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Mechanism of Water Splitting on Gadolinium

Doped CeO₂ (111): A DFT+U Study

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ABSTRACT

Ceria-based materials have attracted considerable interest due to their potential applications in the electrocatalytic splitting of water for hydrogen production. In this work, the reaction mechanism of water splitting on gadolinium-doped ceria (GDC) is investigated using DFT+U calculations. We found that H₂ evolution preferentially proceeds on the overly hydroxylated surfaces of pure ceria and GDC via the formation of Ce-H and Gd-H intermediates respectively, which is much more efficient than the H₂ evolution over their partially hydroxylated surfaces. Notably, GDC is more easily and strongly reduced through formation of oxygen vacancies and hydroxyls compared to pure ceria. Thus, the facile formation of the overly hydroxylated states by the incorporation of Gd leads to the improved electrocatalytic activity of water splitting on ceria. These results indicate that a dopant that stabilizes the reduced ceria and favors the formation of Metal-H moiety is capable of effectively improving the reaction activity of ceria for water splitting.

INTRODUCTION

Ceria is widely used in many catalytic processes not only as a support but also as an efficient catalyst in redox reactions, due to its particular redox cycle between Ce^{4+} and Ce^{3+} . Ceria can be used to store oxygen in three-way catalysts¹⁻³ and in the water-gas shift reaction⁴⁻⁶. It also provides a sustainable alternative to fuel production using solar thermochemical cycles, with high conversion efficiencies.^{7,8} As a good ionic or mixed ionic and electronic conductor, doped ceria is a promising material for oxygen ion-conducting solid electrolytes in solid oxide fuel cells (SOFC)^{9,10} and solid oxide electrolyser cells (SOEC).^{11,12}

SOEC is a highly efficient technology for hydrogen production through the water splitting reaction at high temperature. By utilization of waste heat at high temperature, an SOEC can produce hydrogen with smaller overpotential losses than low temperature electrolysis cells.¹³ There is, however, pronounced degradation at the electrochemical interfaces (gas/electrode/electrolyte boundaries) in SOEC during high operating temperature, which results from oxygen incorporation into the oxygen conductor, eventually weakening and cracking the reaction interface.^{13,14} The hydrogen evolution reaction (HER) usually takes place at triple phase boundaries (TPB) between the gas channels, electronic and ionic conductors. The efficiency of the HER is significantly restricted by the degradation.^{13,14} Replacing the traditional yttria-stabilized zirconia (YSZ) ionic conductor with ceria will extend the TPB reaction zones to a double-phase boundary, where HER proceeds readily at the ceria-gas interface.^{15,16} Computational studies has showed that water dissociation for hydrogen production at the ceria/gas interface would be facile once oxygen vacancies can diffuse to the surface.¹⁷ Improved ionic conductivity increases the reaction efficiency of ceria, and doping ceria is a promising

approach for improving the ionic conductivity and the electrochemical activity for HER. Gadolinium doped ceria has been demonstrated to have the highest ionic conductivity among ceria-based materials¹⁸ and allows the electrochemical reactions at intermediate temperatures (773-1073 K).^{19,20} Therefore, ceria-based materials are promising for hydrogen production, through H₂O electrolysis in SOEC.

In the past few decades, the reactions associated with H₂, H₂O and ceria have been studied extensively, showing that the catalytic behavior of ceria is directly linked to its mixed valence Ce³⁺/Ce⁴⁺ redox states and the mobility of oxygen ions.^{11,17,21} Recently, the excellent performance of solar thermochemical redox reactions in ceria has been shown to be attributed to the positive entropy contribution associated with the $f^0 \rightarrow f^1$ transition.²² Electrocatalytic water splitting in ceria includes reaction steps of oxygen vacancy diffusion to the surface, water adsorption on the surface, water reaction with the oxygen vacancy and oxygen ions into hydroxyl ($\text{H}_2\text{O}_{\text{ads}} + 2\text{Ce}^{3+} + \text{V}_\text{o} + \text{O}^{2-} \rightarrow 2\text{OH}^- + 2\text{Ce}^{3+}$), and finally hydroxyl decomposition into H₂ and oxygen ions ($2\text{OH}^- + 2\text{Ce}^{3+} \rightarrow \text{H}_2 + 2\text{Ce}^{4+} + 2\text{O}^{2-}$). A competing pathway for the water splitting reactions when lattice O²⁻ is unavailable at the ceria surface proceeds through a Ce-H intermediate ($\text{H}_2\text{O}_{\text{ads}} + 2\text{Ce}^{3+} + \text{V}_\text{o} \rightarrow \text{OH}^- + \text{Ce}^{4+} + \text{Ce}^{4+}\text{H}^- \rightarrow \text{H}_2 + 2\text{Ce}^{4+} + \text{O}^{2-}$).¹⁷ The localization of the excess electrons after creating an oxygen vacancy varies with different DFT descriptions of the 4f orbitals on cerium.^{17,23,24} Oxygen diffusion to the surface for reaction with adsorbed water and the following step of water dissociation into stable hydroxyl are facile steps, having barriers of 0.65 and 0.06 eV, respectively.¹⁷ Recently, both theoretical and experimental studies indicate that the rate-determining step of the water splitting reaction on ceria involves the charge transfer for H₂ production through hydroxyl decomposition.^{11,17} Experimentally, surface hydroxyls can be stabilized up to 400-600 K under UHV conditions.^{25,26} Increasing the surface

