https://doi.org/10.1016/j.ceramint.2018.11.072

Unlocking the nature of the co-doping effect on the ionic conductivity of CeO_2-based electrolyte

Meina Chen[1)*] Huiying Gao[1)] Lei Zhang[1)] Yan Xuan[1)] Junfeng Ren[1)] Meng Ni[2)*] Zijing Lin[3)]

[1)] School of Physics and Electronics, Shandong Normal University, Jinan 250358, China

[2)] Department of Building and Real Estate, The Hong Kong Polytechnic University, Hong Kong, China

[3)] Department of Physics, University of Science and Technology of China, Hefei, 230026, China

Email: mnchen@sdnu.edu.cn

Email: bsmengni@polyu.edu.hk

Abstract:

Doped CeO_2 is a very promising electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs). To further improve the performance of the CeO_2-based electrolyte, co-doping two different elements into CeO_2 is a feasible method, however the co-doping effect on the ionic conductivity is not well understood and whether it is synergistic or average is even controversial. In order to gain a fundamental understanding of the co-doping effect, the microscopic properties of co-doped CeO_2 are calculated using the DFT+U method. Density of states, band structures, oxygen vacancy formation energies, defect association energies, and oxygen vacancy migration energies are systematically calculated for In^{3+}, Sm^{3+} single-doped and co-doped CeO_2. Based on our calculations, we find that the coexistence of the two doped ions in the local structures of the doped CeO_2 can suppress the reduction of Ce^{4+} to Ce^{3+}, which is beneficial for the decrease of the internal short circuit current of the CeO_2-based electrolyte. For In^{3+} and Sm^{3+} co-doped CeO_2, when the distance between the two doped ions is the first nearest neighbor, the co-doping effect is average. However, when the distance between the two doped ions extends to the second nearest neighbor, the availability of the free oxygen vacancies is synergistically enhanced. Therefore whether the co-doping effect on the ionic conductivity is average or synergistic is highly dependent on the local structures of the co-doped CeO_2 which are difficult to control in experiments, offering a reasonable explanation for controversial experimental results. Our work provides a new atomistic level insight into the co-doping effect in CeO_2 which would be helpful for high performance electrolyte development.

Key words: Co-doping effect; Ionic conductivity; Electrolyte; IT-SOFC; First principles calculation

1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) are promising power sources due to their high energy conversion efficiency and low pollution emissions [1-6]. The key to develop efficient and durable IT-SOFC is to develop stable electrolytes with high ionic conductivity. Recently, CeO_2-based electrolytes has received increasing attention due to their higher ionic conductivity than that of the conventional yttria-stabilized zirconia (YSZ) electrolyte [7-9].

Actually, CeO_2 can be doped with one or more than one elements. In the past few years, many studies have been conducted on CeO_2 doped with one element [10-24]. Nakayama and Martin [25] conducted first principle calculations on Sc, Y, La, Nd, Sm, Gd, Dy and Lu single-doped CeO_2 using density functional theory (DFT) without taking localized 4f states into consideration. For simplify, they assumed that only doped ions on the nearest neighboring positions affect the oxide ion hopping and concluded that the radius of the doped ions could influence the defect association energy and oxygen vacancy migration energy to some degree. Shi et al. [17, 18] did DFT calculations using PBE+U method on Mn, Pr, Sn and Zr single-doped CeO_2. It is found that the decrease of the oxygen vacancy formation energy is mostly caused by the electronic modification as well as the structural distortion. Yahiro et al. [22] experimentally verified that among lanthanide series, Sm and Gd single-doped CeO_2 (commonly referred to as SDC and GDC) have the highest ionic conductivity, therefore SDC and GDC have been widely used in IT-SOFCs recently. Ou et al. [26] used electron energy loss spectroscopy together with area electron diffraction method to study Sm, Gd, Dy and Yb single-doped $CeO_{2.}$ It is found that the oxygen-vacancy local ordering would decrease the mobility of oxygen vacancies and lead to a lower ionic conductivity. Thus, controlling dopants segregation and doping more than one elements into CeO_2 are suggested as two promising ways to control the oxygen vacancy local ordering for improving the ionic conductivity of CeO_2-based electrolytes.

Recently, several co-doped CeO_2 materials has demonstrated high ionic conductivity. Kashyapa et al. [27] reported that Sr^{2+} and Gd^{3+} co-doped CeO_2 could increase the ionic conductivity to 6.3×10^{-3} S cm^{-1} while that of the Gd^{3+} single-doped CeO_2 is only 1.1×10^{-2} S cm^{-1} at 600°C. Jaiswal et al. [28] synthesized Sr^{2+} and Sm^{3+} co-doped CeO_2. It is found that the ionic conductivity of $Ce_{0.82}Sm_{0.16}Sr_{0.02}O_{1.9}$ (2.67×10^{-2} S cm^{-1}) is about two times higher than that of $Ce_{0.8}Sm_{0.2}O_{1.9}$ (1.33×10^{-2} S cm^{-1}) at 600°C. Yamamura et al. [29] performed experimental research on Ca^{2+}/Sr^{2+} and La^{2+} co-doped CeO_2. They concluded that the suppression of the local ordering of oxygen vacancies maybe the main reason for the ionic conductivity improvement of the co-doped CeO_2. Tao et al. [30] reported that In^{3+} and Sm^{3+} co-doped CeO_2 could not only significantly improve the ionic conductivity but also suppress the electronic conductivity, which in turn decreases the ohmic loss and leakage current.

The above-mentioned experimental studies observed a synergistic effect of co-doping on ionic conductivity of CeO_2-based materials, which means the ionic conductivity of co-doped CeO_2 is higher than either of the respective single-doped CeO_2. However, different results are also observed. For example, Kasse and Nino [31] found that the ionic conductivity of Sm^{3+} and Nd^{3+} co-doped CeO_2 was between those of Sm^{3+} doped CeO_2 and Nd^{3+} doped CeO_2. Similar results were also reported by Yoshida et al. [23] on La^{3+} and Y^{3+} co-doped CeO_2. Thus the co-doping effect on the ionic conductivity of CeO_2-based materials is still controversial in experimental researches.

Compared with many experimental researches, very few theoretical calculations are available on the co-doping effect of CeO_2 and no consensus has been reached yet. Without considering long-range cation ordering, grain boundaries, impurity segregation, etc., Burbano et al. [32] investigated the ionic conductivity of Nd, Sm and Sc, La co-doped CeO_2 by molecular dynamics (MD) method. Their results showed that the ionic conductivity of co-doped CeO_2 was an average of the conductivity of the respective single-doped CeO_2. Alaydrus et al. [33] calculated the co-doping effect on ionic conductivity of Sm, Gd co-doped CeO_2. They found that the dopant vacancy association between the oxygen vacancy and the two different co-doped ions is beyond the simple logic of superposition. Andersson et al. [34] studied Nd, Sm and Pr, Gd co-doped CeO_2 by first principles calculations and predicted synergistic co-doping effect of such combinations on ionic conductivity. However, the subsequent experiment on Nd, Sm co-doping structures [31] showed a contrary result. The contradictory results in the literature indicates the need of systematic study on the co-doping effect in CeO_2-based materials.

