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Structural characterization and oxygen nonstoichiometry of ceria-zirconia (Ce_{1-x}Zr_xO_{2- δ}) solid solutions

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Abstract

The oxygen nonstoichiometry and crystalline structure of ceria-zirconia $Ce_{1-x}Zr_xO_{2-\delta}$ (CZO) (x = 0.05, 0.1, 0.2, 0.5, and 0.8) solid solutions, commercially used as oxygen storage materials, have been examined using thermogravimetry, X-ray diffraction, and Raman spectroscopy. In this study detailed data describing oxygen vacancy concentrations, obtained at intermediate to high pO_2 , are interpreted with the aid of point defect equilibria relationships. For cubic CZO ($x \le 0.2$), the ease of reducibility dramatically increased with increasing Zr content, as reflected by an ultimate >40% decrease in reduction enthalpy, with a corresponding shift in onset of reduction to higher pO_2 . The impact of pre-existing oxygen vacancies on the larger reduction enthalpy found for Y doped CZO, as compared with this study, is discussed, as is evidence that Zr increases the electron migration energy in ceria by 50%. The reducibility of tetragonal CZO ($x \ge 0.2$) was found to increase following redox cycling. This enhanced reducibility is believed to be related to ordering and is partially negated by a high temperature (1000 °C) heat treatment.

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1. Introduction

Three way emission control catalysts (TWC) are designed to limit harmful emissions from automobile exhausts by fully oxidizing carbon monoxide and hydrocarbons to carbon dioxide and water, while simultaneously reducing nitrogen oxides to nitrogen and oxygen. A stoichiometric air to fuel ratio is required for optimal conversion [1], but inevitable variations induced by irregular driving conditions can be compensated for by the use of oxygen storage materials (OSM), which act, in effect, as chemical air to fuel ratio regulators. Excess oxygen, under fuel-lean conditions in the gas phase, is stored in the OSM by filling

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oxygen vacancies, while oxygen deficiency under fuel-rich conditions is compensated by the release of oxygen from the lattice, thereby forming oxygen vacancies. Under the operating conditions of a TWC, oxygen buffering needs to proceed rapidly to allow quick adjustment of the oxygen partial pressure (pO_2), thus requiring high oxygen surface exchange rates (elevated k_{ex}) across the gas/solid interface, as well as fast oxygen transport within the lattice (high D_v). Since oxygen is stored by filling oxygen vacancies in the OSM the potential for large deviations in oxygen nonstoichiometry δ , in for example $CeO_{2-\delta}$, is desirable, maximizing the oxygen storage capacity. Through the reduction/oxidation of Ce^{4+} (Ce_{Ce}^x) and Ce^{3+} (Ce'_{Ce}), $CeO_{2-\delta}$ has the ability to release and incorporate oxygen according to the reaction:

$$2Ce_{Ce}^{x} + O_{O}^{x} \iff 2Ce_{Ce}^{/} + V_{o}^{\bullet} + \frac{1}{2}O_{2}(gas)$$
(1)

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with O_o^x and V_o^{\bullet} denoting oxygen ions on oxygen lattice sites and doubly charged oxygen vacancies, using the Kröger–Vink notation [2], respectively.

A significant reduction in ceria occurs only at relatively low pO_2 and elevated temperatures [3,4], resulting in limited oxygen nonstoichiometry under TWC operating conditions. Substituting isovalent cations such as Zr⁴⁺ for Ce⁴⁺ has been found to substantially enhance the reducibility of ceria and hence its oxygen storage capacity [5-7], resulting in the implementation of $Ce_{1-x}Zr_xO_{2-\delta}$ (CZO) in TWCs and heterogeneous catalysis [5,6,8]. This finding is at first surprising, given that Zr^{4+} is a fixed valent ion and also isovalent with the host Ce^{4+} ion, so that it cannot induce the creation of charge compensating defects (as, for example, with Gd^{3+}) or valency change (as, for example, with $Pr^{3+/4+}$) [9–12]. Instead, the underlying mechanism appears to be strain related, whereby the considerably smaller Zr⁴⁺, compared with Ce⁴⁺, prefers a 7-fold coordination, in contrast to the 8-fold coordination of the fluorite cation, resulting in a driving force for the formation of oxygen vacancies associated with structural relaxation through reduction of Ce^{4+} to the larger Ce^{3+} [13–15]. According to first principle calculations, the Zr dopant serves as low energy regions for oxygen vacancy formation and clustering [13]. Additionally, the long-term thermal morphological and/or redox stability of pure ceria has been shown to be improved by the addition of Zr [5,13,14,16]. CZO is being investigated in other energy-related applications as well, such as solid oxide fuel cells and solar water splitting, where it may improve the structural and thermal stability and catalytic activity [16-18].

