Experimental and theoretical study on the complete phase separation of ceria-zirconia solid solution into two end members, ceria and zirconia

Seol Hee Oh, Hyun-Kyu Kim, Jason Kim, Yeong-Cheol Kim, Sun-Young Park, Sungeun Yang, Ho-Il Ji, Kyung Joong Yoon, Ji-Won Son and Jong-Ho Lee

1 Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
2 School of Energy Materials and Chemical Engineering, Korea University of Technology and Education, Cheonan 31253, Republic of Korea
3 Department of Convergence IT Engineering, Pohang University of Science and Technology, Pohang 37673, Republic of Korea
4 Technology Support Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
5 Division of Nano Science & Technology, University of Science and Technology, Seoul 02792, Republic of Korea

* Author to whom any correspondence should be addressed.

E-mail: jongho@kist.re.kr

Keywords: Ce$_{0.75}$Zr$_{0.25}$O$_2$, ceria-zirconia solid solution, phase stability, complete dissociation, enhanced cation diffusion

Supplementary material for this article is available online

Abstract
Solid solution CeO$_2$–ZrO$_2$ has long been used as a non-noble metal oxide promoter for three-way catalysts owing to its high oxygen storage capacity. However, the stability issue of the CeO$_2$–ZrO$_2$ has been controversial for a long time. In particular, the phenomena observed by phase instability are so diverse and inconsistent that the related causal analysis is still a matter of debate. In this study, for the first time, it was demonstrated theoretically and experimentally that a Ce$_{0.75}$Zr$_{0.25}$O$_2$ (CZO) solid solution must be completely separated into CeO$_2$ and ZrO$_2$ phases owing to its inherent thermodynamic instability. According to an extensive evaluation via defect chemical calculations and well-controlled model experiments with grain-boundary-free epitaxial thin film samples, CZO materials undergo phase separation until they are completely separated, and the separation rate is particularly high in a reducing atmosphere. The underlying inherent stability problem and enhanced phase separation kinetics of the CZO material are attributed to the enhanced cation diffusion in a reducing atmosphere, where more mobile cationic defects (interstitial cations) are generated and an easier pathway with a lower migration energy is available.

1. Introduction

CeO$_2$–ZrO$_2$ is widely used in three-way catalysts (TWCs) to remove CO, NO$_x$, and hydrocarbons from exhaust gases emitted from gasoline vehicles owing to its high oxygen storage capacity (OSC) [1, 2]. CeO$_2$–ZrO$_2$ plays an important role in TWCs as a stabilizer for noble metal catalysts as well as an oxygen buffer, compensating for fluctuations in the composition of the exhaust gas stream [3]. CeO$_2$–ZrO$_2$ also has highly versatile catalytic properties and can thus be used in many catalytic reactions, such as CO oxidation and the water-gas-shift reaction [4, 5]. In addition to catalytic promoters, CeO$_2$–ZrO$_2$ has been recognized as a potential oxide electrocatalyst for high-temperature electrochemical devices such as solid oxide fuel cells (SOFCs) owing to its high catalytic activity and favorable mixed ionic electronic conductivity [6]. Despite this high versatility, however, many long-standing questions remain regarding its phase stability.

Some studies have suggested that the homogeneous solid solution phase in CeO$_2$–ZrO$_2$ materials is unstable, resulting in a shift to heterogeneous phases over a wide range of compositions [7, 8]. Based on density functional theory (DFT) calculations, Grau-Crespo et al reported that the Zr solubility in the CeO$_2$ lattice was below 2 mol% at a maximum of 1373 K [7]. Our previous calculation work with $2 \times 2 \times 2$ supercell also confirmed that the free energy of mixing, $\Delta G_{\text{mix}}$ of CeO$_2$–ZrO$_2$ solid solutions remains
positive over wide temperature range (0–1500 K), which indicates that it is thermodynamically unstable in most of thermodynamic conditions [9]. Hori et al also observed through scanning electron microscopy (SEM) that at most, only 1–3 mol% Zr was dissolved in a cubic CeO$_2$ lattice at 1000 °C [8]. In addition, numerous experimental observations of phase separation phenomena caused by the thermodynamic instability of CeO$_2$–ZrO$_2$ solid solutions have been reported incoherently over a wide range of compositions, even in the Ce-rich phase, which has long been believed to be stable [10]. Moreover, even the thermodynamic conditions under which phase separation occurs are difficult to specify because phase separation occurs over a very wide range of thermodynamic conditions, regardless of oxidizing or reducing atmospheres, over a broad temperature range of 900 °C–1200 °C [8, 11–18]. These highly unspecified tendencies of phase instability phenomena hinder a detailed discussion of the origin or mechanism of phase separation in CeO$_2$–ZrO$_2$ solid solutions. Only a few explanations of the driving force of phase separation, such as the difference in surface energy according to particle size [11, 12] or between the particle surface and the interphase [11, 12], have been reported thus far, and even those studies lack consistency in the interpretation of the phase separation mechanism.