reduction by creating oxygen vacancies or forming hydroxyls can improve the reaction activity for H_2 production.^{17,27} Among ceria-based materials, GDC holds great promise to improve the water splitting reaction rate.^{18–20} So far, computational studies on GDC have been limited to electronic structures and properties related to oxygen diffusion.^{28–30} Therefore, the fundamental understanding of the reaction mechanism for water splitting in SOEC on pure ceria and especially doped ceria remains elusive.

In this work, we present detailed DFT investigations on the formation and diffusion of oxygen vacancies, as well as hydroxyl formation and decomposition on ceria and GDC, respectively. The effect of Gd-doping on the stability of the reduced ceria surface by creating oxygen vacancies and formation of hydroxyl groups, and the impact of Gd-doping on the reaction pathways for water dissociation are discussed to obtain a more clear understanding of the water splitting reaction on the reduced ceria-based materials.

METHODS

Density-functional-theory (DFT) calculations are performed using the Vienna Ab-initio Simulation Package (VASP).^{31–33} The ionic cores are described by PAW potentials³⁴ and the wave functions are expanded in plane waves with an energy cutoff of 550 eV. The exchange and correlation are approximated by the PBE functional³⁵ including aspherical gradient corrections within the PAW augmentation spheres. Because of the electron self-interaction error in the Kohn-Sham formalism, the DFT+U approach³⁶ was used to describe electron localization on the 4f states of Ce^{3+} . We do not include a U correction on gadolinium, because the 4f shell of gadolinium is always found to be filled with seven electrons ($4f^7$) and the U contribution on describing the electron localization on the $4f^7$ shell can be negligible³⁷. the Spin polarization was

considered with ferromagnetic ordering, because the energy difference between antiferromagnetic and ferromagnetic state is small (<0.01 eV).³⁸

The optimal value of the Hubbard U parameter for cerium varies in the range of $0 < U_{\text{eff}} < 10$ eV ($U_{\text{eff}} = U - J$) depending on the quantity of interest.^{36,39–41} PBE+ U usually overestimates the lattice constant.^{40,41} The reduction energy of ceria is well described already at $U_{\text{eff}} \approx 2.0$ eV³⁹ while the calculated band gap is consistent with experiments for $U_{\text{eff}} > 5.5$ eV⁴⁰. We find a strong dependence of the oxygen vacancy formation energy (E_{Vo}) and the barrier for hydroxyl decomposition over the $\text{CeO}_2(111)$ on the values of U_{eff} , as shown in Figures S1-S3 in the supporting information. As noted in Figure S1, E_{Vo} linearly decreases with increasing U_{eff} when U_{eff} is higher than 3.5 eV. For $U_{\text{eff}} < 3.5$ eV there is a zone of weak electron localization on the 4f orbitals of ceria, which is consistent with the results by Castleton *et al.* that charge starts to become localized at $U_{\text{eff}} \approx 3.0$ eV⁴⁰. The degree of localization reaches a maximum at $U_{\text{eff}} \approx 5.5$ eV for the GGA+ U method.⁴⁰ The calculated barrier for hydroxyl decomposition on the $\text{CeO}_2(111)$ increases with U_{eff} because of the higher stability of reduced cerium when using a larger U_{eff} as shown in Figure S3 and S4. Overall, $U_{\text{eff}} = 4.5$ eV is often used for investigations on vacancy diffusion and related reactions on ceria, which has been proved to be an appropriate correction to ensure describe chemical properties of ceria.^{42–45} In addition, the vacancy formation energy and the activation barrier for hydroxyl decomposition on the $\text{CeO}_2(111)$ calculated in this work are well consistent with previously reported DFT results.^{23,45,46} Thus, $U_{\text{eff}} = 4.5$ eV used in this work is appropriate to describe the electrochemical properties of ceria during the water splitting reaction.