CZO is known to exhibit a cubic to tetragonal fluorite phase transition with increasing Zr content, ultimately forming the monoclinic phase at high Zr concentrations [19,20]. The tetragonal phase (t-phase), with a c- to a-axis bond length ratio (c/a) equal to 1.4, exhibits two distortions t'(c/a)a = 1.01) and t''(c/a = 1), all belonging to the P4₂/nmc space group. From measurement of lattice parameters one can distinguish between the t' and t'' phases, though due to similarities between the t'' and cubic structures, Raman and other vibrational spectroscopy methods are typically used to distinguish the primarily oxygen ion distortions between the two phases [19,21]. The phase change from cubic to t'' leads to significant changes in ionic bond strength and an increase in the number of vibrational modes [22–24]. Small changes in oxygen ion-cation coordination, not always detectable as additional peaks (or peak splitting) by X-ray diffraction (XRD), are often detectable by Raman spectroscopy. Similar to the cubic to tetragonal distortion in CZO, relaxation of oxygen atoms away from their ideal fluorite positions and the formation of ordered zones or domains have been observed in cubic fluorite Ca-stabilized zirconia and hafnia by electron diffraction [25].

The appearance of cubic, t', and t'' phases in CZO depends strongly on the Zr content and, based on Raman spectroscopy and XRD analysis, a phase diagram was proposed by Yashima et al. for CZO fabricated by the solid-

state reaction method [19]. The cubic-tetragonal (c-t'')phase boundary at room temperature was indicated at a zirconium content of $0.1 \le x \le 0.2$, while transition to t' occurs at around x = 0.3. In a more recent study [26] CZO prepared by the solid-state method showed a cubic structure up to $x \approx 0.3$. For $0.6 \le x \le 0.8$, after calcination at 1650 °C, mixtures of the cubic, t and t' phases were observed [27]. For nanocrystalline CZO, with an average particle size of 8-20 nm, synthesized by a nitrate-glycine gel combustion process, the phase boundaries for cubic/t''and t''/t' were x = 0.15 and 0.32, respectively [28]. Comparison of CZO powders with different particle sizes between ~ 6 and 80 nm revealed a shift in the apparent phase boundaries to slightly higher zirconia concentrations, as the particle size decreased and the solubility of zirconia in each phase increased [29]. In summary, the position of the phase boundaries for CZO can only be taken as approximate as t' and t'' are metastable phases and the degree of distortion of the cubic fluorite structure strongly depends on the synthesis method, particle size and thermal history [26].

While a number of studies have shown the enhanced reducibility of ceria on doping with isovalent Zr [7,30,31], more complete nonstoichiometry data, as well as a detailed analysis of the thermodynamics of defect formation, are lacking. A defect model presented by Otake et al. [32] focused on the nonstoichiometry of Y-doped CZO, and a similar model was used to analyze electrical conductivity measurements in nanocrystalline CZO by Boaro et al. [33]. Janvier et al. [34] also used a similar defect model to describe the surface oxygen nonstoichiometry of undoped ceria and CZO, although their study was limited to a very narrow range of pO_2 (0.01–0.21 atm). Other electrical conductivity measurements focused on high, >80 mol.%, Zr- or Y-doped CZO [35,36]. Kim et al. and Zhou et al. measured the thermodynamics of reduction, finding dramatically reduced enthalpies of reduction for several CZO compositions, although no defect model was explicitly described [7,30]. Computational studies have also confirmed a decrease in reduction enthalpy and oxygen vacancy formation energy in ceria upon addition of Zr [37,38].

To address the lack of a systematic examination of the undoped CZO system with respect to nonstoichiometry, particularly at intermediate to high pO_2 , a series of solid solutions of CZO with low (1%) to high (80%) concentrations of Zr were prepared and studied. Structural features were examined by XRD and Raman spectroscopy. Oxygen nonstoichiometry was systematically studied as a function of Zr content, pO_2 , and temperature. The results obtained were analyzed with respect to the defect model described below and compared with data from the literature.

2. Theory

The equilibrium mass action equation for the reduction reaction described in Eq. (1) is:

$$K_{\text{Red}} = \frac{[\text{Ce}_{\text{Ce}}^{/}]^{2} [V_{\text{o}}^{\bullet}] (p O_{2})^{1/2}}{[\text{Ce}_{\text{Ce}}^{x}]^{2} [O_{\text{o}}^{x}]}$$
(2)

where K_{Red} is the equilibrium constant and square brackets signify the concentration of defect species. It follows that at low pO_2 the majority of defects in ceria will be V_o^{\bullet} and Ce_{Ce}^{\prime} , leading to the approximate charge neutrality relation

$$[\mathrm{Ce}_{\mathrm{Ce}}^{\prime}] \approx 2[\mathrm{V}_{\mathrm{o}}^{\bullet}] \tag{3}$$

Mass conservation dictates the following two equations for the anion and cation sub-lattices.