Therefore, in this study, we examined the phase stability of Ce$_{0.75}$Zr$_{0.25}$O$_2$ (CZO) using theoretical and experimental analyses, thereby aiming to solve the long-standing controversy regarding the stability of CZO. First, we fabricated a single-phase epitaxial CZO thin film and investigated its phase stability while minimizing the grain boundaries or interfacial effects between the CZO particles. To identify the underlying driving force and reaction kinetics of the phase separation in CZO, we estimated the cation migration energy and diffusivity using DFT calculations based on chemical analysis of point defects.

2. Methods: experimental and theoretical calculation

2.1. Thin film fabrication

The Ce-rich material CZO, which has been widely used as an excellent OSC material, was selected for model experiments. The CZO powders were prepared using the glycin-nitrate process (GNP). The starting raw materials were Ce(NO$_3$)$_3$·6H$_2$O (Sigma–Aldrich, 99.99%) and ZrO(NO$_3$)$_2$·xH$_2$O (Sigma–Aldrich, 99.99%). Glycine (Daejung, 99.0%, C$_2$H$_5$NO$_2$) was used as the oxidizer and fuel. Nitrates and glycine were dissolved in distilled water at a glycine-to-nitrate ratio of 0.55. The solution was stirred for 24 h and then dried at 350 °C until combustion occurred. The GNP-produced CZO ash was calcined at 600 °C for 5 h to remove residual carbon. A fully dense CZO target for pulsed laser deposition (PLD) was obtained by the cold isostatic pressing method at a pressure of 200 MPa with sintering at 1500 °C for 5 h. Using the PLD technique, 25 nm thick CZO (001) thin films were epitaxially grown on SrTiO$_3$ (STO) substrates heated to 750 °C. A KrF excimer laser (λ = 248 nm) with an energy density of 2 J cm$^{-2}$ and repetition rate of 5 Hz was applied to ablate the CZO target under an oxygen partial pressure of 50 mTorr. The crystallographic structures of the deposited films were investigated by x-ray diffraction (XRD) and transmission electron microscopy (TEM). θ–2θ scans and ϕ scans were carried out using an x-ray diffractometer (Rigaku Smart Lap) with CuK$_{α1}$ radiation (λ = 0.154056 nm). The fabricated thin films were exposed to a high temperature in an oxidizing or reducing atmosphere by flowing air or a 4%H$_2$–96%Ar mixed gas, respectively, in a tube furnace. To observe the microstructural evolution of the CZO thin film, the surface morphology of the film heat-treated at 1000 °C for up to 60 h was measured using a field-emission SEM (Inspect 50, FEI). The cross-sectional elemental distribution of the CZO thin films was determined using scanning transmission electron microscopy (STEM, Talos F200X) in conjunction with energy dispersive spectroscopy (EDS). STEM-EDS samples were prepared using a focused ion beam (FIB, Helios NanoLab 600).

2.2. Defect chemical analysis

For the mechanistic study of the phase separation phenomena in CZO films, we first performed defect chemical analysis to calculate the concentration of all point defects and to identify the major defect type in each anionic and cationic sublattice as a function of temperature (T) and oxygen partial pressure (pO$_2$). For simplicity, we performed a defect chemical analysis of CeO$_2$ instead of CZO because of the increased complexity associated with Zr inclusion. Hence we used CeO$_2$ instead of CZO while expecting CZO as a kind of homovalent-Zr-doped CeO$_2$, whose defect structure is not significantly different from that of undoped CeO$_2$. Nevertheless, considering any possible doping effect caused by the inadvertent inclusion of impurities, the acceptor dopant concentration was set to 2 × 10$^{-4}$ mol% for the calculation, as suggested by Beschmitt et al [19]. The concentrations of major point defects in CeO$_2$ were calculated by solving the system of equations listed in table S1, which describes eight critical relations for the formation of six intrinsic defects.
and their charge and site equivalency [19]. The system of equations was solved using particle swarm optimization [20] at wide $T$ and $pO_2$ ranges of 1000–1300 K and 0.21–10$^{-16}$ atm, respectively.