To gain a fundamental understanding of the co-doping effect, we performed DFT+U method on In^{3+}, Sm^{3+} single-doped and co-doped CeO_2 to calculate a series of microscopic properties, including density of states, band structures, oxygen vacancy formation energies, defect association energies, and oxygen vacancy migration energies. Based on experimental results [30] and our calculations, we proposed a new explanation for the co-doping effect in CeO_2, which can provide an atomistic level understanding of co-doping effect in CeO_2 and help further development of co-doped electrolyte materials for IT-SOFCs.

2. Computational methods

All calculations in this paper were carried out using spin-polarized DFT+U method and implemented in the Vienna Ab initio Simulation Package (VASP) [35, 36]. The projector augmented wave (PAW) method [37] was used, and the exchange-correlation effects were described by the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [38]. The cut off energy of the plane wave basis set was 400 eV and the energy convergence criterion was 10^{-4} eV. Structural optimization was carried out until the Hellmann-Feynman force on each atom was smaller than 0.02V/Å. The Gaussian smearing was set to be 0.05 eV. A $2 \times 2 \times 2$ k-points of Monkhorst–Pack meshes [39] centered at the Γ point was applied for Brillouin zone integration. To account for strong on-site Coulomb repulsion among the 4f electrons of Ce and Sm, DFT+U method was adopted. The U values of 5.0 eV for Ce [40] and 7.35eV for Sm [41] were adopted respectively. The climbing-image nudged elastic band (CI-NEB) method was adopted to calculate the oxygen vacancy migration barriers, and the force tolerance for the transition state (TS) calculations was 0.02 eV/Å.

3. Results and discussion

3.1 Crystal structures

Pure bulk CeO_2 has a fluorite structure with the cations (Ce^{4+}) residing at the face-centered-cubic (fcc) arrangement and the anions (O^{2-}) occupying the tetrahedral holes. The calculated lattice constant of pure CeO_2 is 5.442Å, which is very close to the experimental value of 5.412Å [42]. A 2×2×2 supercell with 96 atoms including 32 Ce and 64 O was adopted to model pure CeO_2. To construct In^{3+}, Sm^{3+} co-doped CeO_2, two

Ce atoms in the supercell were replaced by Sm and In atoms, and then one oxygen atom was removed. As shown in Fig.1 and Fig.2, nine different co-doping configurations were calculated in this paper, named M1, M2, M3, M4, M2-2, M3-2, M4-2, M2-3 and M4-3. In Fig.2 and the rest of this paper, we used N, NN, and NNN to represent the first nearest neighbor, the second nearest neighbor, and the third nearest neighbor respectively.

Total energy calculations were performed on these nine configurations. Comparing energies in different columns of M2, M3, M4 and M2-2, M3-2, M4-2 (as shown in Fig.2), we conclude that if we keep the distance between the doped ions and the oxygen vacancy unchanged, the energies of the corresponding configurations will decrease first and then increase with increasing distance between the doped ions. The configuration of M3 and M3-2 is found to possess the lowest energy in the corresponding column, in which the distance between Sm^{3+} and In^{3+} are both NN. Similarly, when comparing the energies in each row in Fig.2, no matter how far the two doped ions are from each other, the lowest energy can be found in the configuration with the distance between Sm^{3+} and oxygen vacancy being NN and In^{3+} and oxygen vacancy being N. This phenomenon may be attributed to the competition interactions of the two different doped ions on the oxygen vacancy. More detailed discussions are provided in section 3.4 of this paper.

Furthermore, it can be seen from Fig.2 that the most energetically stable configurations are M1 and M3-2, both with the energy of -772.24eV. Therefore, our subsequent calculations will be performed on these two configurations.

3.2 Density of states and band structures

A comparative analysis of density of states (DOS) was performed on different structures, including perfect structure CeO_2 (Fig. 3(a)), reduced CeO_2 (Fig. 3(b)), In^{3+} or Sm^{3+} single doped CeO_2 of different concentrations (Fig. 3(c), 3(d), 3(e), 3(f)), and Sm^{3+} , In^{3+} co-doped CeO_2 with different configurations of M1 or M3-2 (Fig. 3(g), 3(h)). For these different structures, the corresponding band structures were also calculated. The band gaps between the valence band top and the conduction band bottom are listed in Table 1.

From Fig. 3(a) and Table 1, we can conclude that the CeO_2 with perfect structure is a pronounced wide gap insulator with a band gap of 2.372eV, which is very close to the earlier DFT calculations of 2.377eV [14] and a little lower than the experimental result of 3eV [43], indicating that our DFT+U calculations are reliable. It's worth noting that the underestimation of the energy gap is a common feature of the DFT+U calculations.

Different from the unreduced CeO_2, the reduced CeO_2 (Fig. 3(b)) possesses a small Ce 4f state just below the Fermi level, which can be attributed to the local reduction from Ce^{4+} to Ce^{3+} around the oxygen vacancy [44]. Meanwhile, the corresponding band gap of the reduced CeO_2 is narrowed to be 0.796eV (Table 1). Thus, we can derive that the reduced CeO_2 may possess a little electronic conductivity, which is in good agreement with the experimental results [45, 46].

From Fig. 3(c), Fig. 3(d), Fig. 3(e), and Fig. 3(f), we can conclude that for Sm^{3+} or In^{3+} single-doped CeO_2, whether the gap state of Ce 4f appears or not depends on the doping concentration or the local structure of the doped CeO_2. When there are only one doped trivalent ions surrounding the oxygen vacancy, one Ce^{4+} around the oxygen vacancy will be reduced to Ce^{3+} for the charge compensation mechanism of the oxygen vacancy. As shown in Fig. 3(c) and Fig. 3(e), the Ce 4f state will appear near the Fermi level, which means in such condition, In^{3+} or Sm^{3+} single-doped CeO_2 will possess a small amount of electronic conductivity. Meanwhile, when the oxygen vacancy is surrounded by two doped trivalent ions (Fig. 3(d) $Ce_{30}In_2O_{63}$, Fig. 3(f) $Ce_{30}Sm_2O_{63}$), no Ce^{4+} is reduced to Ce^{3+}, as the trivalent ions are enough to compensate for the charge of the oxygen vacancy. Therefore, the Ce 4f gap state near the Fermi level will not exist. From Table 1, we can see that the corresponding band gap is 2.119 eV for $Ce_{30}In_2O_{63}$ and 2.316eV for $Ce_{30}Sm_2O_{63}$, which means in such conditions, In^{3+} or Sm^{3+} single-doped CeO_2 is non-conductive.

As the local concentrations or local structures of the doped CeO_2 is difficult to control in experiment, these two conductive conditions could coexist in the actual material. Therefore the conductive behavior of the single doped CeO_2 is complicated. This finding also well explains the small electronic conductivity of SDC in experiment [9, 47].

