Transitional Area of Ce4+ to Ce3+ in SmxCayCe1-x-yO2- with Various Doping and Oxygen Vacancy Concentrations: A GGA + U Study (Postprint)

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Abstract

In this work, we perform DFT+U periodic calculations to investigate the geometric and electronic structures, as well as oxygen vacancy formation energies, of SmxCayCe1-x-yO2- systems (x = 0.0312, 0.0625, 0.125, and 0.250; y = 0.0312, 0.0625, 0.125, and 0.250; = 0.0312, 0.0625, 0.125, 0.250, and 0.50) with varying oxygen vacancy and doping concentrations. The calculated results show that V1-Sm3+-V2 structures, where V1 and V2 (both nearest to Sm3+) are positioned along a face diagonal, exhibit the lowest energy configurations. Electronic structure analysis of the SmxCayCe1-x-yO2- systems reveals that excess electrons generated from oxygen vacancies are localized on the f-level traps of neighboring Ce ions, and that Ca2+ and Sm3+ co-doping effectively suppresses the reduction of Ce4+. To prevent the formation of Ce3+, both x and y must be greater than 0.0625 when = 0.125, or must be less than 0.125 when x = y = 0.0625. The Ce3+/Ce4+ transformation ratio k exhibits a clear monotonic increase with increasing oxygen vacancy concentration. The introduction of Sm3+ reduces k. Furthermore, doped Sm3+ can suppress the reduction of Ce4+ when the V1-Sm3+-V2 structure with a face-diagonal positional relationship exists in a less reducing atmosphere. It should be noted that the Sm0.25Ce0.75O1.5 system should be considered as Sm-doped Ce2O3.

Full Text

Transitional Area of Ce4+ to Ce3+ in SmxCayCe1-x-yO2- with Various Doping and Oxygen Vacancy Concentrations: A GGA + U Study

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ABSTRACT

In this work, we perform DFT+U periodic calculations to investigate the geometric and electronic structures as well as oxygen vacancy formation energies of SmxCayCe1-x-yO2- systems (x = 0.0312, 0.0625, 0.125 and 0.250; y = 0.0312, 0.0625, 0.125 and 0.250;   = 0.0312, 0.0625, 0.125, 0.250 and 0.50) with varying oxygen vacancy and doping concentrations. Our calculations reveal that the V1-Sm3+-V2 structures, where V1 and V2 (both nearest to Sm3+) adopt a face-diagonal positional relationship, represent the lowest-energy configurations. Analysis of the electronic structures shows that excess electrons originate from oxygen vacancies and become localized on the f-level traps of neighboring Ce atoms, while Ca2+ and Sm3+ co-doping effectively suppresses the reduction of Ce4+ to Ce3+. To prevent the formation of Ce3+, both x and y must exceed 0.0625 when   = 0.125, or   must be less than 0.125 when x = y = 0.0625. The Ce3+/Ce4+ transformation ratio k exhibits a clear monotonic increase with rising oxygen vacancy concentration, while the introduction of Sm3+ reduces k. Furthermore, Sm3+ doping can inhibit Ce4+ reduction when the V1-Sm3+-V2 structure with a face-diagonal relationship exists in less reduced atmospheres. It should be noted that the Sm0.25Ce0.75O1.5 system is best described as Sm-doped Ce2O3.

Keywords: cerium oxide; oxygen vacancies; doping; electronic structures; GGA+U

1 INTRODUCTION

CeO2-based materials are important components in solid oxide fuel cells (SOFC) due to their high ionic conductivity. Pure CeO2 is a mixed ionic and electronic conductor. When a neutral oxygen vacancy is created in CeO2, the two excess electrons left behind become localized on the f-level traps of two neighboring Ce atoms, formally reducing Ce4+ to Ce3+. To improve ionic conductivity and reduce electronic conductivity, CeO2 is commonly doped with alkaline earth or rare earth metals such as Ca2+, Gd3+, Sm3+, and La3+, or through their co-doping.