2.3. DFT calculation of diffusivity

DFT calculations of the migration enthalpy of the constituent elements were performed to understand the kinetics of the phase separation behavior in CZO. In general, the concentration and mobility of cationic defects are much lower than those of anionic defects in fluorite structural oxides such as CZO and thus cation diffusion is the rate-limiting step for the phase separation reaction. Hence, we calculated the cation diffusion as a function of $T$ and $pO_2$ using the concentration of major cationic defects and their migration enthalpy obtained from defect chemical and DFT calculations, respectively. As in previous defect chemical analyses, cation migration was considered in a simple CeO$_2$ model system to avoid the complexity associated with the Zr inclusion.

To calculate the migration enthalpy ($\Delta H_{\text{mig}}$) of the cations, three possible migration pathways were considered: cation interstitial, interstitialcy and vacancy mechanisms (figure 1). In this study, the $\Delta H_{\text{mig}}$ values of Ce defects were calculated in a $2 \times 2 \times 2$ CeO$_2$ supercell expanded from the CeO$_2$ unit cell. Most of the pathways were computed by using the climbing image nudged-elastic-band method [21], but in the case of the interstitialcy pathway of Ce$^{	ext{i}}$′′′′, the calculation was performed by fixing Ce$^{	ext{i}}$′′′′ at various positions and relaxing the surrounding atoms, as suggested by Beschotted et al [19]. The influence of adjacent oxygen vacancies ($V_{\text{O}}$) on the cation-migration energetics was considered for all cation pathways (figures 1(d)–(f)) whereas it was considered only for the cation vacancy pathways in the previous report [19]. It seems more reasonable to consider all cation pathways because a large number of the predominant defects, $V_{\text{O}}$ will definitely affect all possible cation-migration energetics in ceria. In addition, the clustering of $V_{\text{O}}$ around Ce defects was also considered for both Ce interstitial and Ce vacancies.

Figure 2 shows a CeO$_2$ unit cell that contains a Ce$^{	ext{i}}$′′′′ and a $V_{\text{Ce}}^{''''}$ (top), as well as Ce$^{	ext{i}}$′′′′ and Ce$^{''''}$ surrounded by eight O atoms (middle). A $V_{\text{O}}$ was created around a Ce defect to determine whether the $V_{\text{O}}$ could be gathered around the Ce defect. The number of $V_{\text{O}}$s was increased to determine the number of $V_{\text{O}}$s that could be gathered around the Ce defect shown at the bottom. One $V_{\text{O}}$ was located away from the Ce defect as a reference to identify the maximum number of clustered $V_{\text{O}}$ s ($N (V_{\text{O}}_{\text{clus}})$) around the Ce defect.

All DFT calculations were performed using the Vienna ab initio simulation package (VASP) code [22, 23]. The electron wave functions were described using the projector augmented wave method of Blochl, as implemented in the VASP code by Kresse and Joubert [24, 25]. The exchange correlation energy was described via the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [26]. The GGA + $U$ method was employed to consider the strongly localized Ce 4f electrons with an effective Hubbard $U$ parameter. We used the values (eV) of $U = 5$ and $J = 0$, as recommended in [27–29]. The cutoff energy was 500 eV and the Monkhorst Pack $k$-point mesh was $2 \times 2 \times 2$ [30]. Ionic and electronic optimizations of the supercell with or without defects were considered to converge when the total energy difference between successive calculation steps was less than $10^{-2}$ and $10^{-3}$ eV, respectively.
3. Results and discussion

The out-of-plane XRD pattern of the CZO thin film on STO (001) is shown in figure 3(a). Only the (00l) reflections of the CZO thin film without impurities were observed, clearly demonstrating the pure c-axis growth of the CZO thin film. Satellite peaks called pendellosung fringes were observed near 33.5°, and an enlarged graph is shown in figure 3(b). The fringe was caused by the interference of the diffraction patterns in a very thin layer, and the thickness of the thin film was determined using the following equation [31]:

\[ t = \frac{\lambda}{2 \Delta \theta \cos \theta} \]  

where \( \lambda \) is the wavelength of the x-ray source, \( \Delta \theta \) is the periodicity of the fringe, and \( \theta \) is the peak position of the thin films. The thickness of the CZO thin film was calculated to be 24.3 nm. Figure 3(c) shows that the \( \varphi \) scans of the CZO \{111\} and STO \{111\} planes have a set of four peaks with a periodicity of 90°. The CZO peaks shifted by 45° with respect to the STO peaks, indicating an epitaxial 45° in-plane rotation between the CZO and STO lattices. The lattice constant of the fluorite structure of CZO was consistent with the diagonal value of the STO lattice constant (\( a_{CZO} = 5.395 \text{ Å} \approx \sqrt{2} a_{STO} = 5.522 \text{ Å} \)). The coherency of these two lattices was determined by high-resolution TEM (HR-TEM). Figure 3(e) shows an HR-TEM image of the interface between the CZO thin film and STO substrate and selected area electron diffraction (SAED) patterns for (f) the thin film and (g) the substrate regions. For the same plane, the zone axes of CZO and STO were [110] and [100], respectively.