For Sm^{3+}, In^{3+} co-doped CeO_2 with different configurations of M1 and M3-2, we can conclude from Fig. 3(g), Fig. 3(h) and Table 1 that they are both non-conductive and the bandgaps of 2.249 eV for M1 and 2.258 eV for M3-2 are just between the bandgaps of 2.316 eV for $Ce_{30}Sm_2O_{63}$ and 2.119 eV for $Ce_{30}In_2O_{63}$, reflecting an average effect of In^{3+}, Sm^{3+} co-doping on the bandgaps.

3.3 Oxygen vacancy formation energy

Oxygen vacancy formation energy E_{vac}^{f} is an important factor determining the formation of oxygen vacancies [34], which can be defined as

$$E_{vac}^{f} = E_{M+vac} - E_{M} + 1/2\,\mu_{O_2}$$

where M represents the doping ions such as Sm^{3+} or In^{3+}, E_{M+vac} is the total energy of the supercell containing the dopant-vacancy complex, E_{M} is the total energy of the supercell with doped ions, and μ_{O_2} is the chemical potential of O_2. A negative value of E_{vac}^{f} means that the formation of the oxygen vacancy is an exothermic reaction, thus the oxygen vacancy can form spontaneously. While a positive value of E_{vac}^{f} means the opposite.

For comparative analysis, E_{vac}^{f} was calculated for a series of CeO_2-based materials, including pure CeO_2, Sm^{3+} or In^{3+} single-doped CeO_2 and Sm^{3+}, In^{3+} co-doped CeO_2. For simplicity, we used different expressions to represent the different structures and configurations. For example, in the expression of $Ce_{30}InSmO_{63}$ (NN)-NN,N, $Ce_{30}InSmO_{63}$ represents the structure of In^{3+}, Sm^{3+} co-doped CeO_2, NN in the bracket means that the distance between the two doped ions is the second nearest neighbor, NN,N behind the dash represents the distances between the oxygen vacancy and the two doped ions, where the NN in front of the comma means the distance between the oxygen vacancy and the Sm^{3+} is the second nearest neighbor and the N after the comma means the distance between the oxygen vacancy and the In^{3+} is the first nearest neighbor. The rest of the expressions in Table 2 follow the same naming principle.

As shown in Table 2, the E_{vac}^{f} for pure cerium oxide ($Ce_{32}O_{63}$) is calculated to be 3.332eV, which is very close to 3.10eV calculated by Tang at al [17] (with the U value to be 4.5eV) and 3.61eV by Andersson at al [48] (with the U value to be 6.0eV). Such positively large E_{vac}^{f} value indicates the difficulty to form oxygen vacancy in the pure cerium oxide, which is consistent with the experimental results [46, 49].

For In^{3+} or Sm^{3+} single doped CeO_2 as shown in Fig.2, it can be seen that the local structure of the doped CeO_2 is an important factor influencing the E_{vac}^{f} to a large degree. When there is only one doped ion in the supercell, the values of E_{vac}^{f} for either In^{3+} doped CeO_2 or Sm^{3+} doped CeO_2 are all positive, indicating the difficulty to form oxygen vacancies under such condition. Moreover, it is found that the difference of E_{vac}^{f} between $Ce_{31}SmO_{63}$-N and $Ce_{31}SmO_{63}$-NN is 0.069eV, which is smaller than that for In^{3+} single doped CeO_2 to be 0.497eV (between $Ce_{31}InO_{63}$-N and $Ce_{31}InO_{63}$-NN).

When there are two doped ions in the supercell, all E_{vac}^{f} values become negative, indicating that in such situation the oxygen vacancies can form spontaneously. The difference of E_{vac}^{f} between $Ce_{30}Sm_2O_{63}$(N)-N,N and $Ce_{30}Sm_2O_{63}$(N)-NN,N is as low as 0.003eV, indicating that there are almost the same formation probabilities of the oxygen vacancies on these two sites. The E_{vac}^{f} difference between $Ce_{30}In_2O_{63}$(N)-N,N and $Ce_{30}In_2O_{63}$(N)-NN,N is 0.607eV, which is obviously lager than that in Sm^{3+} doped CeO_2 and indicates that compared with the NN,N site, oxygen vacancy tends to form at the N,N site. Thus, we can conclude that In^{3+} has a stronger trapping effect on the oxygen vacancies than Sm^{3+} (More details will be discussed in section 3.4 and 3.5).

It's worth noting that when the distance between the two doped ions is enlarged to NN, the E_{vac}^{f} value for Sm^{3+} single doped CeO_2 ($Ce_{30}Sm_2O_{63}$(NN)-NN,N) increases 0.31eV compared with the configuration of $Ce_{30}Sm_2O_{63}$(N)-NN,N. However, such increase of E_{vac}^{f} for In^{3+} single doped CeO_2 is only 0.011eV, which is much smaller than that of Sm^{3+} single doped CeO_2. Therefore, the distance between the two doped ions has a greater impact on Sm^{3+} single-doped CeO_2 than the In^{3+} single doped CeO_2. And the In^{3+} single doped CeO_2 is more sensitive to the distance between the oxygen vacancy and the doped ions. Such difference may be helpful for the E_{vac}^{f} reduction of the co-doped CeO_2.

For In^{3+}, Sm^{3+} co-doped CeO_2, the E_{vac}^{f} were calculated for the most stable configurations of M1 ($Ce_{30}InSmO_{63}$(N)-N,N) and M3-2 ($Ce_{30}InSmO_{63}$(NN)-NN,N) as discussed in section 3.1. The E_{vac}^{f} for M1 is -0.533eV, the value of which is between -0.421eV for $Ce_{30}Sm_2O_{63}$(N)-N,N and 0.889eV for $Ce_{30}In_2O_{63}$(N)-N,N, reflecting the average co-doping effect on the oxygen vacancy formation of M1. While the E_{vac}^{f} for M3-2 is -2.160 eV, which is lower than -0.108eV for $Ce_{30}Sm_2O_{63}$(NN)-NN,N and -0.293eV for $Ce_{30}In_2O_{63}$(NN)-NN,N, reflecting the synergistic co-doping effect on the oxygen vacancy formation in M3-2. Moreover, M3-2 also possesses the lowest E_{vac}^{f} among all the structures calculated in Table 2, which is beyond our simple logic of superposition. It is worth noting that we also calculated the E_{vac}^{f} of $Ce_{30}InSmO_{63}$ (NN)-N,NN (M3), the result of which also reflects the synergistic co-doping effect on the oxygen vacancy formation.

So we can conclude that in In^{3+}, Sm^{3+} co-doped CeO_2, whether the co-doping effect on the oxygen vacancy formation is average or synergistic depends on the distance between the two doped ions. The NN distance of the two doped ions is more beneficial for the oxygen vacancy formation.