The $\text{CeO}_2(111)$ surface is built as a 2×3 repeated surface unit cell consisting of nine atomic layers ($\text{Ce}_{18}\text{O}_{36}$). Three atomic layers in the bottom are fixed as shown in Figure S4 in the

Supporting Information. Vacuum with a thickness of 15 Å is added to reduce interaction between the periodic images. The calculated equilibrium lattice constant of bulk ceria is 5.497 Å, which is well consistent with reported DFT result^{28,45} but overestimates the experimental lattice constant of 5.411 Å⁴⁷ by 1.6 %. The lattice constant has a 1.4% mismatch with the experimental lattice constant of Ce_{0.8}Gd_{0.2}O_{1.9} (5.423 Å)⁴⁸. The lattice with the same mismatch has been used by Aparicio-Anglès *et al.* for investigations of dopant clustering near the GDC(111) surface.²⁸ The highest ionic conductivity is obtained in ceria with 10% Gd doping.^{28,49} In this work, two cerium atoms in Ce₁₈O₃₆(111) are replaced with two gadolinium atoms for a Gd concentration of 11%. The selected system size allows for investigations of compensating oxygen vacancies near the optimal doping level, because two Gd³⁺ dopants are expected to induce the formation of one oxygen vacancy. The Gd₂Ce₁₆O₃₅(111) surface was investigated as the GDC model.

Transition states (TS) are identified for oxygen vacancy diffusion, water dissociation into hydroxyls and hydroxyl decompositions, using the climbing image nudged-elastic band method⁵⁰ in VASP. Each band is optimized until the maximum force on the band is less than 0.03 eV /Å.

RESULTS AND DISCUSSIONS

Distribution of Gd and oxygen vacancies (Vo) in Gd₂Ce₁₆O₃₅(111). We first investigate the surface without a compensating oxygen vacancy by substituting one Gd atom into the surface layer and another Gd atom into either the surface or subsurface layer. The distribution of the two Gd atoms is labeled from Type1 to Type4 with increasing Gd-Gd distance as shown in Figure 1(a). The uncompensated situation was normally investigated for aliovalent dopants in CeO₂^{28,37}. Based on the four uncompensated configurations of the Gd₂Ce₁₆O₃₆(111), a

compensating oxygen vacancy (Vo) was then introduced into the different oxygen atomic layers leading to the formation of the $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}$ (111). The Vo formation energy is defined as:

$$E_{Vo} = E_{\text{Gd}_2\text{Ce}_{16}\text{O}_{35}} - E_{\text{Gd}_2\text{Ce}_{16}\text{O}_{36}} + \frac{1}{2}E_{\text{O}_2},$$

where $E_{\text{Gd}_2\text{Ce}_{16}\text{O}_{35}}$ is the total energy of the system after creating one oxygen vacancy, $E_{\text{Gd}_2\text{Ce}_{16}\text{O}_{36}}$ is the total energy of the uncompensated system and E_{O_2} is the energy of an oxygen molecule. The formation energy of one oxygen vacancy in the subsurface ($\text{Vo}^{\text{subsurface}}$) and top surface ($\text{Vo}^{\text{surface}}$) in the uncompensated system to form $\text{Gd}_2\text{Ce}_{18}\text{O}_{35}$ (111) is list in Table 1. Creating a $\text{Vo}^{\text{subsurface}}$ in Type3 is more facile than in other types of Gd distribution, which is taken as a reference. Compared with the $\text{Vo}^{\text{subsurface}}$ in Type3, the relative energy of the Vo in each oxygen atomic layer in $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}$ (111) with four types of Gd distribution as a function of the distance from the top oxygen layer (depth) is given in Figure 1(b). For Type 1 GDC, the Vo favors to be created in the top surface, in comparison with creating one Vo in the subsurface and deeper layers. However, for Type2, Type3 and Type4 with two gadolinium atoms siting in two different atomic layers, the most favorable oxygen vacancy sits in the subsurface oxygen layer. The relative energy of the Vo in these GDC model increases when the vacancy is created in the deeper oxygen layers (depth > 1.5 Å) and the two excess electrons remain localized on the two gadolinium atoms. The energy difference between the $\text{Vo}^{\text{surface}}$ with four types of Gd distribution is lower than 0.006 eV, as displayed in Table1. Compared to the $\text{Vo}^{\text{surface}}$, a slightly larger energy difference (within 0.23 eV) between the $\text{Vo}^{\text{subsurface}}$ is noticed, which is consistent with Aparicio-Anglès's findings (within 0.25 eV)²⁸. However, the energy difference between the four different types of Gd distribution in $\text{Gd}_2\text{Ce}_{16}\text{O}_{36}$ is within 0.065 eV as presented in the Table 1. In addition, we found that the calculated energy difference between the formation energy of $\text{Gd}_2\text{Ce}_{18}\text{O}_{35}$ (111) having one oxygen vacancy in the top surface with four types of Gd