$$(1-x)[Ce_{1-x}Zr_{x}O_{2}] = [Ce_{ce}^{x}] + [Ce_{ce}^{\prime}]$$
(4)

$$2[\operatorname{Ce}_{1-x}\operatorname{Zr}_{x}\operatorname{O}_{2}] = [\operatorname{O}_{O}^{x}] + [\operatorname{V}_{o}^{\bullet}]$$
(5)

where $[Ce_{1-x}Zr_xO_2]$ is the concentration of CZO, of the order of 10^{22} cm⁻³. The nonstoichiometry (δ) is defined by

$$\delta = \frac{[\mathbf{V}_{o}^{\star}]}{[\mathbf{C}\mathbf{e}_{1-x}\mathbf{Z}\mathbf{r}_{x}\mathbf{O}_{2}]} \tag{6}$$

For the case of small deviations from stoichiometry, where $[V_o^*] \ll [O_0^x]$ and $[Ce_{Ce}^{/}] \ll [Ce_{Ce}^x]$, the denominator in Eq. (2) is approximately constant for a change in pO_2 . Substituting Eq. (3) into Eq. (2) and writing the vacancy concentration in terms of δ using Eq. (6) it can readily be shown that

$$\delta \sim K_{\text{Red}}^{1/3} (pO_2)^{-1/6} \tag{7}$$

A key parameter defining the material reducibility, the enthalpy of reduction (H_{Red}) , is defined in the following equation:

$$K_{\text{Red}} = K_{\text{Red}}^0 \exp\left(-\frac{H_{\text{Red}}}{kT}\right) \tag{8}$$

where K_{Red}^0 is a constant which includes the vibrational entropy. By fitting Eq. (7) to δ vs. $\log pO_2$ isotherms and plotting the resulting K_{Red} terms on an Arrhenius plot, H_{Red} is obtained.

Due to large changes in the nonstoichiometry upon reduction, interactions among defects and lattice ions may alter the enthalpy of reduction [12,39–42]. Therefore, as an additional approach to analyzing the thermodynamics of defect formation, the partial molar enthalpy and entropy of reduction were derived as a function of δ , following the approach of Mizusaki and co-workers [41–43]. The oxygen chemical potential μ_O of CZO in equilibrium with the gas phase at a certain oxygen partial pressure is given by

$$\mu_{\rm O} - \mu_{\rm O}^0 = \frac{RT}{2} \ln p O_2 \tag{9}$$

where μ_0^0 corresponds to the equilibrium in 1 atm O₂. Additionally, the chemical potential can be correlated with the partial molar reduction enthalpy h_0 and entropy s_0 :

$$\mu_{\rm O} = h_{\rm O} - Ts_{\rm O} \tag{10}$$

From Eqs. (9) and (10) and the Gibbs–Helmholtz equation we obtain:

$$h_{\rm O} - h_{\rm O}^0 = \frac{R}{2} \frac{\partial \ln p O_2}{\partial \frac{1}{T}} \tag{11}$$

and

$$s_{\rm O} - s_{\rm O}^0 = -\frac{1}{2} \frac{\partial RT \ln p O_2}{\partial T}$$
(12)

3. Experimental details

Solid solutions of $Ce_{1-x}Zr_xO_{2-\delta}$ (x = 0.01, 0.05, 0.2, 0.5 and 0.8, denoted CZO_100x) were prepared by the Pechini method [44], which favors a homogeneous, uniform mixing and distribution of metal cations, on the molecular scale, in multicomponent materials. Stoichiometric amounts of Ce(NO₃)₃·6H₂O (Sigma-Aldrich, St Louis, MO) and $ZrO(NO_3)_2 \cdot xH_2O$ (x = 2.5) (Alfa Aesar, Ward Hill, MA) were dissolved in distilled water. The water content of the metal nitrate-hydrate complexes was confirmed by oxidizing the compounds at elevated temperatures in air and measuring the weight change by thermogravimetry. An excess amount of ethylene glycol (Alfa Aesar, Ward Hill, MA) and citric acid (Alfa Aesar, Ward Hill, MA) was added to the metal nitrate solution, followed by heating to about 100 °C under stirring. The polymeric precursor obtained was dried overnight at about 120 °C and then fired at 600 °C for 5 h. The powders obtained were confirmed as single phase CZO solid solutions by XRD analysis (Cu Ka, 45 kV and 40 mA, PANalytical X'Pert Pro Multipurpose Diffractometer, Almelo, The Netherlands) performed at room temperature in air.

The powders were uniaxially pressed into pellets and sintered in air for several hours at 1200-1400 °C. The relative densities were 76%, 68% and 70% for the CZO 1, CZO 5 and CZO_20 pellets, respectively, while the CZO_50 and CZO 80 pellets exhibited 52% and 60% relative density, respectively. The powders were characterized at room temperature in air by XRD as above and Raman scattering (Kaiser Optical Hololab 5000R Raman Microscope, Kaiser Optical Systems, Ann Arbor, MI, 785 nm laser wavelength). Undoped ZrO₂ (99.7%, $H_f < 75$ ppm, Alfa Aesar, Ward Hill, MA) and CeO₂ (REacton[®], 99.99%, Alfa Aesar, Ward Hill, MA) powders were also examined by Raman spectroscopy for comparison with the CZO fabricated here. Lattice parameters were obtained from the XRD patterns by Rietveld analysis using HighScorePlus (PANalytical, Almelo, The Netherlands). Chemical analysis was performed by wavelength dispersive spectrometry (WDS) in a JEOL JXA-8200 Superprobe (JEOL, Peabody, MA), with the Zr fraction in reasonably good agreement with the target compositions of the different CZO pellets given in Table 1.