3.4 Dopant-vacancy association energy

Dopant-vacancy association energy E_{ass} is defined as the interaction between the doped ions and the oxygen vacancy, which can reflect the ability of hindering the oxygen vacancies from being mobile [10, 34]. Thus the E_{ass} combined with E_{vac}^{f} can determine the availability of the free oxygen vacancies for ionic conductivity.

E_{ass} can be evaluated by calculating the energy difference between a supercell with a vacancy nearby the doped ions and a supercell in which the doped ions and the vacancy are sufficiently far away from each other. As shown in Table 3, E_{ass} can be divided into two parts, one is electronic interactions (symbolized as E_{ele}) mediated by redistribution of the electronic structures, the other is elastic interactions (symbolized as E_{ela}) caused by lattice deformations. E_{ele} can be calculated as the same energy difference as E_{ass} in unrelaxed supercells. E_{ela} can be extracted by subtracting E_{ele} from E_{ass} [34].

For comparison, E_{ass}, E_{ele} and E_{ela} are calculated for In^{3+}, Sm^{3+} single-doped and co-doped CeO_2 in different configurations of M1, M3-2 and M3. As shown in Table 3, all the calculated E_{ass} which is balanced between the repulsive elastic part ($E_{ela}>0$) and the attractive electronic part ($E_{ele}<0$) are negative, indicating that it is the total attractive interactions between the doped ions and the oxygen vacancies for M1, M3-2 and M3 in either In^{3+}, Sm^{3+} single doped or co-doped CeO_2.

Table 3 shows that for both M1 and M3-2 (the configurations of M3 and M3-2 for single doped CeO_2 are equivalent), the E_{ass} values for In^{3+} single doped CeO_2 are lower than that for Sm^{3+} single doped CeO_2, reflecting that the In^{3+} ions have a stronger trapping effect on the oxygen vacancies than the Sm^{3+} ions. This may be attributed to the smaller ionic radius of the In^{3+} ions (0.92Å) than that of the Sm^{3+} ions (1.079Å) under the same effective charges.

For In^{3+}, Sm^{3+} co-doped CeO_2 with the configuration of M1, an intermediate E_{ass} value is obtained between the corresponding single doped structures, reflecting an average co-doping effect. However, for M3-2, the E_{ass} value of the co-doped CeO_2 is higher than both of the In^{3+} or Sm^{3+} single doped structures, reflecting neither average effect nor synergistic enhancement effect, which is beyond our expectations. For further comparison, we have also calculated the E_{ass} of M3, of which the E_{ass} value is lower than the corresponding single doped structures. It's worth noting that the only difference between M3 and M3-2 is the relative position of the oxygen vacancy (as shown in Fig.2).

The difference of the co-doping effect on the E_{ass} between the configuration of M3 and M3-2 can be attributed to the competition interactions on the oxygen vacancy between In^{3+} and Sm^{3+}. As the In^{3+} ion has a stronger trapping effect than the Sm^{3+} ions, the configuration with the oxygen vacancy N to the In^{3+}, and NN to the Sm^{3+} (M3-2) is more energetically stable (section 3.1) and possesses lower E_{vac}^{f} (section 3.3) than M3, from which we can infer that it is much harder for the oxygen vacancies to move in M3-2. This well explains the E_{ass} calculation results.

Moreover, for the co-doped configuration of M3 or M3-2, the E_{ele} value is either lower or higher than that of the corresponding single doped structures, which has the same trend with the corresponding E_{ass} value. While the E_{ela} value shows the opposite trend with the corresponding E_{ass} value. So we can conclude that compared with elastic interactions E_{ela}, electronic interactions E_{ele} plays a dominant role in the E_{ass}.

Therefore, the local structure in doped CeO_2 plays an important role in $E_{ass.}$ The E_{ass} for the co-doped structure of M1 can be described as an average effect of co-doping. While the E_{ass} for the co-doped structure of M3 or M3-2 is beyond the simple logic of superposition and can be described as a synergistic enhancement or decrement effect of co-doping.

For M3-2, the E_{ass} is 0.44eV or 0.091eV higher than that of the corresponding Sm^{3+} or In^{3+} single doped CeO_2, which is a hinder for the ionic conductivity. For comparison, the E_{ass} increase value is much smaller than the E_{vac}^{f} decrease value of 2.052eV or 1.867eV as discussed in section 3.3. Therefore, for M3-2 the co-doping effect on the availability of the free oxygen vacancies is synergistically enhanced.

3.5 Oxygen vacancy migration energy

Actually there are many different migration paths in In^{3+}, Sm^{3+} single-doped and co-doped CeO_2, for the sake of efficiency and due to our limited computational resources, we choose only four migration paths for M1 or M3-2 to calculate. As shown in Fig.4, we use "V" to represent the initial position of the oxygen vacancy and "O1", "O2", "O3" and "O4" to represent the final position of the oxygen vacancy. The corresponding results of the migration energy barriers are summarized in Table 4.

From Table 4, we can conclude that there are three important factors influencing the migration energy barriers of the doped CeO_2: (1) Dopant-vacancy association energy E_{ass}; (2) the energy difference between the initial state and the final state of the oxygen vacancy migration; (3) edge atoms besides the migration paths of the oxygen vacancy.

For the path of V→O1 (N,N→N,NN), we can see that the forward barriers of In^{3+} single doped CeO_2 and In^{3+}, Sm^{3+} co-doped CeO_2 are both lager than the Sm^{3+} single doped CeO_2. This can be attributed to the stronger trapping effect of In^{3+} on the oxygen vacancy than Sm^{3+} as concluded in section 3.3 and 3.4. Moreover, the energy differences of the In^{3+} single doped or co-doped CeO_2 are all lager than the Sm^{3+} single doped CeO_2 which may also be an additional reason.

It's worth noting that although In^{3+} single doped CeO_2 has smaller edge atoms (In^{3+}, Ce^{4+}) than that of the Sm^{3+} single doped CeO_2 (Sm^{3+}, Ce^{4+}), it still has a larger forward energy barrier than the Sm^{3+} single doped CeO_2. Thus, we can conclude that compared with edge atoms, E_{ass} plays a more important role in the migration energy barrier of the oxygen vacancies.

For the path V→O2 (N,N→NN,N), the migration energy barriers for In^{3+} or Sm^{3+}

single doped CeO_2 are the same with that of M1 (V→O1), for their migration paths are equivalent. The forward migration energy barrier for co-doped CeO_2 is much lower than that of M1 (V→O1), which can be attributed to two reasons: (1) the edge atoms of In^{3+} and Ce^{4+} for M1(V→O2) are smaller than the Sm^{3+} and Ce^{4+} for M1(V→O1); (2) the smaller energy differences between the initial configuration and the final configuration of the migration paths.

For the path V→O3 (N,N→N,N), the migration energy barrier can be arranged in the decreasing order as: $Ce_{30}Sm_2O_{63}$ (Sm^{3+}, Sm^{3+}) > $Ce_{30}InSmO_{63}$ (Sm^{3+}, In^{3+}) > $Ce_{30}In_2O_{63}$ (In^{3+}, In^{3+}). The difference, which can be can be interpreted as: for the initial configuration and the final configuration of this migration path are equivalent, the radius of the edge atoms (In^{3+} (0.92Å) < Ce^{4+} (0.97Å) < Sm^{3+} (1.079Å)) can dominate the migration energy barriers as shown in Table 4.