The ionic and electronic conductivities of CeO2 have been widely studied. Mogensen' s investigation of Ca- or Gd-single-doped CeO2 systems found that the conduction carrier depends on the atmosphere, with conductivity measured in air being primarily ionic and the electronic contribution negligible. In reduced atmospheres, both ionic conductivity (i) and electronic conductivity (e) are related to oxygen partial pressure. The highest i for CeO2 doped with 20 mol% Ca reaches 0.209 S/cm in H2 atmosphere at 850 °C, which is larger than that in air. Ce1-xMxO2- (M = Gd3+ or Sm3+) at x = 0.15, 0.2 and (Ce0.8Sm0.2)1-0.05Ca0.05O2- compounds exhibit the largest ionic conductivity, with the latter achieving 0.126 S/cm at 800 °C in air. Additionally, the ionic radii and valence of dopants, oxygen vacancy and dopant concentrations, and dopant-vacancy and vacancy-vacancy defect associations—which decrease the number of mobile vacancies available—all affect the ionic conductivity of CeO2.

Theoretically, the distributions of oxygen vacancies and dopants, their formation energies, geometric and electronic structures, and oxygen ion migration energies of CeO2 systems have been investigated at the atomic level. Among rare earth metals, Sm3+ and among alkaline earth metals, Ca2+ yield the smallest oxygen ion migration energies in CeO2 systems, and their doping can effectively suppress electronic conductivity. Both theoretical and experimental studies have shown that Ca2+ and Sm3+ co-doping can better improve ionic conductivity. Previous work has examined the effects of different oxygen vacancy and doping concentrations on the distributions of oxygen vacancies, dopants, and Ce3+ in CeO2 systems. Murgida’ s study demonstrated that oxygen vacancy concentration affects the distribution of Ce3+, with excess electrons preferring to localize on cation sites that maximize the mean Ce3+ coordination number, and two vacancies tending to be second-nearest neighbors. For doped CeO2- , studies have found that dopants prefer to occupy nearest neighbor (NN) and next-nearest neighbor (NNN) positions relative to oxygen vacancies. Independent of oxygen vacancy and doping concentrations, Ce3+ is distributed around the nearest neighbor oxygen vacancy.

However, a systematic theoretical study on the Ce3+/Ce4+ electronic properties of CeO2 with different oxygen vacancy and doping concentrations is lacking. Since Ca and Sm doping can effectively restrain the reduction of Ce4+ to Ce3+ and doped CeO2 exhibits high ionic conductivity, we investigate the effects of various oxygen vacancy and Ca-, Sm-doping concentrations on the electronic structures (Ce3+/Ce4+) of CeO2 systems. We select different numbers of oxygen vacancies or Ca and Sm dopants in the same supercell to obtain a series of vacancy and doping concentrations, ultimately mapping the transitional area of Ce4+ to Ce3+ and the Ce3+/Ce4+ change ratio k under different conditions.

2 MODELS AND COMPUTATIONAL DETAILS

2.1 Models

CeO2 has a fluorite-type structure (Fm3m space group) with one formula unit per primitive unit cell. In this work, we consider various numbers of oxygen vacancies or Ca2+ and Sm3+ dopants to produce different oxygen vacancy and doping concentrations in a 2×2×2 supercell, namely SmxCayCe1-x-yO2- systems with various x, y and (x = 0.0312, 0.0625, 0.125 and 0.250; y = 0.0312, 0.0625, 0.125 and 0.250; = 0.0312, 0.0625, 0.125, 0.250 and 0.50), see Table 1 . When the doping concentration exceeds 0.30, SmxCayCe1-x-yO2- systems transition from doped to alloyed compositions; however, for descriptive convenience, we refer to all compositions as doped systems.