distributions is < 0.066 eV. With an oxygen vacancy in the subsurface, the energy difference is < 0.291 eV (see Table S1 in the supporting information). Our results suggest that Gd can distribute freely between the top surface or subsurface of $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}(111)$ at 11% Gd concentration. These results are in line with the previously reported findings.²⁸

In addition, the calculated formation energy of an oxygen vacancy in the top surface of the clean $\text{Ce}_{18}\text{O}_{36}(111)$ is 2.18 eV, which is close to 2.15 eV calculated by using $p(3\times 3)$ unit cell and $U_{\text{eff}}=4.5$ eV⁴⁵. The calculated formation energy for a slightly larger $p(3\times 4)$ unit cell is only 0.16 eV smaller than using a $p(2\times 3)$ unit cell, agreeing well with the report by Hui-Ying et al⁵¹ that the interaction between O vacancy in neighboring supercells could be neglected. Because the inducing of a compensating oxygen vacancy into the uncompensated $\text{Gd}_2\text{Ce}_{16}\text{O}_{36}$ system is preferred, the V_O formation energies in $\text{Gd}_2\text{Ce}_{16}\text{O}_{36}$ with four types of Gd distribution are negative values.

Figure 1: (a) The configurations of the most favorable vacancy in the top surface (depth = 0.0 Å) of the $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}(111)$ with Type1, Type2, Type3 and Type4 Gd distribution. Color legend: yellow for cerium, green for gadolinium and red for oxygen atoms. The balls with crosses represent the fixed atoms, while red balls with a dashed perimeter marks the oxygen vacancy. (b)

Relative energy of an oxygen vacancy at different depths in the $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}(111)$ with four types of Gd distribution. The depth is measured from the top of the surface.

Table 1. The minimum Gd-Gd distance in the four types of Gd distribution in the $\text{Gd}_2\text{Ce}_{16}\text{O}_{36}(111)$ and the relative energy between them. The formation energy of one oxygen vacancy (Vo) in the uncompensated system to form the $\text{Gd}_2\text{Ce}_{18}\text{O}_{35}(111)$. Vo in the subsurface and in the top surface layer is abbreviated as $\text{Vo}^{\text{subsurface}}$ and $\text{Vo}^{\text{surface}}$, respectively.

Gd distribution type	Gd-Gd Distance /Å	Relative Energy/eV	$\text{Vo}^{\text{subsurface}}$ /eV	$\text{Vo}^{\text{surface}}$ /eV
Type1	3.982	0	-0.725	-0.783
Type2	4.014	0.040	-0.927	-0.789
Type3	5.489	0.039	-0.957	-0.787
Type4	6.717	0.065	-0.855	-0.783
$\text{Ce}_{18}\text{O}_{36}(111)$	/	/	1.808	2.184

Reduced GDC and ceria. Increased surface reduction has been observed to improve the activity for H_2 production.^{17,27} In the following, we investigate reduced ceria and GDC with oxygen vacancies (Vo) and hydroxyls formed by water dissociation on lattice oxygen ions. For ceria, the surface reduction reactions can be written as $2\text{Ce}^{4+} + \text{O}^{2-} \rightarrow 2\text{Ce}^{3+} + \text{Vo} + \frac{1}{2}\text{O}_2$ and $\text{H}_2\text{O}_{\text{ads}} + 2\text{Ce}^{3+} + \text{Vo} + \text{O}^{2-} \rightarrow 2\text{OH}^- + 2\text{Ce}^{3+}$. The hydroxylated GDC forms via similar reactions. The magnetization of the reduced cerium or gadolinium atoms are labeled and presented in the Figures S5-S7 in the supporting information. Among the four considered types of Gd distribution, the Vo formation energies in Type2 and Type3 are the lowest. Because the formation energy of oxygen vacancies in Type2 and Type3 are very close, only Type2 is considered for the further investigations. Although the subsurface Vo in Type1 is 0.202 eV less stable than the subsurface Vo in Type2, the difference in the formation energy of a Vo in the top surface of Type1 and Type2 is very small (6 meV), which indicates a similar reactivity of the top

surface vacancy in GDC regardless of the distribution of the Gd. A comparison of the most favorable configurations of hydroxylated surfaces and mixed hydroxyl-vacancy phases, among Type1, Type2 and ceria is presented in the Figures S5-S7 in the supporting information. Here, the hydroxyl coverage $\theta_H = N_H/N$ is used to distinguish surfaces with different degrees of reduction by forming hydroxyls, which is defined as the number of hydroxyls (N_H) in to the total number of oxygen ($N=6$) in the top layer. The more reduced surfaces have higher coverage of hydroxyls.