For the path V→O4 (N,N→NN,NN), it is worth noting that when we perform the geometry relaxation on the final configuration of In^{3+} single dope CeO_2, it will convert to the initial configuration of this path, which means that the final configuration of this path for In^{3+} single dope CeO_2 does not exist. So we can infer that the forward migration energy barrier of this path for In^{3+} single doped CeO_2 is zero and the backward migration energy barrier is infinity. Regarding the Sm^{3+} single doped CeO_2 and the In^{3+}, Sm^{3+} co-doped CeO_2, we can see that the co-doped CeO_2 possesses higher forward migration energy than the Sm^{3+} single doped CeO_2. For the stronger trapping effect of In^{3+} on the oxygen vacancy than Sm^{3+}, the energy difference between the initial configuration and the final configuration of this path for the co-doped CeO_2 is larger than that of the Sm^{3+} single doped CeO_2, which will cause the lager energy barrier for the co-doped CeO_2 than the Sm^{3+} single doped ones.

For the migration energy barriers of M3-2, the influencing factors as concluded above are the same with those of M1, so for simplicity, no repeated analysis will be presented in the paper.

We have also calculated the average migration energy barriers for the limited paths in M1 and M3-2. From table 4, we can see that the average forward barrier for the co-doped CeO_2 has demonstrated an intermediate value between the corresponding single doped CeO_2 either for M1 or for M3-2, reflecting an average co-doping effect on the migration energy barriers of both M1 and M3-2.

To verify the accuracy of our calculations, we further compared our calculated data with the experimental results. At low or intermediate temperatures, the ionic conductivity σ of the dilute concentration doped CeO_2 can be expressed in the Arrhenius equation [34, 50]:

$$\sigma = \sigma_0/T \cdot \exp(-\frac{E_a}{k_B T})$$

where σ_0 is a temperature-independent prefactor, T is the temperature, k_B is the Boltzman constant and E_a is the activation energy for oxygen vacancy diffusion corresponding to the sum of dopant-vacancy association energy E_{ass} and average oxygen vacancy migration energy E_m.

However, as reported [33-34] and discussed in section 3.4, E_{ass} depends on the concentration and distribution of the doped ions, the latter of which (or in other words the local structure) is difficult to control in experiments. That’s why even for the same composition, the E_a values reported by different experiments are always slightly different [50-54]. As Andersson et al. [34] concluded, the highest E_{ass} can be reached when the configuration is the most stable (corresponding to our configuration of M1 and M3-2 as discussed in section 3.4) and when the temperature is sufficiently high, most vacancies will be dissociated, then the E_{ass} can be considered to be zero.

Based on these two limits, the activation energy for our calculated 6.25% Sm doped CeO_2 can be estimated to be 0.61~1.16eV (0.73~1.16eV for M1 and 0.61~0.94eV for M3-2), which is in good accordance with the similar composition experimental results of 0.8eV for 9% Sm doped CeO_2 [54] and 0.71eV for 10% Sm doped CeO_2 [55]. In addition, since we have fully considered the existence of the extreme cases, for the common 20% Sm doped CeO_2, the experimental E_{a} value of 0.69~1eV [50-54] is also within our estimated range. Therefore, our calculation results are reliable and meaningful for the further development of the CeO_2-based electrolyte.

4. Summary

To figure out the co-doping effect on electrolyte performance of CeO_2-based materials, a series of microscopic properties including density of states, band structures, oxygen vacancy formation energies, defect association energies, and oxygen vacancy migration energies for In^{3+}, Sm^{3+} single doped and co-doped CeO_2 are performed using DFT+U method. The results show that the most energetically stable configurations for In^{3+}, Sm^{3+} co-doped CeO_2 are M1 and M3-2, which are both non-conductive and possess an average co-doping effect on bandgaps.

For both E_{vac}^{f} and E_{ass}, whether the co-doping effect is average or synergistic has a strong relationship to the distance of the two doped ions. When the distance between two doped ions is the first nearest neighbor (M1), the co-doping effects are average. However, when the distance between the two doped ions extends to the second nearest neighbor (M3-2, M3), the availability of the free oxygen vacancies is synergistically enhanced.

From CINEB calculation, we can conclude that the migration energy barrier is related to three influencing factors, including: (1) Dopant-vacancy association energy E_{ass}; (2) the energy difference between the initial state and the final state of the oxygen vacancy migration; (3) edge atoms besides the migration paths of the oxygen vacancy. Although the co-doping effect on the oxygen vacancy migration may be complicated, our calculated average migration energy barriers based on the limited migration paths for M1 and M3-2 reflect the average co-doping effect on the oxygen vacancy migration.

Therefore based on our calculation results, a new explanation for the controversial co-doping effect can be proposed. That is in In^{3+}, Sm^{3+} co-doped CeO_2, whether the co-doping effect on the ionic conductivity is average or synergistic has a strong relationship with the local structures of the co-doped ions which is difficult to control in experiments. The results from this paper provide insights in explaining the controversial experimental results for CeO_2-based materials with complex configurations.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51602183 & 11674197), the Shandong Provincial Natural Science Foundation, China (Grant No. ZR2014BP003), the China Postdoctoral Science Foundation (Grant No.2015M572074), and the Undergraduate Scientific Research

Foundation of Shandong Normal University, China (Grant No.2017BKSKY35). The authors acknowledge Supercomputing Center of USTC for their supporting.

References

[1] S.P. Jiang, W. Wang, Fabrication and performance of GDC-impregnated (La, Sr) MnO_3 cathodes for intermediate temperature solid oxide fuel cells, J. Electrochem. Soc. 152 (2005) A1398-A1408. https://doi.org/10.1149/1.1928167.

[2] M. Ni, D.Y. Leung, M.K. Leung, Electrochemical modeling and parametric study of methane fed solid oxide fuel cells, Energ. Convers. Manage. 50 (2009) 268-278. https://doi.org/10.1016/j.enconman.2008.09.028.

[3] Z. Shao, S. M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, Nature 431 (2004) 170-173. https://doi.org/10.1038/nature02863.

[4] T. Hong, M. Zhao, K. Brinkman, F. Chen, C. Xia, Enhanced Oxygen Reduction Activity on Ruddlesden–Popper Phase Decorated $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ 3D Heterostructured Cathode for Solid Oxide Fuel Cells, ACS Appl. Mater. Interfaces 9 (2017) 8659-8668. https://doi.org/10.1021/acsami.6b14625.

[5] J. Chen, F. Liang, L. Liu, S. Jiang, B. Chi, J. Pu, J. Li, Nano-structured (La, Sr)(Co, Fe)O_3+YSZ composite cathodes for intermediate temperature solid oxide fuel cells, J. Power Sources 183 (2008) 586-589. https://doi.org/10.1016/j.jpowsour.2008.05.082.

