general $\eta_{\text{solar-to-fuel}}$ rapidly decreases towards higher $T_{\text{ox}}$ as the re-oxidation with H₂O gets thermodynamically less favorable and an increasing amount of excess steam has to be heated in order to fully oxidize the reduced material. Towards lower $T_{\text{ox}}$, $\eta_{\text{solar-to-fuel}}$ decreases as the temperature difference between oxidation and reduction increases and towards lower $\delta_{\text{red}}$ it decreases as the amount of H₂ produced (equal to $\delta_{\text{red}}$) decreases compared to the sensible energy required to heat the oxide. Qualitatively these results are in agreement with calculations reported in literature for pure ceria,⁷,³¹,³² and indicate the tradeoffs between an isobaric redox cycle driven by temperature swing and an isothermal redox cycle driven by pressure swing. Heat recovery, not accounted for in Fig. 9, can significantly boost $\eta_{\text{solar-to-fuel}}$.⁷ When heat recovery is used for generating steam at $T_{\text{ox}}$, $\eta_{\text{solar-to-fuel}}$ peaks at 19% for CeO₂ and 18% for CZO₀.₅. If, in addition, heat recovery is used to heat the redox material from $T_{\text{ox}}$ to $T_{\text{red}}$, $\eta_{\text{solar-to-fuel}}$ peaks at 41% and 44% for CeO₂ and CZO₀.₅, respectively. Results for CZO₂₀ are not shown because thermodynamic data are not available at $\delta \leq 0.03$ and also because calculations always predict maximum $\eta_{\text{solar-to-fuel}}$ at lowest $T_{\text{ox}}$ (400 K) and highest $\delta_{\text{red}}$ (0.1).

Maximum $\eta_{\text{solar-to-fuel}}$ as a function of $P_{O_2}$ is shown in Fig. 10 for CeO₂ (solid lines), CZO₀.₅ (dashed lines) and CZO₂₀ (dotted lines) where $\delta_{\text{red}} = 0.1$ (a) and $\delta_{\text{red}} = 0.05$ (b). Additionally, $T_{\text{red}}$ where maximum $\eta_{\text{solar-to-fuel}}$ is obtained is shown in Fig. 10. Estimates of

Fig. 9 $\eta_{\text{solar-to-fuel}}$ shown as contour lines for CeO₂ (a) and CZO₀.₅ (b) as a function of $\delta_{\text{red}}$ and $T_{\text{ox}}$ assuming reduction at $P_{O_2} = 10^{-6} \text{ atm}$ and subsequent complete re-oxidation with steam.

Fig. 10 Maximum $\eta_{\text{solar-to-fuel}}$ and $T_{\text{red}}$ versus $P_{O_2}$ for CeO₂ (solid lines), CZO₀.₅ (dashed lines) and CZO₂₀ (dotted lines) assuming $\delta_{\text{red}} = 0.1$ (a) and $\delta_{\text{red}} = 0.05$ (b).
$T_{\text{red}}$ of CZO_20 were calculated according to the methodology described by Yang et al. using the thermodynamic data of Kuhn et al. It is observed that CeO$_2$ shows the highest $T_{\text{solar-to-fuel}}$ under all conditions investigated and CZO_20 shows the lowest $T_{\text{solar-to-fuel}}$. Although CZO_20 reduces at substantially lower temperatures compared to CZO_5 and CeO$_2$, the lower energy input during reduction cannot compensate the higher energy input during oxidation with H$_2$O. In general, $T_{\text{solar-to-fuel}}$ increases with decreasing $p_{O_2}$ meaning less energy is required to reduce the oxide by lowering $p_{O_2}$ compared to increasing $T_{\text{red}}$.

**Conclusions**

Oxygen nonstoichiometry measurements of Zr$^{4+}$ doped ceria at elevated temperatures presented in this work are largely in agreement with the trends observed in works performed at lower temperatures (<1573 K), namely: for a given $T_{\text{red}}$ and $p_{O_2}$ the reduction extent increases and the reduction enthalpy decreases with increasing Zr$^{4+}$ concentration. Extracted thermodynamic properties are also largely in agreement with previous data, but they deviate at low nonstoichiometries especially for the case of pure ceria. This is likely due to the fact that they are slightly temperature dependent, especially at higher temperatures (>1623 K) where different sub-phases can be expected. Interestingly, in the case of 5 mol% Zr$^{4+}$ doped ceria, a single defect model is capable of describing the nonstoichiometry data over the entire measurement range ($\delta = 0.01$ to 0.04) and therefore the thermodynamic properties can be assumed to be independent of temperature. This is an important distinction when extrapolating nonstoichiometries to conditions that have not yet been measured experimentally.