To evaluate the stability under various operating conditions, epitaxial CZO thin films were thermally annealed in air and a reducing atmosphere using a tube furnace. As mentioned previously, the instability of CZO remains controversial. According to previous theoretical [7] and experimental investigations on the mixing enthalpy of CZO [32], a positive value was always obtained over the entire temperature range of the analysis. These calculation results indicate that the CZO solid solution is inherently thermodynamically unstable and eventually dissociates. However, according to our experiment, the dissociation of CZO occurs selectively depending on the experimental conditions. Such dissociation seems to occur only when an energetically favorable environment is created.

Figures 4 shows the XRD patterns and SEM images, respectively, representing the variation in the crystalline structure and surface morphologies of the CZO thin film with respect to the heat treatment time. According to the analysis results shown in figures 4(a–c), the CZO thin films retained their crystallinity without any secondary phases, even after heat treatment at 1000°C for 60 h in an air atmosphere, and clean surfaces were observed, except for the presence of pits resulting from lattice shrinkage. However, as shown in figures 4(a), (d), and (e), as the exposure time increased in a reducing atmosphere, the original diffraction peak of the CZO thin film became less intense, and the peaks shifted to higher angles. These results indicate that the CZO lattice is distorted and compressed. After 30 h, Ce oxide and Zr oxide peaks appeared, and precipitated phases were observed on the thin film surface by SEM (figure 4(d)). Finally, after 60 h, the epitaxia thin film CZO peak almost disappeared and mainly separated phases remained. The corresponding surface image in figure 4(e) shows two types of particles with different sizes. As shown in figure 4(e), a lot of...
small nano-meter sized particles and some relatively larger particles are planarly separated from each other on the surface of the substrate.

Figure 5 presents cross-sectional STEM images with individual elemental mapping of the CZO thin films after 60 h in an oxidizing or reducing atmosphere at 1000°C, and these data can be used to identify the aforementioned precipitated phases. The Ce and Zr of the oxidized thin film on the left side were evenly distributed, whereas the reduced thin film on the right side was completely separated by Ce oxide and Zr oxide. Compared to the results of the previous SEM image shown at the top of figure 4(e), during the phase separation of CZO, Ce oxide precipitated in the form of large particles and Zr oxide precipitated in the form of small particles. For better understanding, new cross-section TEM images where two different phases do
Figure 5. Cross-sectional STEM images with EDS mapping for oxidized (top) and reduced (bottom) CZO/STO thin films at 1000°C for 60 h.

Figure 6. Defect concentration as a function of $T$ predicted by the defect chemical analysis at $pO_2$ values of (a) 0.21 and (b) $10^{-15}$ atm. The acceptor dopant concentration was fixed to $2 \times 10^{-4}$ mol per mol oxide.

not overlap each other even in cross-sectional images, to the supplementary materials (figure S2). As shown in figure S2, the completely separated ceria- and the zirconia phase are clearly identified. All these results suggest that phase separation of the CZO thin film is an irreversible reaction that occurs until Ce and Zr are completely separated. These results are completely different from previous reports [7, 8, 10–18] that the phase separation phenomenon is limited to segregation of some components or that the separated phase has an arbitrary intermediate composition even when phase separation occurs.

What’s even more interesting is that the dissociation of CZO varied considerably depending on the experimental conditions: phase separation is accelerated in a reducing atmosphere rather than in an oxidizing atmosphere. Such a difference in the phase separation behavior in the oxidizing and reducing atmospheres was attributed to the difference in the reaction kinetics for the phase separation owing to the difference in the thermodynamic environment. As mentioned above, because cation diffusion is the rate-limiting step for the phase separation reaction in fluorite structure oxides, we estimated the cation migration energy and diffusivity based on a point defect chemical analysis of a CeO$_2$ model system used to represent CZO.