Doped atoms are uniformly distributed in the 2×2×2 supercell to obtain systems with various doping concentrations. Hooper' s study on Sm-doped CeO2 systems found that dopant-vacancy interactions follow a hybrid NN/NNN mixture distribution as Sm3+ concentrations increase, with NN distributions being most favored. Our previous studies found that the first oxygen vacancy (V1) occupies the nearest neighbor (NN) position to the dopant, and we employ the same structural model here. For CeO2 systems where more than one oxygen vacancy is nearest to a single Sm3+, these vacancies are selected according to the NN distribution rule, meaning the second oxygen vacancy nearest to a Sm3+ is introduced and designated as V2. Thus, V1 and V2 can adopt three distinct positional relationships within the cube of eight coordinated O2- for one Sm3+: the side configuration in Fig. 1a [Figure 1: see original paper], the face-diagonal configuration in Fig. 1b, and the body-diagonal configuration in Fig. 1c.

Calculation results show that structures with the face-diagonal relationship between V1 and V2 are the most stable, consistent with pure CeO2 systems containing double oxygen vacancies. For Ca-doped CeO2 systems, we consider models where Ca2+ has either NN or NNN distribution relationships with one oxygen vacancy.

2.2 Computational Details

All calculations were performed using the Vienna ab initio simulation package (VASP). Ce 5s5p6s4f5d, O 2s2p, Ca 3s3p4s, and Sm 5s5p6s4f5d electrons were treated as valence electrons. Structures were relaxed until forces on each ion fell below 0.02 eV/Å and total energy converged within 1×10   eV. A plane-wave cutoff energy of 400 eV, a 3×3×3 Monkhorst-Pack k-point mesh, and a Gaussian smearing parameter of 0.20 eV were employed.

Standard DFT formulations often fail to describe strongly correlated electrons due to inadequate treatment of electron correlation. This limitation can be corrected using a DFT+U method, where introducing a Hubbard parameter U modifies the self-interaction error and improves description of correlation effects. This methodology has been widely applied to reduced CeO2 systems. Theoretical work has shown that the U value for Ce should exceed 5.0 eV. In this study, we use U = 6.0 eV for Ce and U = 8.0 eV with J = 0.65 eV for Sm, consistent with previous work. Exchange-correlation effects were described using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The calculated lattice constant from GGA+U is 5.48 Å, in good agreement with the experimental value of 5.41 Å.

The formation energies of oxygen vacancies (E_Vo) for CeO2- systems, E_Vo-Sm for SmxCe1-xO2- systems, and E_Vo-CaSm for SmxCayCe1-x-yO2- systems are defined as:

$$E_V^o = E[X] + \frac{p}{2}E[O_2] - E[Y]$$

where E[X] and E[Y] are the total energies of pure or doped CeO2 systems with and without oxygen vacancies, respectively. E[O2] is the energy of an O2 molecule placed in a 10 Å × 10 Å × 10 Å supercell, and p is the number of oxygen vacancies.

3 RESULTS AND DISCUSSION

3.1 Geometric Structures

Optimized model structures with the lowest energies were obtained. The V1-Sm3+-V2 structures, where V1 and V2 (both nearest to Sm3+) adopt a face-diagonal positional relationship, represent the lowest-energy configurations, consistent with pure CeO2 systems containing double oxygen vacancies. The introduction of Sm3+, Ca2+, and oxygen vacancies into CeO2 produces significant geometric distortions, in agreement with previous work. Representative geometric structures of CeO1.9688, Sm0.0312Ce0.9688O1.9688, Sm0.0312Ce0.9688O1.9375, Sm0.0312Ca0.0312Ce0.9376O1.9688, and Sm0.0312Ca0.0312Ce0.9376O1.9375 systems are displayed in Fig. 2 [Figure 2: see original paper]. Other SmxCayCe1-x-yO2- systems with different oxygen vacancy and doping concentrations exhibit similar geometric distortions.