[6] Z. Zhu, J. Qian, Z. Wang, J. Dang, W. Liu, High-performance anode-supported solid oxide fuel cells based on nickel-based cathode and $Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\delta}$ electrolyte, J. Alloy. Compd. 581 (2013) 832-835. https://doi.org/10.1016/j.jallcom.2013.07.210.

[7] V.V. Kharton, F.M.B. Marques, A. Atkinson, Transport properties of solid oxide

electrolyte ceramics: a brief review, Solid State Ionics 174 (2004) 135-149. https://doi.org/10.1016/j.ssi.2004.06.015.

[8] M. Burbano, S.T. Norberg, S. Hull, S.G. Eriksson, D. Marrocchelli, P.A. Madden, G.W. Watson, Oxygen Vacancy Ordering and the Conductivity Maximum in Y_2O_3-Doped CeO_2, Chem. Mater. (2012) 222-229. https://doi.org/10.1021/cm2031152.

[9] H. Inaba, H. Tagawa, Ceria-based solid electrolytes, Solid State Ionics 83 (1996) 1-16. https://doi.org/10.1016/0167-2738(95)00229-4.

[10] A.K. Lucid, P.R.L. Keating, J.P. Allen, G.W. Watson, Structure and Reducibility of CeO_2 Doped with Trivalent Cations, J. Phys. Chem. C 120 (2016) 23430-23440. https://doi.org/10.1021/acs.jpcc.6b08118.

[11] Z. Fu, Q. Sun, D. Ma, N. Zhang, Y. An, Z. Yang, Effects of Sm doping content on the ionic conduction of CeO_2 in SOFCs from first principles, Appl. Phys. Lett. 111 (2017) 023903-023905. https://doi.org/10.1063/1.4993897.

[12] Y.P. Xiong, K. Yamaji, T. Horita, N. Sakai, H. Yokokawa, Hole and Electron Conductivities of 20 mol% $REO_{1.5}$ Doped CeO_2 (RE= Yb, Y, Gd, Sm, Nd, La), J. Electrochem. Soc. 151 (2004) A407-A412. https://doi.org/10.1149/1.1646149.

[13] S.Q. Shi, J. Gao, Y. Liu, Y. Zhao, Q. Wu, W.W. Ju, C.Y. Ouyang, R.J. Xiao, Multi-scale computation methods: Their applications in lithium-ion battery research and development, Chinese Phys. B 25 (2016) 018212. https://doi.org/10.1088/1674-1056/25/1/018212.

[14] S.Q. Shi, X.Z. Ke, C.Y. Ouyang, H. Zhang, H.C. Ding, Y.H. Tang, W.W. Zhou, P.J. Li, M.S. Lei, W.H. Tang, First-principles investigation of the bonding, optical and lattice

dynamical properties of CeO_2, J. Power Sources 194 (2009) 830-834. https:// doi.org/ 10.1016/j.jpowsour.2009.06.031.

[15] S.Q. Shi, Y.H. Tang, C.Y. Ouyang, L.X. Cui, X.G. Xin, P.J. Li, W.W. Zhou, H. Zhang, M.S. Lei, L.Q. Chen, O-vacancy and surface on CeO_2: A first-principles study, J. Phys. Chem. Solids 71 (2010) 788-796. https://doi.org/10.1016/j.jpcs.2010.02.002.

[16] Y. H. Tang, H. Zhang, L.X. Cui, C.Y. Ouyang, S.Q. Shi, W.H. Tang, H. Li, L.Q. Chen, Electronic states of metal (Cu, Ag, Au) atom on CeO_2(111) surface: The role of local structural distortion, J. Power Sources 197 (2012) 28-37. https://doi.org/10.1016/j.jpowsour.2011.09.026.

[17] Y. H. Tang, H. Zhang, L.X. Cui, C.Y. Ouyang, S.Q. Shi, W.H. Tang, H. Li, J.-S. Lee, L.Q. Chen, First-principles investigation on redox properties of M-doped CeO_2 (M= Mn, Pr, Sn, Zr), Phys. Rev. B 82 (2010) 125104-125109. https://doi.org/10.1103/PhysRevB.82.125104.

[18] Y. H. Tang, H. Zhang, C.M. Guan, J.Q. Shen, S.Q. Shi, W.H. Tang, Effects of Mn, Pr, Sn, Zr, Se and Te doping on redox properties of CeO_2, Sci. Sin-Phys. Mech. Astron. 42 (2012) 914-925. https://doi.org/10.1360/132012-59.

[19] L. X. Cui, Y.H. Tang, H. Zhang, L.G. Hector, Jr., C. Ouyang, S.Q. Shi, H. Li, L. Chen, First-principles investigation of transition metal atom M (M = Cu, Ag, Au) adsorption on CeO_2(110), Phys. Chem. Chem. Phys. 14 (2012) 1923-1933. https://doi.org/10.1039/c2cp22720g.

[20] L. J. Chen, Y.H. Tang, L.X. Cui, C.Y. Ouyang, S.Q. Shi, Charge transfer and formation of Ce^{3+} upon adsorption of metal atom M (M = Cu, Ag, Au) on CeO_2 (100) surface, J. Power Sources 234 (2013) 69-81.

https://doi.org/10.1016/j.jpowsour.2013.01.121.

[21] R. Gerhardt-Anderson, A. Nowick, Ionic conductivity of CeO_2 with trivalent dopants of different ionic radii, Solid State Ionics 5 (1981) 547-550. https://doi.org/10.1016/0167-2738(81)90313-1.

[22] H. Yahiro, K. Eguchi, H. Arai, Electrical properties and reducibilities of ceria-rare earth oxide systems and their application to solid oxide fuel cell, Solid State Ionics 36 (1989) 71-75. https://doi.org/10.1016/0167-2738(89)90061-1.

[23] H. Yoshida, T. Inagaki, K. Miura, M. Inaba, Z. Ogumi, Density functional theory calculation on the effect of local structure of doped ceria on ionic conductivity, Solid State Ionics 160 (2003) 109-116. https://doi.org/10.1016/S0167-2738(03)00153-X.

[24] M. Mogensen, N.M. Sammes, G.A. Tompsett, Physical, chemical and electrochemical properties of pure and doped ceria, Solid State Ionics 129 (2000) 63-94. https://doi.org/10.1016/ S0167-2738(99)00318-5.

[25] M. Nakayama, M. Martin, First-principles study on defect chemistry and migration of oxide ions in ceria doped with rare-earth cations, Phys. Chem. Chem. Phys. 11 (2009) 3241-3249. https://doi.org/10.1021/cm2031152.

[26] D.R. Ou, T. Mori, F. Ye, J. Zou, G. Auchterlonie, J. Drennan, Oxygen-vacancy ordering in lanthanide-doped ceria: Dopant-type dependence and structure model, Phys. Rev. B 77 (2008) 024108 - 024116. https://doi.org/10.1103/PhysRevB.77.024108.