Figure 6 shows the point defect concentration ($[\text{def}]$) in CeO$_2$ estimated by solving the system of equations presented in table S1. For this calculation, we used CeO$_2$ lattice instead of CZO because the process of solving the system of equations becomes too complicated when Zr inclusion is considered, even though it may affect the defect concentration in the CZO film. The calculations were performed under two atmospheric conditions ($pO_2$: 0.21 and $1 \times 10^{-15}$ atm) in the temperature range of 1000–1300 K, which was of our experimental interest. For the oxidizing atmosphere ($pO_2 = 0.21$ atm), figure 6(a) shows that the cation vacancy, [$V_{\text{Ce}}^{+++}$], is a major cationic defect whose concentration is overwhelmingly larger than that of the interstitial cation, [$\text{Ce}_{\text{i}}^{+++}$]. This result agrees with that reported in [19]. On the other hand, in figure 6(b), for a reducing atmosphere ($pO_2 = 10^{-15}$ atm), the concentration of the cation interstitial, [$\text{Ce}_{\text{i}}^{++}$], was
shows the migration enthalpy, \( \Delta E_{\text{clus}} = E_{\text{clus}} - E_{\text{ref}} \) between Ce defects and \( \text{V}_{\text{O}} \)s in the \( 2 \times 2 \times 2 \) \( \text{CeO}_2 \) supercell. \( E_{\text{clus}} \) is the energy when \( \text{V}_{\text{O}} \)s are clustered around the Ce defects, and \( E_{\text{ref}} \) is the energy when one \( \text{V}_{\text{O}} \) among the clustered \( \text{V}_{\text{O}} \)s is placed away from the Ce defects.

| Ce defect | \( N(\text{V}_{\text{O}, \text{clus}}) \) | \( \Delta E_{\text{clus}} \) (eV) |
|-----------|-----------------|-----------------|
| \( \text{Ce}^{\text{i}'''} \) | 1 | -0.42 |
| | 2 | 0.43 |
| \( \text{V}_{\text{Ce}}^{''''} \) | 1 | -0.84 |
| | 2 | -1.27 |
| | 3 | 0.07 |
| | 4 | 1.22 |

Table 2. Migration enthalpy (\( \Delta H_{\text{mig}} \)) of Ce defects with and without clustered \( \text{V}_{\text{O}} \)s. Two values for the vacancy pathway with four \( \text{V}_{\text{O}} \)s present the forward/reverse \( \Delta H_{\text{mig}} \), indicating that the initial and final reactions are structurally not equivalent. The bolded data were used to calculate the diffusion coefficients for interstitial and vacancy pathways.

| Diffusing Ce defect | Pathway | \( N(\text{V}_{\text{O}, \text{clus}}) \) | \( \Delta H_{\text{mig}} \) (eV) |
|---------------------|---------|-----------------|-----------------|
| \( \text{Ce}^{\text{i}'''} \) | Interstitial | 0 | 5.30 | 6.31 |
| | | 1 | 1.92 |
| | Interstitialcy | 0 | 3.68 | 4.19 |
| | | 1 | 2.42 |
| \( \text{V}_{\text{Ce}}^{''''} \) | Vacancy | 0 | 3.41 | 4.35 |
| | | 2 | 6.54 | 5.87 | 4.94 |

greatly increased, the gap with \( [\text{V}_{\text{Ce}}^{''''}] \) was reduced in most temperature ranges, and finally, a reversal occurred above 1300 K.

Based on this information on cationic defect concentrations in oxidizing and reducing atmospheres, the migration enthalpy (\( \Delta H_{\text{mig}} \)) of cations was calculated for three possible migration pathways: cation interstitial, interstitialcy, and cation vacancy mechanisms. First, because \( \Delta H_{\text{mig}} \) of cations can vary depending on the surrounding environment on the migration path, especially the presence of \( \text{V}_{\text{O}} \)s [19], the influence of adjacent \( \text{V}_{\text{O}} \)s on the cation-migration energetics was analyzed by calculating the clustering energy (\( \Delta E_{\text{clus}} = E_{\text{clus}} - E_{\text{ref}} \)) between \( \text{V}_{\text{O}} \)s and Ce defects (Ce interstitial or Ce vacancies).

In Table 1, \( E_{\text{clus}} \) is the energy when the \( \text{V}_{\text{O}} \)s are clustered around the Ce defect, and \( E_{\text{ref}} \) is the energy when one \( \text{V}_{\text{O}} \) among the clustered \( \text{V}_{\text{O}} \)s is placed away from the Ce defect. In this case, the negative \( \Delta E_{\text{clus}} \) value indicates that the clustering of Ce defects and \( \text{V}_{\text{O}} \)s is energetically favored. According to the calculation, the \( \Delta E_{\text{clus}} \) value of \( \text{Ce}^{\text{i}'''} \) with two \( \text{V}_{\text{O}} \)s was +0.43 eV, whereas in the case with one \( \text{V}_{\text{O}} \) was negative, indicating that clustering of only one \( \text{V}_{\text{O}} \) with \( \text{Ce}^{\text{i}'''} \) is thermodynamically preferred. The two positively charged defects, \( \text{Ce}^{\text{i}'''} \) and \( \text{V}_{\text{O}} \), should repulse each other because of the same charge. Bader charge analysis showed that the Ce interstitial retains more electrons than the on-site Ce, indicating that the Ce interstitial would be less repulsive to the O vacancy. In contrast, the \( \Delta E_{\text{clus}} \) value of \( \text{V}_{\text{Ce}}^{''''} \) remained negative until two \( \text{V}_{\text{O}} \)s were clustered. Therefore, the two \( \text{V}_{\text{O}} \)s can be stably clustered around \( \text{V}_{\text{Ce}}^{''''} \). It seems reasonable to consider the clustering of Ce defects and \( \text{V}_{\text{O}} \) because the concentration of oxygen vacancies, \( [\text{V}_{\text{O}}] \), is much larger than \( [\text{V}_{\text{Ce}}^{''''}] \) or \( [\text{Ce}^{\text{i}'''}] \) within the lattice in the temperature range of 1000–1300 K.