The average grain size of the as-prepared powders and sintered pellets was determined by transmission electron microscopy (TEM) (JEOL 200CX general purpose electron microscope) and scanning electron microscopy (SEM) (FEI/Philips XL30 FEG ESEM) (Fig. 1) at ~8 and 220–290 nm, respectively.

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Table 1 Microprobe compositional analysis of CZO pellets (measured Zr content error \sim 1–3.5%).

Sample ID	Zr content (%)		Compositional difference (%	
	Target	Measured		
CZO_1	1	0.86	14.5	
CZO_5	5	4.64	7.1	
CZO_20	20	18.34	8.3	
CZO_50	50	46.89	6.2	
CZO_80	80	79.37	0.8	

For nonstoichiometry measurements the porous pellets were placed in an alumina holder in a thermogravimetric analyzer (Cahn 2000, Cahn Instruments Inc., Cerritos, CA). pO_2 was controlled using O_2 – N_2 , CO–CO₂ or H₂– H₂O–N₂ gas mixtures and monitored using a zirconiabased oxygen sensor placed in the vicinity of the sample. The change in oxygen content $\Delta\delta$ with varying pO_2 and temperature was calculated from the sample mass change Δw according to:

$$\Delta \delta = \frac{M_{\rm S} \cdot \Delta w}{M_{\rm O} \cdot m_0} \tag{13}$$

where $M_{\rm S}$ is the molar mass of the sample, $M_{\rm O}$ is the molar mass of oxygen and m_0 is the sample mass at room temperature in air. Equilibrium between the sample and surrounding gas atmosphere was confirmed once stationary values for the sample weight and sample oxygen partial pressure were obtained. The error in mass measurement was ~30 µg, which is reflected by error bars in the figures depicting nonstoichiometry data. Buoyancy effects of gas and temperature on the measured mass changes were corrected, based on reference measurements for an alumina sample of similar geometry.



Fig. 1. Representative SEM image of the porous sintered pellet (CZO_5) used for TGA. (Inset) TEM image of the as-prepared CZO powder (CZO_50).

4. Results

4.1. Structural characterization

The XRD peaks of the powder samples (data not shown) are relatively broad, indicating a small crystallite size, in agreement with that expected from the Pechini method [45] and the calculated particle size of ~ 8 nm based on TEM analysis (Fig. 1). All powders appear to be cubic, single phase, although upon high temperature heat treatment the peaks become sharper due to crystal growth, while secondary phases become evident for high Zr contents (Fig. 2a) [7,46]. The pure cubic phase is observed only for pellets with higher ceria contents ($x \leq 0.2$), while the CZO_50 pellet shows both tetragonal and cubic peaks, and the CZO_80 pellet is single phase tetragonal, in agreement with the literature [7,17,29,47].

Lattice parameters, extracted using Rietveld refinement of the XRD patterns in Fig. 2a, are presented in Table 2 with the crystal structure, space group, and phase fraction. The cubic lattice parameters are plotted in Fig. 2b as a function of Zr content, showing a linear decrease with increasing Zr up to 20 mol.%, in agreement with the literature [7,14,21,28,48,49]. For 50 and 80 mol.% Zr c/a is ~1.02 for the tetragonal phases reported in Table 2, corresponding to the t' phase and in agreement with the phase boundaries in the CZO phase diagram [19,29].

The Raman spectra of the CZO powders and sintered pellets are given in Fig. 3. The measured Raman spectra of undoped ZrO₂ and CeO₂ commercial powders are also shown for comparison. The Raman spectra measured here are similar to previous studies examining phases in zirconia- or yttria-doped CZO ([26,29]), with Raman modes assigned based on Lopez et al. [24], Merle et al. [50], and Bolon and Gentleman [51]. There is a clear change in the spectra with increasing Zr content, indicating a transition from cubic $(x \leq 0.2)$ to tetragonal distortion, t'', $(0.5 \le x \le 0.8)$, to monoclinic (x = 1). The Raman spectra for the cubic phase ($x \le 0.2$) show a strong peak at ~ 465 – 480 cm⁻¹ (Fig. 4a), assigned to the O-Ce-O or O-Zr-O stretching mode in F2g symmetry [24,29]. Additionally, CZO_1, CZO_5, and CZO_20 also exhibit a small peak at around 600 cm⁻¹, not observed for pure ceria, which has previously been shown to arise from lattice distortions due to the presence of cation defects (i.e. Zr in the CeO₂ lattice) [29,52] and is separate from the peak believed to be related to oxygen vacancies occurring at \sim 560 cm⁻¹ [53]. In Fig. 3b–d, an apparent plateau at the top of the F_{2g} peak is observed for CZO_5 and CZO_20 powders and, to a lesser extent, for the sintered samples (i.e. CZO_50). Similarly to the XRD spectra, the cubic peaks of the sintered pellets also exhibit a smaller full width at half maximum (FWHM) than the powders (Fig. 4b), in agreement with the increased crystallinity/reduced microstrain indicated by a prior study on undoped ceria [54]. For both cubic CZO powders and pellets the position of the F_{2g} peak blue shifts to higher wavenumbers with increasing Zr content, while the