Figure 2. The formation energy of hydroxyl (E_H) as a function of hydroxyl coverage (θ_H) in Type1 GDC (a) and Type2 GDC (c), compared with the E_H in the CeO_2 ; The formation energy of creating an oxygen vacancy (E_{Vo}) as a function of θ_H in Type1 GDC (b) and Type2 GDC (d), compared with the E_{Vo} in the CeO_2 .

Figure 2 shows the average and differential formation energy of hydroxyls, E_H , and oxygen vacancy formation energies, E_{Vo} , as a function of hydroxyl coverage in Type1 and Type2 GDC compared to ceria. As noticed from Figure 2, the average E_H increases with the increasing θ_H . When the GDC surface has one or two hydroxyls, the differential E_H in GDC is about 1.4 eV more negative than in ceria, which again is due to the strong driving force to create Gd^{3+} rather than Ce^{3+} . The magnetization of the reduced cerium or gadolinium atoms is shown in Figures S5-S7 in the supporting information. After two hydroxyls form on GDC, Ce^{4+} ions are reduced to Ce^{3+} near these surface hydroxyls because of the further reduction, leading to the differential E_H in Type1 and Type2 close to that in ceria as hydroxyl coverage ranging from 0.5 to 0.83. Forming one more hydroxyl at higher θ_H , the differential E_H increases dramatically, which indicates the repulsive interaction between the hydroxyls and the reduced surface. When the hydrogen coverage increases beyond 1.0, the additional hydrogen reacts with subsurface oxygen ions to form one subsurface hydroxyl (subO-H), which is unfavorable compared to surface hydroxyls. The differential energy required for the formation of the subO-H in Type2 GDC is much more negative than that in ceria and Type 1 GDC, which means that the formation of the subO-H is relatively favorable in Type 2 GDC. Overall, the average E_H in both Type1 and Type2 GDC is much more negative than that in ceria. Therefore, the reduced ceria via forming hydroxyls is significantly favorable by incorporation of Gd.

At the hydroxylated surfaces, E_{V_o} increases with increasing coverage of hydroxyls. However, E_{V_o} in GDC is more negative than in ceria, which reveals that creating a $V_o^{\text{subsurface}}$ or V_o^{surface} in the hydroxylated GDC is much easier than in the hydroxylated ceria. To create one V_o in hydroxylated ceria surface, $V_o^{\text{subsurface}}$ is more favorable than V_o^{surface} at $\theta_H < 0.4$. In Type2, forming a $V_o^{\text{subsurface}}$ can be favored until at a high hydroxyl coverage ($\theta_H > 0.8$). By contrast, the V_o^{surface} is always more favorable than the $V_o^{\text{subsurface}}$ in Type1 at all hydroxyl coverages. For comparison, the V_o formation energy in the bulk (a $2 \times 2 \times 2$ cubic cell) is 3.16 eV, which is close to the value of 3.10 eV calculated by Tang et al.⁵². The V_o in the Type2 GDC surface is more stable than the bulk V_o when the surface is fully hydroxylated. By contrast, the V_o is unstable in the Type1 GDC surface and in ceria at $\theta_H > 0.67$. A more detailed explanation of the relative stability of subsurface and surface oxygen vacancy in CeO_2 with and without Gd doping at different H coverages are given in the supporting information at Page S8-S10. Therefore, GDC especially Type2 can easily be reduced by forming hydroxyls and creating V_o . Since the reduced Type2 is the more favorable than reduced Type1, Type2 GDC is used as the GDC model for the following kinetic studies of V_o diffusion, water dissociation and hydroxyl decomposition.

The reaction barriers for V_o diffusion, water dissociation and hydrogen formation at reduced GDC and reduced ceria.