[27] D. Kashyap, P.K. Patro, R.K. Lenka, T. Mahata, P.K. Sinha, Effects of Gd and Sr co-doping in CeO_2 for electrolyte application in solid oxide fuel cell (SOFC), Ceram. Int. 40 (2014) 11869-11875. https://doi.org/10.1016/j.ceramint.2014.04.021.

[28] N. Jaiswal, S. Upadhyay, D. Kumar, O. Parkash, Sm^{3+} and Sr^{2+} co-doped ceria prepared by citrate–nitrate auto-combustion method, Int. J. Hydrogen Energ. 39 (2014) 543-551. https://doi.org/10.1016/j.ijhydene.2013.10.009.

[29] H. Yamamura, E. Katoh, M. Ichikawa, K. Kakinuma, T. Mori, H. Haneda, Multiple doping effect on the electrical conductivity in the $(Ce_{(1-x-y)}La_{(x)}M_{y})O_{2-delta}$ (M=Ca, Sr) system, Electrochemistry 68 (2000) 455-459.

[30] Z. Tao, H. Ding, X. Chen, G. Hou, Q. Zhang, M. Tang, W. Gu, The co-doping effect of Sm and In on ceria for electrolyte application in IT-SOFC, J. Alloy. Compd. 663 (2016) 750-754. https://doi.org/10.1016/j.jallcom.2015.12.164.

[31] R.M. Kasse, J.C. Nino, Ionic conductivity of $Sm_{x}Nd_{y}Ce_{0.9}O_{2-\delta}$ codoped ceria electrolytes, J. Alloy. Compd. 575 (2013) 399-402. https://doi.org/10.1016/j.jallcom.2013.05.204.

[32] M. Burbano, S. Nadin, D. Marrocchelli, M. Salanne, G.W. Watson, Ceria co-doping: synergistic or average effect?, Phys. Chem. Chem. Phys. 16 (2014) 8320-8331. https://doi.org/10.1039/c4cp00856a.

[33] M. Alaydrus, M. Sakaue, S.M. Aspera, T.D. Wungu, T.P. Linh, H. Kasai, T. Ishihara, T. Mohri, A first-principles study on defect association and oxygen ion migration of Sm^{3+} and Gd^{3+} co-doped ceria, J. Phys-Condens. Mat. 25 (2013) 225401-225408. https://doi.org/10.1088/0953-8984/25/22/225401.

[34] D.A. Andersson, S.I. Simak, N.V. Skorodumova, I.A. Abrikosov, B. Johansson, Optimization of ionic conductivity in doped ceria, Proc. Natl. Acad. Sci. USA 103 (2006) 3518-3521. https://doi.org/10.1073/pnas.0509537103.

[35] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169-11186. https://doi.org/10.1103/PhysRevB.54.11169.

[36] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comp. Mater. Sci. 6 (1996) 15-50. https://doi.org/10.1016/0927-0256(96)00008-0.

[37] P.E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953-17979. https://doi.org/10.1103/PhysRevB.50.17953.

[38] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865-3868. https://doi.org/10.1103/PhysRevLett.77.3865.

[39] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188-5192. https://doi.org/10.1103/PhysRevB.13.5188.

[40] Z. Yang, T.K. Woo, K. Hermansson, Effects of Zr doping on stoichiometric and reduced ceria: a first-principles study, J. Chem. Phys. 124 (2006) 224704-224711. https://doi.org/10.1063/1.2200354.

[41] J. Feng, B. Xiao, C.L. Wan, Z.X. Qu, Z.C. Huang, J.C. Chen, R. Zhou, W. Pan, Electronic structure, mechanical properties and thermal conductivity of $Ln_2Zr_2O_7$ (Ln=La, Pr, Nd, Sm, Eu and Gd) pyrochlore, Acta Mater. 59 (2011) 1742-1760. https://doi.org/10.1016/j.actamat.2010.11.041.

[42] L. Gerward, J.S. Olsen, L. Petit, G. Vaitheeswaran, V. Kanchana, A. Svane, Bulk modulus of CeO_2 and PrO_2—An experimental and theoretical study, J. Alloy. Compd.

400 (2005) 56-61. https://doi.org/10.1016/j.jallcom.2005.04.008.

[43] E. Wuilloud, B. Delley, W.D. Schneider, Y. Baer, Spectroscopic Evidence for Localized and Extended f-Symmetry States in CeO_2, Phys. Rev. Lett. 53 (1984) 202-205. https://doi.org/10.1103/PhysRevLett.53.2518.

[44] M. Nolan, J.E. Fearon, G.W. Watson, Oxygen vacancy formation and migration in ceria, Solid State Ionics 177 (2006) 3069-3074. https://doi.org/10.1016/j.ssi.2006.07.045.

[45] K. Kaviyarasu, X. Fuku, G.T. Mola, E. Manikandan, J. Kennedy, M. Maaza, Photoluminescence of well-aligned ZnO doped CeO_2 nanoplatelets by a solvothermal route, Mater. Lett. 183 (2016) 351-354. https://doi.org/10.1016/j.matlet.2016.07.143.

[46] A. Corma, P. Atienzar, H. García, J.-Y. Chane-Ching, Hierarchically mesostructured doped CeO_2 with potential for solar-cell use, Nat. Mater. 3 (2004) 394-397. https://doi.org/10.1038/nmat1129.

[47] L. Wei, S.M. Haile, Impedance Spectroscopy as a Tool for Chemical and Electrochemical Analysis of Mixed Conductors: A Case Study of Ceria, J. Am. Ceram. Soc. 88 (2010) 2979-2997. https://doi.org/10.1111/j.1551-2916.2005.00740.x.

[48] D.A. Andersson, S.I. Simak, B. Johansson, I.A. Abrikosov, N.V. Skorodumova, Modeling of CeO_2, Ce_2O_3, and CeO_{2-x} in the LDA+U formalism, Phys. Rev. B 75 (2007) 035109-035115. https://doi.org/10.1103/PhysRevB.75.035109.

[49] M.A. Panhans, R.N. Blumenthal, A thermodynamic and electrical conductivity study of nonstoichiometric cerium dioxide, Solid State Ionics 60 (1993) 279-298. https://doi.org/10.1016/0167-2738(93)90006-O.

[50] H. Yoshida, H. Deguchi, K. Miura, M. Horiuchi, T. Inagaki, Investigation of the relationship between the ionic conductivity and the local structures of singly and doubly doped ceria compounds using EXAFS measurement, Solid State Ionics 140 (2001) 191-199. https://doi.org/10.1016/S0167-2738(01)00854-2.

[51] S. Sameshima, H. Ono, K. Higashi, K. Sonoda, Y. Hirata, Y. Ikuma, Electrical conductivity and diffusion of oxygen ions in rare-earth-doped ceria, J. Ceram. Soc. Jpn. 108 (2000) 1060-1066. https://doi.org/10.2109/jcersj.108.1264_1060.