Fig. 2. (a) XRD patterns of $Ce_{1-x}Zr_xO_{2-\delta}$ sintered pellets. * denotes tetragonal phase peaks. (b) The cubic lattice parameters of CZO plotted as a function of Zr content. The lattice parameter of undoped CeO₂ is from the literature [48,49]. The dashed line represents a linear fit for $0 \le x \le 0.2$.

FWHM increases (Fig. 4a and b). In this range of Zr content a predominantly cubic phase exists, allowing changes in the oxygen–cation–oxygen nearest neighbor stretching mode to be followed. As previously shown for yttria-stabilized zirconia thin films [54,55], the blue shift typifies strengthening of bonds, consistent with a decrease in the lattice parameters. At the same time there should be an incipient elongation along the *c* direction, ultimately leading to a phase transition to tetragonal for larger Zr contents [19]. The effective blue shift of the F_{2g} mode by 15 wavenumbers is comparable with findings on Raman measurements during symmetry reduction (cubic to t'') observed for yttria-doped and pure zirconia [56].

For larger concentrations of Zr (>20 mol.% Zr) the original F_{2g} stretching mode splits into the B_{1g} and E_g bands for the cubic to tetragonal phase transition, as observed in Fig. 3e. The B_{1g} modes represent an asymmetric cation– oxygen–cation stretching mode, while E_g accounts for an asymmetric cation–oxygen–cation stretching mode arising from fully symmetric coupling of the B_{1g} mode [24]. Additionally, a symmetric Zr–O–Zr stretching mode, the A_{1g} band, is also observed for CZO_80 [24,51]. The existence of all six expected Raman modes for the t'' phase for CZO_80 indicates a complete phase transition, as opposed to CZO_50, in which only four modes are obvious, indicating an incomplete phase transition.

Table 2

Lattice parameters of CZO determined by Rietveld refinement from the XRD patterns shown in Fig. 2a.

Material	Crystal system/ space group (wt.% of phase)	a (Å)	b (Å)	<i>c</i> (Å)
CZO_1	Cubic/Fm-3 m	5.40815 (3)		
CZO_5	Cubic/Fm-3 m	5.39678 (5)		
CZO_20	Cubic/Fm-3 m	5.3544 (1)		
CZO_50	Cubic/Fm-3 m (62%)	5.33797 (7)		
	Tetragonal/P4 ₂ /nmc (38%)	5.1484 (1)	5.1484 (1)	5.2400 (2)
CZO_80	Tetragonal/P42/nmc	5.1491 (1)	5.1491 (1)	5.2414 (2)

4.2. Nonstoichiometry of CZO

Fig. 5 shows a comparison of the measured oxygen nonstoichiometry of CZO for different Zr contents as a function of pO_2 at 600–1000 °C. At high pO_2 (~air–O₂) the change in mass with pO_2 was less than the error in the measurement, indicating nearly full oxidation of the sample. Therefore, for the measurement at the lowest temperature (600 °C) and highest pO_2 (100% O_2), δ was approximated as zero, consistent with other treatments for ceria-based materials [57,58]. As further evidence that with increasing Zr content δ remains approximately zero at high pO₂ and low temperature, δ was predicted from the room temperature lattice parameter contraction (ε) using the formula $\varepsilon = \alpha_{\rm M} x_{\rm Zr} + \alpha_{\rm V}(2\delta)$, where $\alpha_{\rm M}$, $x_{\rm Zr}$, and $\alpha_{\rm V}$ are the contraction due to the smaller ionic radius of zirconium (-0.055)[59], site fraction of Zr, and contraction due to relaxation of the lattice around oxygen vacancies (-0.044) [60], respectively (modified from Eq. (6) in Marrocchelli et al. [61]). Recent work [60] has shown that Zr addition to CeO_2 dramatically reduces α_V from that of pure ceria to cubic-stabilized zirconia, presumably due to localization of vacancies near Zr cations. Negative and small values for δ , 0 to -0.007, are predicted, signifying a negligible vacancy concentration.

With decreasing pO_2 and increasing temperature, δ increases, as expected from the reduction reaction given by Eq. (1). Compared with undoped ceria [4], the reduction isotherms of CZO are shifted to higher pO_2 , indicating an earlier onset of reduction (enhanced reducibility). In some cases the reducibility increased after re-oxidation and, for the first reduction cycle, CZO_20 exhibits the maximum reducibility.