Barriers for V_o diffusion. Forming the V_o^{surface} in ceria, one Ce^{3+} ion locates in its nearest-neighbored site and the other Ce^{3+} sites in the next-nearest-neighbored (NN-NNN) position. The same local distribution of localized electrons around the most stable V_o^{surface} has been reported by Su et al.⁴⁵ and Ganduglia-Pirovano *et al.*²³, using $U_{\text{eff}} = 4.5$ eV. The calculated formation energy of the V_o^{surface} (2.18 eV) is close to the formation energy of 2.15 and 2.34 eV calculated

by Su et al. and by Ganduglia-Pirovano et al, respectively. Although the same local configuration is reported by using PBE+U ($U_{\text{eff}}=3.0$ eV)¹⁷, the total formation energy of the $\text{Vo}^{\text{surface}}$ (2.78 eV) is about 0.6 eV larger than the values calculated using $U_{\text{eff}} = 4.5$ eV in this work. This difference is caused by the lower stability of electrons localized in the 4f orbitals of ceria using lower U values, as discussed in the part of ‘Methods’.

The most favorable Vo in GDC has electrons localized on two gadolinium atoms (Figure S4). Creating one more Vo, the most favorable configuration has the second Vo in the subsurface, where the two more compensating electrons localized on 2Ce^{3+} in the NN positions relative to the Vo. The formation energy of creating two Vo in the top surface is very close to creating one Vo in the top surface and the other Vo near the Gd in the subsurface. The less stable configuration is that the second Vo sites next to 2Ce^{3+} . We calculate the barriers for oxygen vacancy diffusion from the subsurface configuration to the surface configuration in ceria with one Vo, and in GDC with one or two oxygen vacancies. In one vacancy system, the diffusion barrier is 0.15 eV in GDC and 0.65 eV in ceria, as shown in Figure 3(a). A 0.64 barrier for oxygen vacancy diffusion at the same Vo concentration in ceria has been reported by Chen et al.⁵³ By contrast, the barrier for vacancy diffusion from the subsurface to the surface increases to 1.5 eV when two vacancies are created in GDC as presented in Figure S8 in the supporting information. Although the mobility of oxygen decreases when two vacancies are present in GDC, it is still a facile reaction compared to the hydroxyl decomposition step for breaking the strong O-H bond (having a 2.93 eV activation barrier¹⁷). The ionic conductivity in ceria is improved significantly by the incorporation of gadolinium in the “one-vacancy” system.

Figure 3. (a) Oxygen vacancy diffusion from the subsurface to the surface in ceria and GDC, respectively. (b) Water dissociation into hydroxyl groups over the ceria, the 5H covered ceria and the 5H covered GDC, respectively.

Barriers for water dissociation. It is easy for water adsorption on ceria or GDC surface after creating oxygen vacancy. The most stable configuration for adsorption of one water molecule on the CeO₂(111) surface is that it adsorbs next-nearest-neighbor to the oxygen vacancy. The water adsorption energy in ceria agrees well with previously reported results as shown in Table S2. On a highly reduced surface having five hydroxyls and an oxygen vacancy, the most stable site for water adsorption is near a cerium or gadolinium atom next to the V_O^{surface} as shown in Figure S9. The reaction barriers for water dissociation into hydroxyls are calculated and presented in Figure 3(b). On the ceria surface having one V_O^{surface} (the dotted line), the water dissociates into two hydroxyls via the reaction of $\text{H}_2\text{O}_{\text{ads}} + 2\text{Ce}^{3+} + \text{V}_\text{o} + \text{O}^{2-} \rightarrow 2\text{OH}^- + 2\text{Ce}^{3+}$. The migration of the V_O from the subsurface to the surface provides a V_O site in the surface and can accommodate one OH coming from H₂O slitting. The other H from H₂O forms a second OH with the nearest-neighbor surface O. The reaction barrier for water dissociation is

close to zero and thus it is facile to perform water dissociation at the ceria surface. A similar reaction pathway and barrier for water dissociation has been demonstrated previously.¹⁷ No reaction path for water dissociation via the reaction of $\text{H}_2\text{O}_{\text{ads}} + 2\text{Gd}^{3+} + \text{V}_\text{o} + \text{O}^{2-} \rightarrow 2\text{OH}^- + 2\text{Gd}^{3+}$ on the GDC with one $\text{V}_\text{o}^{\text{surface}}$, is presented, because the activation energy is negligible.