Although the nonstoichiometry increases with increasing Zr$^{4+}$ dopant concentration, oxidation with steam becomes thermodynamically less favorable and has to be conducted at lower temperatures or with excess amounts of steam. This ultimately results in lower theoretical solar-to-fuel energy conversion efficiencies compared to that for pure ceria. Therefore, when screening potential redox materials it is important to consider both steps of the cycle, i.e. the materials ability to release lattice oxygen and its oxidation potential with H$_2$O and CO$_2$. We have assumed that reduction and oxidation are driven to completion, but maximum efficiencies may be found at lower extents. In general, when we compare with the thermodynamic properties of pure ceria, a relatively lower partial molar enthalpy and a relatively higher partial molar entropy are desired, resulting in $\Delta G_{\text{red}} < 0$ at lower $T_{\text{red}}$ and $\Delta G_{\text{ox},H_2O} < 0$ at higher $T_{\text{ox}}$ which in turn yields a smaller temperature swing between the redox steps. Besides thermodynamic aspects, fast reaction kinetics and long term chemical and morphological stability are obviously essential.

**Nomenclature**

$C$  
Flux concentration ratio of incident radiation

$C_{\text{Ce}^x}$  
Cerium atom on cerium lattice site

$C_{\text{Ce}^z}$  
Electron localized on cerium lattice site

$\left(C_{\text{Ce}^x}V_{\text{O}}^{-}\text{Ce}_{\text{Ce}^z}\right)^x$  
Oxygen vacancy–polaron association

$C_p$  
Heat capacity of CeO$_2$ (kJ mol$^{-1}$ K$^{-1}$)

$\Delta G$  
Standard Gibbs free energy change of H$_2$O dissociation (kJ mol$^{-1}$)

$\Delta G_{\text{O}}$  
Partial molar free energy (kJ mol$^{-1}$)

$\Delta G_{\text{ox}}$  
Standard Gibbs free energy change of ceria oxidation (with O$_2$) (kJ mol$^{-1}$)

$\Delta G_{\text{ox},H_2O}$  
Standard Gibbs free energy change of ceria oxidation (with H$_2$O) (kJ mol$^{-1}$)

$\Delta G_{\text{red}}$  
Standard Gibbs free energy change of ceria reduction (kJ mol$^{-1}$)

$\Delta h_{\text{H}_2O}$  
Energy to heat water (kJ mol$^{-1}$)

$\Delta h_{\text{ox},H_2O}$  
Higher heating value of H$_2$ (kJ mol$^{-1}$)

$\Delta h_{\text{red}}$  
Partial molar enthalpy (kJ mol$^{-1}$)

$I$  
Enthalpy change of reduction (kJ mol$^{-1}$)

$K_1$  
Normal beam insolation (W m$^{-2}$)

$K_2$  
Ideal solution model equilibrium constant

$K_w$  
Defect interaction model equilibrium constant

$M_0$  
Molar mass of O (g mol$^{-1}$)

$m_s$  
Weight of reactive sample (mg)

$M_s$  
Molar mass of reactive sample (g mol$^{-1}$)

$\Delta m_s$  
Relative weight loss of reactive sample

$n_{\text{H}_2}$  
Molar amount of H$_2$ at equilibrium (mol)

$n_{\text{H}_2O}$  
Initial molar amount of H$_2$O (mol)

$\eta_{\text{solar-to-fuel}}$  
Oxygen atom on oxygen lattice site

$\eta_{\text{oxygen}}$  
Oxygen partial pressure (atm)

$\eta_{\text{input,min}}$  
Minimum amount of input energy to produce H$_2$ (kJ mol$^{-1}$)

$\eta_{\text{universal}}$  
Universal gas constant (J mol$^{-1}$ K$^{-1}$)

$\eta_{\text{partial}}$  
Partial molar entropy (J mol$^{-1}$ K$^{-1}$)

$\text{Temperature (K)}$  
Temperature (K)

$\text{Reduction temperature (K)}$  
Oxidation temperature (K)

$D_{\text{ion}}$  
Doubly ionized oxygen vacancy

$D_{\text{ion}}$  
Molar dopant concentration of Zr$^{4+}$

$\beta$  
Stoichiometric coefficient of H$_2$O

$\delta$  
Stoichiometric coefficient of CO$_2$

$\delta_{\text{ox}}$  
Degree of oxygen nonstoichiometry

$\delta_{\text{red}}$  
Degree of oxygen nonstoichiometry after reduction

$\eta_{\text{abs}}$  
Degree of oxygen nonstoichiometry after oxidation

$\eta_{\text{abs}}$  
Solar absorption efficiency

$\eta_{\text{Carnot}}$  
Carnot efficiency

$\sigma$  
Solar-to-fuel energy conversion efficiency

$\text{Stefan–Boltzmann constant (W m}^{-2}\text{K}^{-4})$  
Stefan–Boltzmann constant (W m$^{-2}$ K$^{-4}$)

**Acknowledgements**

We gratefully acknowledge the financial support by the Swiss Competence Center Energy & Mobility, the Helmholtz-Gemeinschaft Deutscher Forschungszentren (Virtuelles Institut SolarSyngas),
and the European Research Council under the European Union’s ERC Advanced Grant (SUNFUELS – no. 320541).

References