After re-oxidation at intermediate pO_2 (CO–CO₂ gas mixtures) the reduction measurements for CZO_50 and CZO_80 were repeated at low pO_2 , revealing a second isotherm with an increased magnitude of δ (Fig. 5), and for CZO_50 δ is even larger than that for CZO_20. The difference in the two reduction isotherms was greatest at lower



Fig. 3. Raman spectrum of ceria, CZO, and zirconia. For x = 0.01, 0.05, 0.2, 0.5 and 0.8 spectra are shown for powders (solid line) and sintered pellets (dashed-dotted line).



Fig. 4. (a) Position and (b) FWHM of the cubic F_{2g} Raman peak as a function of Zr content x.

temperature and became negligible at $1000 \text{ °C. CZO}_{20}$ was confirmed to be insensitive to redox cycling at 600, 800 and 1000 °C, as confirmed by the repeatability shown in Fig. 5.

The nonstoichiometry for CZO_20, CZO_50 and CZO_80 at 600, 700 and 800 °C was compared with data from the literature measured by Zhou et al. using coulometric and flow titration [7]. For CZO_50 (Fig. 6) and CZO_80 (not shown) significant discrepancies were observed. In the case of CZO_50 the literature data show higher reduction (Fig. 6), whereas for CZO_80 some data exhibit higher nonstoichiometry. δ of CZO_20 (not shown) agreed well with the literature at high pO_2 and low temperature, but was larger in the low pO_2 range.

In order to examine the validity of the proposed defect model and extract K_{Red} , $\log \delta$ was plotted vs. $\log pO_2$, as shown in Fig. 7 for CZO_20. Indeed, at intermediate to high pO_2 an approximate -1/6 slope is observed, consistent with the expected behavior predicted by Eq. (7). At the lowest $pO_2 \delta$ strongly deviates negatively from this slope and becomes increasingly pO_2 insensitive with decreasing pO_2 , behavior previously observed for pure ceria, often attributed to defect interaction/ordering effects [10,62,63].

In order to determine the equilibrium constant K_{Red} , a straight line fit using a -1/6 slope to each δ isotherm in the intermediate pO_2 region was performed, with the value of the intercept with the *y*-axis yielding K_{Red}^0 . In the cases of CZO_50 and CZO_80 only the first reduction isotherms were fitted, as the data in the considered intermediate pO_2 region were not affected by the second reduction experiment. The K_{Red} values were then used to predict δ in Fig. 5, as shown by the curves. As in Fig. 7, the predicted δ agrees well with the data in the intermediate to high pO_2 region.

From the slope of the straight line fit of K_{Red} for CZO_20 in Fig. 8 (inset), H_{Red} was calculated using Eq. (8), with the resulting values for each CZO composition reported as a function of x in Fig. 8. As clearly observed in the figure, substitution of Ce by Zr results in a large decrease in H_{Red} , in comparison with that for pure ceria, with an apparent minimum at 20–50 mol.% Zr. The similar

magnitude of H_{Red} for CZO_20 and CZO_50 is reflected in their similar oxygen nonstoichiometries at high and intermediate pO_2 (Fig. 5). Also, in agreement with the lower reducibility of CZO_80 relative to that of CZO_50, as evidenced in Fig. 5, H_{Red} increases to ~3.5 eV, approaching the value for CZO_5.

The thermodynamics of reduction were also derived via Eqs. (12) and (13), particularly useful at large δ where the defect equilibria model does not fit the data. $R/2 \ln pO_2$ and $RT/2 \ln pO_2$ were obtained by interpolation of the oxygen nonstoichiometry data as a function of δ (data not shown). $h_O - h_O^0$ and $s_O - s_O^0$ were obtained as the slopes of the linear fits and are shown in Fig. 9a and b as a function of δ for all compositions. Both the partial molar enthalpy and entropy exhibit a dependence on nonstoichiometry and, compared with the data of Zhou et al. [7], the calculated values are in good agreement with the literature except for x = 0.2 (Fig. 9a) and x = 0.5 and 0.86 (Fig. 9b). At low nonstoichiometry, the partial molar enthalpy of reduction is close to the values shown in Fig. 8.