The oxygen vacancy creates a region of effective positive potential, causing neighboring O2- ions to move toward the vacancy while neighboring Ce4+ ions move away. In the CeO1.9688 system (Fig. 2a), three of the four O2- ions near the oxygen vacancy move toward it while the fourth moves away. As discussed in the electronic structure analysis below, this O2- is bridged by two Ce3+ ions that have greater negative potential than Ce4+. In the Sm0.0312Ce0.9688O1.9688 system (Fig. 2b), the behavior is similar to CeO1.9688, except that one of the two Ce3+ ions is replaced by Sm3+. In the Sm0.0312Ce0.9688O1.9375 system (Fig. 2c), the movement of four O2- ions toward the two vacancies and two O2- ions toward Sm3+ results from the combined attraction of V1 and V2 to O2-, meaning an O2- bridged by Sm3+ and Ce3+ is not repelled, unlike in systems with a single oxygen vacancy. In the Sm0.0312Ca0.0312Ce0.9376O1.9688 system (Fig. 2d), the four O2- ions near oxygen vacancies are driven toward the vacancy while neighboring Ce4+ ions move away. The Sm0.0312Ca0.0312Ce0.9376O1.9375 system (Fig. 2e) is similar to the Sm0.0312Ce0.9688O1.9375 system (Fig. 2c).

3.2 Oxygen Vacancy Formation Energies

Oxygen vacancy formation energies (E_Vo) for CeO2- systems, E_Vo-Sm for SmxCe1-xO2- systems, and E_Vo-CaSm for SmxCayCe1-x-yO2- systems are listed in Table 1 . E_Vo increases monotonically with increasing , as shown in Table 1 and Fig. 3 [Figure 3: see original paper]. For SmxCe1-xO2- and

SmxCayCe1-x-yO2- systems, E_Vo-Sm with a given x and E_Vo-CaSm with given x and y are larger at higher , while both decrease with increasing x (or x and y) at fixed . Notably, the introduction of Ca and Sm promotes spontaneous oxygen vacancy formation, similar to Fergus' s findings for Sm-doped CeO2 systems.

3.3 Electronic Structures

When oxygen vacancies form in CeO2, the Ce 4f state splits into two states: an empty Ce 4f_empty state and an occupied defect Ce3+ 4f_full state in the range between O 2p and Ce 4f_empty, consistent with our previous work and other studies, see Fig. 4 [Figure 4: see original paper]. Total electronic densities of states (DOS), partial electronic densities of states (PDOS), and localization electronic densities of states (LDOS) from the defect state of Ce3+ were calculated for various SmxCayCe1-x-yO2- systems with different x, y, and , as shown in Figs. 4 and 5 [Figure 5: see original paper].

3.3.1 Excess Electron Distribution The PDOS of the Ce 4f state for CeO1.9688, CeO1.9375, CeO1.875, and CeO1.75 systems (Fig. 4a) shows a new peak appearing in the -1.2 to 0 eV range for CeO1.9688, CeO1.9375, and CeO1.875 systems, and in the -0.80 to 0.60 eV range for the CeO1.75 system. These peaks are fully occupied by Ce3+ electrons. Compared to the CeO1.75 system, the Fermi level of the other systems shifts upward by approximately 0.50 eV due to decreased oxygen vacancy concentration. Excess electrons arise from oxygen vacancies and localize on the f-level traps of neighboring Ce atoms, as visually confirmed by the corresponding LDOS of the defect Ce3+ state in Figs. 4b-e. These findings are consistent with theoretical studies of CeO1.9843, CeO1.9687, CeO1.9375, and CeO1.875 and CeO2(111), (110), and (100) surfaces.

The PDOS of the Ce 4f state for SmxCe1-xO2- (0.0312   x   0.25, 0.0312   0.5) systems (Fig. 5a) shows similar behavior to CeO2- systems, with a new peak appearing in the O 2p–Ce 4f_empty range. The corresponding LDOS of the defect Ce3+ state (Figs. 5c-j) reveals that excess electrons from oxygen vacancies localize on the f-level traps of neighboring Ce atoms, as in CeO2- systems. For the Sm0.0312Ce0.9688O1.9375 system (Fig. 5j), two oxygen vacancies in the 2×2×2 supercell should induce four charge-compensating cations; however, calculations find only three, possibly due to the V1-Sm3+-V2 structure with a face-diagonal relationship in less reduced atmospheres, where doped Sm3+ can suppress Ce4+ reduction.