Because of the low barrier for water dissociation into hydroxyls, it is able to form more hydroxyls on the ceria and GDC surface. When the ceria and GDC surface is covered by five hydroxyls, we need to create one oxygen vacancy in the surface in order to form more hydroxyls via water dissociation. The water dissociates on such highly reduced ceria surface via the reaction of $\text{H}_2\text{O}_{\text{ads}} + 7\text{Ce}^{3+} + 5\text{OH}^- + \text{V}_\text{o} + \text{O}^{2-} \rightarrow 7\text{OH}^- + 7\text{Ce}^{3+}$, where one OH from H_2O takes the place of the V_o while the H of H_2O reacts with one subsurface oxygen ion of the ceria to form one subsurface hydroxyl (subO-H). This subO-H is unfavorable compared to other surface hydroxyls as noticed from Figure 2. On the 5OH covered GDC surface, water dissociates into hydroxyls via the reaction of $\text{H}_2\text{O}_{\text{ads}} + 2\text{Gd}^{3+} + 5\text{Ce}^{3+} + 5\text{OH}^- + \text{V}_\text{o} + \text{O}^{2-} \rightarrow 7\text{OH}^- + 2\text{Gd}^{3+} + 5\text{Ce}^{3+}$, where one OH from water takes the place of the V_o while the H of water reacts with the subsurface oxygen that is nearest-neighbor to the Gd. Compared with the facile formation of the 2OH on the surface, the kinetic barrier for water dissociation to form the 7OH on the ceria and GDC increases slightly to 0.2 and 0.3 eV, respectively. Thus, it is easy to form fully and overly hydroxylated ceria and GDC via reactions between water and an oxygen vacancy.

Barriers for hydroxyl decomposition. After oxygen vacancies have diffused to the surface and reacted with the adsorbed water to form two hydroxyls on the ceria surfaces, the last step for hydrogen production is the hydroxyl decomposition, which is widely reported as the rate-determining step during many hydroxyl-associated reactions.^{11,17,44,52} The reaction barriers

for hydroxyl decomposition on the ceria ($\text{Ce}_{18}\text{O}_{36}$), GDC ($\text{Gd}_2\text{Ce}_{16}\text{O}_{36}$) and GDC with a compensating subsurface Vo (GDC_subVo, $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}$) are presented in Figure 4. The hydroxyl decomposition on the ceria surface proceeds via the reaction $2\text{OH}^- + 2\text{Ce}^{3+} \rightarrow \text{H}_2 + 2\text{Ce}^{4+} + 2\text{O}^{2-}$. The reaction is $2\text{OH}^- + 2\text{Gd}^{3+} \rightarrow \text{H}_2 + 2\text{Gd}^{3+} + 2\text{O}^{2-} + 2h^+$ on the GDC surface and is $2\text{OH}^- + 2\text{Gd}^{3+} + V_0 \rightarrow \text{H}_2 + 2\text{Gd}^{3+} + V_0 + 2\text{O}^{2-}$ on the GDC_subVo surface.

The reaction pathways for hydroxyl decompositions are asymmetric and the transition states appear early when breaking the first O-H bond.^{17,46} A vibrational analysis of the transition state for hydroxyl decomposition on these hydroxylated surfaces reveals a single mode with an imaginary frequency. The mode corresponds to an H moving over a Gd/Ce ion while shortening the H-H bond. At the TS for hydroxyl decomposition on the ceria, one O-H bond is broken and one Ce^{3+} is oxidized to Ce^{4+} , where the total magnetization of the ceria decreases from 1.96 to $0.98 \mu_B$, as shown in Figure 4(b). The breaking of an O-H bond and an H-H bond length of 2.02 Å in the transition state agree well with previous literature reports.^{17,54} After the transition state, breaking the second O-H bond is downhill in energy as shown in Figure 4(a), which finally leads to the formation of one hydrogen molecule. This asymmetric reaction pathway leads to a 3.4 eV barrier for hydroxyl decomposition over the ceria surface.

Similarly, the asymmetric reaction pathway is found for the hydrogen formation on the GDC and GDC_subVo, which respectively leads to a 5.2 eV activation barrier and a 2.8 eV barrier. The barrier decreases dramatically for hydrogen formation over the GDC reduced by creating one $\text{Vo}_{\text{subsurface}}$ and forming two hydroxyls, compared with the partially hydroxylated (2H) GDC. This is because the final formation of the GDC_subVo ($\text{Gd}_2\text{Ce}_{16}\text{O}_{35}$) after the hydroxyl decomposition is more favored than the formation of the uncompensated GDC ($\text{Gd}_2\text{Ce}_{16}\text{O}_{36}$) surface as discussed in the section of “Distribution of Gd and oxygen vacancies (Vo) in

Gd₂Ce₁₆O₃₅ (111)". Therefore, our results indicate that the hydroxyl decomposition may proceed more easily over the highly hydroxylated GDC surface by creating oxygen vacancy and formation of hydroxyls. It has not been possible to identify Ce(Gd)-H as a stable intermediate structure on the 2H* surface because they easily relax into H₂ or 2OH.