[52] T. H. Yeh, C. C. Chou, Ionic conductivity investigation in samarium and strontium co-doped ceria system, Phys. Scripta 2007 (2007) 303. https://doi.org/10.1088/0031-8949/2007/T129/067.

[53] H. Yahiro, Y. Eguchi, K. Eguchi, H. Arai, Oxygen ion conductivity of the ceria-samarium oxide system with fluorite structure, J. Appl. Electrochem. 18 (1988) 527-531. https://doi.org/10.1007/BF01022246.

[54] W. Huang, P. Shuk, M. Greenblatt, Hydrothermal Synthesis and Properties of $Ce_{1-x}Sm_xO_{2-x/2}$ and $Ce_{1-x}Ca_xO_{2-x}$ Solid Solutions, Chem. Mater. 9 (1997) 2240-2245. https://doi.org/10.1021/cm970425t.

[55] T. Mori, J. Drennan, Influence of microstructure on oxide ionic conductivity in doped CeO_2 electrolytes, J. Electroceram. 17 (2006) 749-757. https://doi.org/10.1007/s10832-006-6311-7.

Figure captions

Fig.1 Location overview of the doped ions and oxygen vacancies in the co-doped CeO_2 supercell.

Fig.2 Local structures and the corresponding energies of the co-doped configurations.

Fig.3 Density of states: (a) $Ce_{32}O_{64}$, (b) $Ce_{32}O_{63}$, (c) $Ce_{31}InO_{63}$, (d) $Ce_{30}In_2O_{63}$, (e) $Ce_{31}SmO_{63}$, (f) $Ce_{30}Sm_2O_{63}$, (g) $Ce_{30}InSmO_{63}$ (M1) (h) $Ce_{30}InSmO_{63}$ (M3-2).

Fig.4 Oxygen vacancy migration paths of the configuration of (a) M1 and (b) M3-2.

Table 1 Bandgap list of the pure and doped CeO_2.

Structure	**Bandgap/eV**
$Ce_{32}O_{64}$	2.372
$Ce_{32}O_{63}$	0.796
$Ce_{30}In_2O_{63}$	2.119
$Ce_{30}Sm_2O_{63}$	2.316
$Ce_{30}InSmO_{63}$ (M1)	2.249
$Ce_{30}InSmO_{63}$ (M3-2)	2.258

Table 2 Vacancy formation energy for un-doped and doped CeO_2 materials.

Structure	**E/eV**
$Ce_{32}O_{63}$	3.332
$Ce_{31}InO_{63}$-N	1.231
$Ce_{31}InO_{63}$-NN	1.728
$Ce_{30}In_2O_{63}$(N)-N,N	-0.889
$Ce_{30}In_2O_{63}$(N)-NN,N	-0.282
$Ce_{30}In_2O_{63}$(NN)-NN,N	-0.293
$Ce_{31}SmO_{63}$-N	1.887
$Ce_{31}SmO_{63}$-NN	1.956
$Ce_{30}Sm_2O_{63}$(N)-N,N	-0.421
$Ce_{30}Sm_2O_{63}$(N)-NN,N	-0.418
$Ce_{30}Sm_2O_{63}$(NN)-NN,N	-0.108
$Ce_{30}InSmO_{63}$ (N)-N,N (M1)	-0.533
$Ce_{30}InSmO_{63}$ (NN)-NN,N (M3-2)	-2.160
$Ce_{30}InSmO_{63}$ (NN)-N,NN (M3)	-1.680

Table 3 E_{ass}, E_{ele} and E_{ela} for doped CeO_2 with different structures.

Structures		E_{ass}/eV	E_{ele}/eV	E_{ela}/eV
M1	**$Ce_{30}In_2O_{63}$**	-1.314	-2.130	0.816
	$Ce_{30}Sm_2O_{63}$	-0.434	-1.946	1.512
	$Ce_{30}InSmO_{63}$	-0.736	-2.045	1.309
M3-2	**$Ce_{30}In_2O_{63}$**	-0.654	-1.256	0.603
	$Ce_{30}Sm_2O_{63}$	-0.305	-1.063	0.758
	$Ce_{30}InSmO_{63}$	-0.745	-1.269	0.524
M3	**$Ce_{30}InSmO_{63}$**	-0.235	-1.017	0.782

Table 4 Migration energy barriers of the oxygen vacancies in In^{3+}, Sm^{3+} single doped and co-doped CeO$_2$.

Migration path		**$Ce_{30}In_2O_{63}$**				**$Ce_{30}Sm_2O_{63}$**				**$Ce_{30}InSmO_{63}$**			
		Edge atom	**Δ E**	**Forward**	**Backward**	**Edge atom**	**Δ E**	**Forward**	**Backward**	**Edge atom**	**Δ E**	**Forward**	**Backward**
M1	**V→O1 N,N→N,NN**	In^{3+} Ce^{4+}	0.568	0.930	0.362	Sm^{3+} Ce^{4+}	0.078	0.717	0.639	Sm^{3+} Ce^{4+}	0.665	0.938	0.273
	V→O2 N,N→NN,N	In^{3+} Ce^{4+}	0.568	0.930	0.362	Sm^{3+} Ce^{4+}	0.078	0.717	0.639	In^{3+} Ce^{4+}	0.072	0.425	0.353
	V→O3 N,N→N,N	In^{3+} In^{3+}	0	0.667	0.667	Sm^{3+} Sm^{3+}	0	1.127	1.127	Sm^{3+} In^{3+}	0.006	0.747	0.741
	V→O4 N,N→NN,NN	Ce^{4+} Ce^{4+}		0	∞	Ce^{4+} Ce^{4+}	0.174	0.512	0.338	Ce^{4+} Ce^{4+}	0.658	0.727	0.069
Average barrier				**0.632**	**--**			**0.768**	**0.686**			**0.709**	**0.359**
M3-2	**V→O1 NN,N→NNNN,N**	In^{3+} Ce^{4+}	0	0.491	0.491	Sm^{3+} Ce^{4+}	0.001	0.706	0.704	In^{3+} Ce^{4+}	0.001	0.401	0.400
	V→O2 NN,N→N,NN	In^{3+} Ce^{4+}	0	0.234	0.234	Sm^{3+} Ce^{4+}	0	0.449	0.449	Ce^{4+} Ce^{4+}	0.521	0.668	0.148
	V→O3 NN,N→NN,N	In^{3+} Ce^{4+}	0.001	0.493	0.493	Sm^{3+} Ce^{4+}	0	0.761	0.761	In^{3+} Ce^{4+}	0.001	0.449	0.448
	V→O4 NN,N→NNN,NN	Ce^{4+} Ce^{4+}	0.519	0.706	0.188	Ce^{4+} Ce^{4+}	0.156	0.615	0.459	Ce^{4+} Ce^{4+}	0.694	0.817	0.123
Average barrier				**0.481**	**0.351**			**0.633**	**0.593**			**0.584**	**0.280**