Table 2 shows the migration enthalpy, \( \Delta H_{\text{mig}} \), of Ce defects with and without clustered \( \text{V}_{\text{O}} \)s. As shown in Table 2, the calculated values of \( \Delta H_{\text{mig}} \) for the Ce defects without \( \text{V}_{\text{O}} \) clustering were slightly lower than those in [19]; however, the general trend remains acceptable. Interestingly, the \( \Delta H_{\text{mig}} \) value of \( \text{Ce}^{\text{i}'''} \) decreased regardless of the pathway when \( \text{Ce}^{\text{i}'''} \) was clustered with one \( \text{V}_{\text{O}} \) (from 5.30 to 1.92 eV for the interstitial pathway and from 3.68 to 2.42 eV for the interstitialcy pathway). This new surprising result was not found in a previous report [19] because they did not consider the influence of adjacent \( \text{V}_{\text{O}} \) on the interstitial pathway. Meanwhile, clustering of \( \text{V}_{\text{Ce}}^{''''} \) in the vacancy pathway was resulted in a higher \( \Delta H_{\text{mig}} \) regardless of the moving directions; 6.54 eV for its initial movement (forward) and 5.87 eV for the subsequent movement (reverse).

The two different values of \( \Delta H_{\text{mig}} \) for the vacancy pathway indicate that the first and second migration reactions occur in a structurally nonequivalent environment. Nevertheless, the \( \Delta H_{\text{mig}} \) values for the movement of \( \text{V}_{\text{Ce}}^{''''} \) were much higher than those of \( \text{Ce}^{\text{i}'''} \) contrary to a previous report [19]. Hence, it can be concluded that \( \text{Ce}^{\text{i}'''} \) migration is much more advantageous than \( \text{V}_{\text{Ce}}^{''''} \) migration when considering only the migration energy values in Table 2. Nonetheless, because cation diffusion needs to consider the concentration of movable cations, we consider the lowest value of migration energy (bold data in Table 2) for both cation interstitial and vacancy pathways for the calculation of diffusion coefficients.
Figure 7 shows the temperature and oxygen partial pressure dependence of cation vacancies or interstitial diffusivity: (a) at oxygen partial pressures of pO$_2$ = 0.21 and 10$^{-15}$ atm and (b) at T = 1300 K. The cation diffusivity was calculated using the following equation:

$$D = [\text{def}] \cdot Z \cdot \frac{1}{6} \cdot d^2 \cdot v_0 \cdot \exp \left( -\frac{\Delta H_{\text{mig}}}{k_B T} \right) \cdot \exp \left( \frac{\Delta S_{\text{mig}}}{k_B} \right),$$

where [def] is the defect concentration, Z is the number of neighboring sites that the defect can jump, d is the jump distance, v$_0$ is the attempt frequency, and $\Delta H_{\text{mig}}$ and $\Delta S_{\text{mig}}$ are the migration enthalpy and entropy, respectively [19]. The $D$ value of Ce$^{2+\cdots}$ (interstitial $D$, $D_{\text{int}}$) and that of $V_{\text{Ce}}^{\cdots\cdots\cdots}$ (vacancy $D$, $D_{\text{vac}}$) were calculated using $\Delta H_{\text{mig}}$ values of 1.92 and 6.94 eV, respectively, in table 2 and Z values of 12. Here, $d = 3.89 \times 10^{-8}$ cm, and we assumed $v_0 = 10^{13}$ Hz and $\Delta S_{\text{mig}} = 0$ [19]. According to the calculation results in figure 7(a), the diffusivity of Ce$^{2+\cdots}$, $D_{\text{int}}$ is always larger than that of $V_{\text{Ce}}^{\cdots\cdots\cdots}$, $D_{\text{vac}}$, regardless of the oxygen partial pressure over the entire temperature range. These results are very surprising in light of the defect concentration calculation results that the cation vacancy, $V_{\text{Ce}}^{\cdots\cdots\cdots}$ is a major cationic defect whose concentration is much larger than that of the interstitial cation, $\text{[Ce}^{2+\cdots}\text{]}$ (figure 6). This is also contrary to the previous study [19], which indicates that although the concentration of cation vacancy is high, its diffusivity, $D_{\text{vac}}$ is lower than that of the interstitial cation, $D_{\text{int}}$ due to the higher migration energy required for its movement.