5. Discussion

In concert with earlier studies, the substitution of Ce⁴⁺ by isovalent Zr⁴⁺ was found to substantially enhance the reducibility of ceria [5-7]. One indeed finds considerably larger deviations from stoichiometry (larger δ values) over the temperature range 600–1000 °C for nearly all reducing conditions (see Fig. 5) and reduced enthalpies of reduction (see Fig. 8) compared with that of pure ceria. These trends are clearest up to 20% substitution of Ce by Zr (i.e. CZO_20), for which the largest values of δ are recorded in the higher pO_2 regime, in which the dilute solution model appears to hold and for which the enthalphy of reduction (H_{Red}) drops to nearly half the value of that for pure ceria (2.75 vs. 4.7 eV, see Fig. 8). It is also within this composition range that both XRD (Fig. 2a and Table 1) and Raman spectroscopy data (Fig. 3) show that CZO remains cubic. Likewise, the blue shift in the F2g Raman peak (Fig. 4a) is consistent with strengthening of the O-Ce-O



Fig. 5. Comparison of the oxygen nonstoichiometry (δ) of CZO for different mol.% Zr as a function of pO_2 at 600–1000 °C. Data from the literature for undoped CeO₂ [4] are also shown. The lines correspond to the fit based on Eq. (7). Open symbols represent a second reduction measurement (see text). The error in the mass measurements of ~30 µg corresponds to an error in δ of ~0.00028–0.00036, for which the respective error bar is smaller than the symbol size.

bond strength with the linearly decreasing lattice parameter with increasing Zr substitution (Fig. 2b). The considerably smaller Zr^{4+} , preferring 7-fold coordination, in contrast to the fluorite cation 8-fold coordination, in turn drives the formation of oxygen vacancies through the reduction of Ce^{4+} to Ce^{3+} [13–15].

As a further indication of the preference for Zr to "bind" oxygen vacancies, we turn briefly to the only other known prior study examining the defect thermodynamics using Eq. (2), on $Zr_{0.164}Ce_{0.654}Y_{0.182}O_{1.91-\delta}$ [32]. Despite

16.4 mol.% Zr doping, this system exhibited $H_{\text{Red}} \approx 3.75 \text{ eV}$, greater than the expected ~3 eV from Fig. 8. However, realizing that 18.2 mol.% Y adds enough vacancies to bind with 9.1 mol.% of the Zr, thus leaving behind 7.3 mol.% Zr without vacancies, one finds for this latter Zr fraction a predicted H_{Red} from Fig. 8 of ~3.5 eV, much closer to the above previously reported value. This indicates that the Zr fraction alone does not dictate reduction thermodynamics, but rather the Zr fraction without associated, or trapped, vacancies, as in the case of Y doping.



Fig. 6. Comparison of the oxygen nonstoichiometry of CZO_50 with data by Zhou et al. [7]. From this work only data for the first reduction treatment are shown. For the data measured in this study the error bars are smaller than the symbol size.



Fig. 7. Isothermal plots of $\log \delta$ vs. $\log pO_2$ for CZO_20. The dashed lines are fits of the -1/6 power law dependence (see Eq. (7)). Data are for the first reduction isotherm.



Fig. 8. Enthalpy of reduction as a function of Zr content. Data for pure ceria is from Tuller and Nowick [3]. The enthalpy of reduction for CZO_50 and CZO_80 is based on the first reduction measurement. (Inset) The fitting parameter K_{Red} as a function of temperature for CZO_20.

Additionally, electrical conductivity measurements on CZO were found to exhibit a power law dependence consistent with Eq. (7), from which activation energies (E_{σ}) were

derived in air [31,35]. The conductivity in ceria (σ) is given by the equation:

$$\sigma = \frac{\sigma_{\rm o}}{T} \exp\left(\frac{-H_{\rm m}}{kT}\right)[i] \tag{14}$$

where σ_o , $H_{\rm m}$, and [i] are a constant, the enthalpy for carrier migration, and the dominant charge carrier concentration [64]. Due to the significantly larger mobility of electrons, and the fact that electrons are at twice the concentration of oxygen vacancies from Eq. (3), the migration and concentration terms in Eq. (14) refer to electrons. Substituting Eq. (8) for K_{Red} in Eq. (7) and inserting the result (via Eq. (3)) in Eq. (14) for [i], one finds that $E_{\sigma} =$ $H_{\rm m} + H_{\rm Red}/3$. Inputting the present value for $H_{\rm Red}$ and the value of E_{σ} from [65] for CZO_20 yields $H_{\rm m} = 0.61$ eV, 50% larger than that for undoped ceria (0.4 eV) [64]. This result indicates that the enthalpy of small polaron migration in CZO is larger than in pure ceria, a not unexpected result given the lattice distortions brought about by Zr, as well as dilution of the Ce concentration by Zr, and thereby an increase in the average hopping distance.

Based on atomistic simulation techniques [38], the addition of up to 10% zirconia was found to decrease the bulk reduction energy of Ce^{4+} by about one-third, while further addition of Zr had little effect on the reduction energy. The calculated reduction energy was found to be comparable with that reported for surface reduction in pure ceria. The lowest energies for oxygen vacancy formation and oxygen migration were calculated for CZO containing 50% zirconia [37], which agrees with the observed "minimum" in Fig. 8b.