To better control excess electrons, we explored SmxCayCe1-x-yO2- (0.0312   x   0.25, 0.0312   y   0.25, 0.0312   0.5) systems with various x, y, and . The DOS in Fig. 5b shows that except for the Sm0.0625Ca0.0625Ce0.875O1.875 system, SmxCayCe1-x-yO2- systems contain no Ce3+. Thus, to avoid Ce3+ formation, both x and y must exceed 0.0625 when   = 0.125, or   must be less than 0.125 when x = y = 0.0625. For these systems, the corresponding LDOS of the defect Ce3+ state (Figs. 5c-k) shows that excess electrons from oxygen vacancies localize on the f-level traps of neighboring Ce atoms, as in CeO2- systems.

3.3.2 Transitional Area of Ce4+ to Ce3+ and Ce3+/Ce4+ Change Ratio k To visually understand the transitional area of Ce4+ to Ce3+ in SmxCayCe1-x-yO2- systems with various oxygen vacancy and doping concentrations, we plotted the transitional areas for SmxCe1-xO2- (Fig. 6a [Figure 6: see original paper]) and SmxCayCe1-x-yO2- systems (Fig. 6b). Fig. 6a shows that no Ce3+ exists in SmxCe1-xO2- systems with x   0.167 and   0.0833, while Ce3+ exists in systems with x   0.0312 and   0.0312, x   0.0625 and   0.0625, x   0.125 and   0.125, x   0.167 and   0.166, and x   0.250 and   0.250.

For SmxCayCe1-x-yO2- systems with y   0, substitution of Ce4+ by Ca2+ creates two excess electrons while substitution by Sm3+ creates one excess electron. To comprehensively reflect the doping concentration effect on the Ce4+ to Ce3+ transition ratio, we transform the effect of one Ca2+ to that of two Sm3+ (ignoring ionic radius differences) and plot the corresponding transitional area in Fig. 6b. This shows that no Ce3+ exists in SmxCayCe1-x-yO2- systems with x   0.0936 and   0.0625, x   0.334 and   0.166, x   0.375 and   0.250, and x   0.750 and   0.50, while Ce3+ exists in systems with x   0.187 and   0.125.

The Ce3+/Ce4+ change ratio k in SmxCe1-xO2- systems with various oxygen vacancy and doping concentrations is shown in Fig. 6c. The ratio k exhibits a clear monotonic increase with vacancy concentration, while Sm3+ introduction reduces k, as seen in Sm0.0312Ce0.9688O1.9375, Sm0.0625Ce0.9375O1.875, Sm0.125Ce0.875O1.75, Sm0.166Ce0.834O1.668, and Sm0.25Ce0.75O1.5 systems. Thus, Sm3+ doping suppresses Ce4+ reduction to Ce3+. Notably, the Sm0.25Ce0.75O1.5 system can be considered as Sm-doped Ce2O3 because it shows no unoccupied defect states between the occupied Ce3+ states and unoccupied Ce 4f_empty (Fig. 5a), consistent with other theoretical work.

4 CONCLUSION

This work investigates the influence of Sm3+ single-doping and Ca2+ and Sm3+ co-doping, along with oxygen vacancies and their concentrations, on the geometric and electronic structures of SmxCayCe1-x-yO2- systems. Geometric structure analysis shows that V1-Sm3+-V2 structures with a face-diagonal positional relationship between V1 and V2 (both nearest to Sm3+) are readily obtained, consistent with pure CeO2 systems. Electronic structure studies reveal that oxygen vacancies contribute excess electrons that localize on the f-level traps of neighboring Ce atoms in SmxCayCe1-x-yO2- systems. The Ce3+/Ce4+ change ratio k depends on both dopant and oxygen vacancy concentrations. Additionally, the presence of V1-Sm3+-V2 structures with face-diagonal relationships in less reduced atmospheres may enable doped Sm3+ to suppress Ce4+ reduction. It should be noted that the Sm0.25Ce0.75O1.5 system can be considered as Sm-doped Ce2O3.

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Note: Figure translations are in progress. See original paper for figures.

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