As shown in figure 7(a), the diffusivity of Ce$^{2+\cdots}$ became larger in the reducing atmosphere ($D_{\text{int}} > D_{\text{vac}}$), as indicated by the blue dotted and solid lines, whereas $D_{\text{vac}}$ became smaller than $D_{\text{vac}}$, as indicated by the red dotted and solid lines. This result indicates that Ce interstitial diffusion was dominant regardless of the oxygen partial pressure, and the gap with Ce vacancy diffusion increased under reducing conditions. In figure 7(b), the cation diffusivities of the two major cationic defects with respect to the oxygen partial pressure pO$_2$ at 1300 K are compared. As shown in the figure, the Ce interstitial diffusivity was always larger than the Ce vacancy diffusivity and became significantly larger by approximately ten orders of magnitude in the reducing atmosphere. Accordingly, the interstitial diffusivity of Ce in the reducing atmosphere was at least four orders of magnitude greater than that in an oxidizing atmosphere. As expected from the results in figure 7(b), because the reducing atmosphere used in our experiment was in a more reducing condition than that in the calculation, the difference between the cation diffusivity in the oxidizing and reducing atmospheres was expected to increase further, which can explain the experimental results presented in figures 4–5. Therefore, it can be concluded that the phase separation phenomena of the CZO material were more accelerated in a reducing atmosphere because cation diffusion was more enhanced in a reducing atmosphere than in an oxidizing atmosphere.

4. Conclusions

CZO has attracted attention as a material with excellent OSC characteristics and can thus be used not only as a TWC, but also as an SOFC electrocatalyst. However, the inherent phase stability of CZO remains controversial. To resolve this long-standing controversy, we report computational results and experimental verification, which indicate that CZO is no longer stable under the environmental conditions in which it is actually used. According to an extensive evaluation of the stability under various operating conditions, CZO materials were found to be unstable and underwent phase separation until Ce and Zr were completely separated from each other. Such a complete phase separation in CZO materials has not been observed in other studies and is reported for the first time in this study. Furthermore, the dissociation of CZO varies...
considerably depending on the experimental conditions, and such dissociation seems to occur only when an energetically favorable environment is created. According to a well-controlled model experiment with grain boundary-free thin film samples, the phase separation rate of CZO was accelerated in a reducing atmosphere (approximately four orders of magnitude greater than oxidizing atmosphere) because of the enhanced cation diffusion, where more mobile cationic defects (cation interstitials) are generated and an easier pathway is available with a lower migration energy.

Data availability statement

All relevant data are within the paper and its supporting information files.

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

This work was supported by the Energy Technology Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by the Ministry of Trade, Industry and Energy, Republic of Korea (No. 20193010032460), and partially supported by the institutional research program of KIST and the Education and Research Promotion Program of KOREATECH in 2022.

Conflict of interest

The authors have declared that no competing interests exist.