As discussed in the Introduction, the cubic-tetragonal (c-t'') phase boundary at room temperature reportedly occurs at a zirconium content of 0.1 < x < 0.3, with the absolute position of the phase boundaries depending strongly on the method of synthesis, particle size and thermal history [26]. In this work the phase transition occurred between x = 0.2 and 0.5, although it is interesting to consider whether the Raman shift and FWHM trends with increasing Zr fraction for $x \le 0.2$ indicate a re-ordering towards the tetragonal phase. For example, the plateau in the peaks for CZO_5 and CZO_20 powders (Fig. 3c and d) and the broadened FWHM of CZO_20 (Fig. 4b) may reflect an incipient splitting of F_{2g} into B_{1g} and E_{g} , resulting from a reduction in symmetry upon transition from the cubic to t'' phase [19,24].

While the cubic structure is observed for $x \le 0.2$ for the CZO pellets in this study, tetragonal distortions become evident for $x \ge 0.50$. In this regime, H_{Red} does not at first change significantly (CZO_50) with further increases in x, before increasing again (CZO_80). However, the difference in reduction enthalpy appears to be less influenced by Zr concentration in the high nonstoichiometry regime (Fig. 10a) [7]. Zhou et al. [7] argued that the difference in nonstoichiometry should instead be attributed to the oxidation entropies.

Values of H_{Red} have been reported for CZO by Zhou et al. [7] and Kim et al. [30], based on nonstoichiometry



Fig. 9. (a) $h_0 - h_0^0$ and (b) $s_0 - s_0^0$ of $Ce_{1-x}Zr_xO_{2-\delta}$ as a function of oxygen nonstoichiometry for different x. Data from Zhou et al. [7] are shown for comparison.

measurements performed by coulometric and flow titration. While the detailed experimental data obtained using the two different techniques seem not to agree with one another (Fig. 6 and Zhou [7]), similar H_{Red} values to those reported here were obtained (Fig. 9a and b), with an overall decrease by a factor of ~1.6 compared with undoped ceria.

In the case of larger concentrations of Zr (x > 0.2) three key features are observed, an increase in H_{Red} with Zr content, deviations from the cubic structure, and, importantly, an apparent increase in reducibility with isothermal reduction/oxidation cycling, discussed below. Previously a change in reducibility of CZO (composition x = 0.38) following a high temperature reduction treatment with subsequent re-oxidation was observed and attributed to ordering of Zr and Ce cations under reducing conditions, frozen in after oxidation [66]. Defect ordering and the appearance of domains of ordered phases have previously been reported in zirconia [25,67]. In order to further investigate the order/disorder behavior, the present CZO_80 sample was heat treated in air at 1000 °C for about 6 h to induce disordering of the cation sub-lattice after the first reduc-



Fig. 10. Reduction isotherms measured for CZO_80 at 600 $^{\circ}$ C during the first reduction (1), after the first reoxidation (2), and after 1000 $^{\circ}$ C heat treatment in air (3). Error bars are smaller than the symbol size.

tion/reoxidation/reduction cycle (corresponding to reduction isotherms 1 and 2, respectively, in Fig. 10). Following this treatment the sample was again reduced at 600 °C and exhibited a decrease in reducibility (isotherm 3 in Fig. 10), showing agreement with the proposed disorder/order phenomenon. The initial reducibility was not completely recovered, however, with longer hold times at elevated temperature and/or higher temperature treatments full recovery may be expected.

In addition to disorder/order phenomena, changes in composition resulting from the formation of Zr-rich/poor secondary phases [7] could also cause the observed changes in nonstoichiometry with redox treatment, resulting in, for example, a mixture of fluorite and pyrochlore structures, wherein the ordered pyrochlore structure could be more reducible [17]. Indeed, pyrochlore-type CZO was shown to exhibit a high oxygen storage capacity [68], although the enhanced homogeneity of Zr and Ce atoms in CZO solid solution postulated to be responsible requires further study.

6. Summary and conclusions

The nonstoichiometry of CZO was studied as a function of x (x = 0.05, 0.2, 0.5 and 0.8), pO_2 and temperature by means of thermogravimetry. The onset of reduction is shifted to higher pO_2 with increasing x up to 0.2, compared with undoped ceria. Reduction enthalpies as a function of composition were obtained by fitting a point defect model to the TGA data at intermediate to high pO_2 . Decreasing H_{Red} with increasing x up to 0.2 is consistent with the observed increase in reducibility on substitution of Zr for Ce. Comparisons between the present values of H_{Red} and prior studies indicates that the pre-existing O vacancy concentration (e.g. from acceptor doping) counteracts the effect of Zr on reducibility and that the substitution of Zr for Ce increases the migration energy for small polaron hopping between Ce ions. At lower pO_2 , defect association and ordering effects lead to a deviation of log δ vs. log pO₂ from a simple -1/6 dependence.

The nonstoichiometry of Zr-rich compounds (x = 0.5 and 0.8) increases after redox cycling. This enhanced reducibility is believed to be related to ordering and is partially negated by a high temperature (1000 °C) heat treatment. A full transition to the tetragonal phase is present for the highest doping levels studied. Phase transitions and ordering can be expected to have an impact on oxygen storage in CZO in harsh environments where the temperature and pO_2 are not constant, with affects on the catalytic properties.

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