ORCID ID

Jong-Ho Lee https://orcid.org/0000-0003-4481-6258

References

[1] Marécot P, Fakche A, Kelali B, Mabilon G, Prigent P and Barbier J 1994 Propane and propene oxidation over platinum and palladium on alumina: effects of chloride and water Appl. Catal. B 3 283–94
[2] Trovarelli A, Zamar F, Llorca J, De Leitenburg C, Dolletti G and Kiss J T 1997 Nanophase fluoride-structured CeO2–ZrO2 Catalysts prepared by high-energy mechanical milling J. Catal. 169 490–502
[3] Vidmar P, Fornasiero P, Kašpar J, Guibitosa G and Graziani M 1997 Effects of trivalent dopants on the redox properties of CexZr1-xO2 mixed oxide J. Catal. 171 160–8
[4] Bunuelsin T, Gorte R and Graham G 1998 Studies of the water-gas-shift reaction on ceria-supported Pt, Pd, and Rh: implications for oxygen-storage properties Appl. Catal. B 15 107–14
[5] Ding X, Chen Y, Pradel K C, Liu M and Wang Z L 2016 In-situ transmission electron microscopy study of oxygen vacancy ordering and dislocation annihilation in undoped and Sm-doped CeO2 ceramics during redox processes J. Appl. Phys. 120 214302
[6] Park S, Vohs J M and Gorte R J 2000 Direct oxidation of hydrocarbons in a solid-oxide fuel cell Nature 404 265–7
[7] Grau-Crespo R, de Leeuw N H, Hamad S and Waghmare U V 2011 Phase separation and surface segregation in ceria–zirconia solid solutions Proc. R. Soc. A 467 1925–38
[8] Hori C E, Fermana H, Ng K S, Brenner A, More K, Rahmoelle K M and Belton D 1998 Thermal stability of oxygen storage properties in a mixed CeO2–ZrO2 system Appl. Catal. B 16 105–17
[9] Oh S H et al 2022 Exploration of a Ce0.65Zr0.25Pr0.1O2−δ-based electrocatalyst that exhibits rapid performance deterioration despite its high oxygen storage capability ACS Appl. Energy Mater. 5 8023–33
[10] Fornasiero P, Balducci G, Di Monte R, Kašpar J, Gubitosa G, Ferrero A and Graziani M 1996 Modification of the redox behaviour of CeO2. Induced by structural doping with ZrO2. J. Catal. 164 173–83
[11] Lan L, Chen S, Cao Y, Zhao M, Gong M and Chen Y 2015 Preparation of ceria–zirconia supported Pd-only three-way catalyst and its supported Pd-only three-way catalyst J. Colloid Interface Sci. 450 404–16
[12] Colon G, Valdivieso F, Pijolat M, Baker R, Calvino J and Bernal S 1999 Textural and phase stability of Ce0.6Zr0.4O1.97 mixed oxides during high temperature oxidising conditions Catal. Today 50 271–84
[13] Martínez-Arias A, Fernández-García M, Hugonía A-B, Conesa J C and Munuera G 2003 Spectroscopic characterization of heterogeneity and redox effects in zirconium—cerium (1:1) mixed oxides prepared by microemulsion methods J. Phys. Chem. B 107 2667–77
[14] Chuang C C, Hsiang H I, Chen C C, Yen F S and Yoshimura M 2013 Phase separation phenomenon and mechanism of Ce0.6Zr0.4O2–δ powders prepared using chemical coprecipitation method J. Am. Ceram. Soc. 96 1629–34
[15] Bozo C, Gaillard F and Guilhaume N 2001 Characterisation of ceria–zirconia solid solutions after hydrothermal ageing Appl. Catal. A 220 69–77
[16] Atribak I, Bueno-López A and García-García A 2009 Role of yttrium loading in the physico-chemical properties and soot combustion activity of ceria and ceria–zirconia catalysts J. Mol. Catal. A 300 105–10
[17] Wang R, Crozier P A, Sharma R and Adams J B 2006 Nanoscale heterogeneity in ceria zirconia with low-temperature redox properties J. Phys. Chem. B 110 18278–85
[18] Keneve K, Valdivieso F, Soustelle M and Pijolat M 2001 Thermal stability of Pd or Pt-loaded Ce0.68Zr0.32O2 and Ce0.50Zr0.50O2 catalyst materials under oxidising conditions Appl. Catal. B 29 93–101
[19] Beschnitt S, Zacherle T and De Souza R A 2015 Computational study of cation diffusion in ceria J. Phys. Chem. C 119 27307–15
[20] Kennedy J and Eberhart R 1995 Particle swarm optimization Proc. ICNN’95-Int. Conf. on Neural Networks (IEEE) pp 1942–8
[21] Sheppard D, Terrell R and Henkelman G 2008 Optimization methods for finding minimum energy paths J. Chem. Phys. 128 134106
[22] Kresse G and Hafner J 1993 Ab initio molecular dynamics for liquid metals Phys. Rev. B 47 558
[23] Kresse G and Furthmüller J 1996 Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 15–30
[24] Blöchl P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953
[25] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758
[26] Perdew J P , Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865
[27] Nolan M, Grigoleit S, Sayle D C, Parker S C and Watson G W 2008 Density functional theory studies of the structure and electronic structure of pure and defective low index surfaces of ceria Surf. Sci. 576 217–29
[28] Zacherle T, Schriever A, De Souza R and Martin M 2013 Ab initio analysis of the defect structure of ceria Phys. Rev. B 87 134104
[29] Shi L, Vathonne E, Oison V, Freyss M and Hayn R 2016 First-principles DFT+U investigation of charged states of defects and fission gas atoms in CeO2 Phys. Rev. B 94 115132
[30] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188
[31] Kato N 1961 A theoretical study of pendellösung fringes. I. general considerations Acta Crystallogr. 14 526–32
[32] Lee T A, Stanek C R, McClellan K J, Mitchell J N and Navrotsky A 2008 Enthalpy of formation of the cubic fluorite phase in the ceria–zirconia system J. Mater. Res. 23 1105–12