Figure 4. (a) Right panel: reaction pathways of the hydroxyl decomposition on ceria, GDC and GDC_subVo surfaces, respectively. (b) Left panel: the configurations of the initial state (IS), transition state (TS) and final state (FS) along each reaction pathways. Bond lengths in surface hydroxyl and H₂, as well as the magnetization (μB) of the each reaction states are labeled. The color for each kinds of atoms is used the same as in Figure 1. The dashed circle indicates the oxygen vacancy in the subsurface of GDC.

The reaction barriers for hydrogen formation on the overly hydroxylated ceria and GDC are presented in Figure 5. As discussed in the section of “Barriers for water dissociation”, the water dissociates into hydroxyls on the 5OH covered ceria surface via the reaction of $H_2O_{ads} + 7Ce^{3+} + 5OH^- + V_o + O^{2-} \rightarrow 7OH^- + 7Ce^{3+}$, where the H of water reacts with one subsurface

oxygen ion of the ceria to form one subsurface hydroxyl (subO-H). This reaction is competed by $H_2O_{ads} + 5OH^- + 7Ce^{3+} + V_o \rightarrow 6OH^- + Ce^{4+} + Ce^{4+}H^- + 5Ce^{3+}$, where the H from water binds to the metal ions and thus form Ce-H moiety in the surface. Two electrons from the 4f shell of $2Ce^{3+}$ contribute to the formation of the $Ce^{4+}H^-$ and one Ce^{4+} (i.e. oxidation of ceria). In this Ce-H system, there are total $5Ce^{3+}$ and the total magnetization of the system is $5.0 \mu B$ as presented in Figure 5 (c). For water dissociation in the GDC system, the Gd-H moiety forms via the reaction of $H_2O_{ads} + 5OH^- + 5Ce^{3+} + 2Gd^{3+} + V_o \rightarrow 6OH^- + 2Ce^{4+} + Gd^{3+}H^- + 3Ce^{3+} + Gd^{3+}$. The 4f¹ of $2Ce^{3+}$ donates two electrons, which contributes to the formation of the $Gd^{3+}H^-$. In the Gd-H system, the magnetization of each Gd^{3+} is $7.0 \mu B$ and there are $3Ce^{3+}$ with the magnetization of $1.0 \mu B$ for each, as shown in Figure 5 (c).

The binding of H to Ce in the surface is about 0.9 eV weaker than the binding to an oxygen in the subsurface as shown in Figure 5 (a). However, the Ce-H bond is 0.28 and 1.15 eV weaker than the O-H bond when using a U_{eff} value of 3.0 and 5.0 eV, respectively, which indicates these bindings are strongly dependent on the values of U_{eff} corrections. The sensitivity to the choice of U_{eff} arises from the fact that there are $5Ce^{3+}$ ions in the surface with formation of one Ce-H and six O-H, while the surface with formation of seven O-H has $7Ce^{3+}$ ions. In the overly hydroxylated GDC, the binding between H and the oxygen next to the Gd in the subsurface is 1.9 eV stronger than the binding between H and Gd in the surface as presented in Figure 5 (b). Because of the strong binding between H and oxygen in the subsurface, the direct breaking of the O-H bond for HER is difficult. Herein, for hydroxyl decomposition on such overly hydroxylated surfaces, the reaction pathways were split into two independent paths via a Ce-H and Gd-H intermediate, respectively on the overly hydroxylated ceria and GDC surface. Path I involves the reaction of breaking the O-H bond in the subsurface to form Me-H (Gd-H or Ce-H)

intermediates. Path II involves the reaction between the Me-H and the nearby O-H, finally leading to the formation of H₂. The reaction along Path I is $OH_{subsurface}^- + 2Ce^{3+} + Gd^{3+} \rightarrow 2Ce^{4+} + Gd^{3+}H^- + O_{subsurface}^{2-}$ on the GDC surface and $OH_{subsurface}^- + 2Ce^{3+} \rightarrow Ce^{4+} + Ce^{4+}H^- + O_{subsurface}^{2-}$ on the ceria surface. The reaction along Path II is $OH_{surface}^- + Gd^{3+}H^- \rightarrow Gd^{3+} + H_2 + O_{surface}^{2-}$ on the GDC surface and $OH_{surface}^- + Ce^{4+}H^- \rightarrow Ce^{4+} + H_2 + O_{surface}^{2-}$ on the ceria surface.

For the reaction along Path I on ceria, breaking the O-H bond in the subsurface of the overly hydroxylated ceria is difficult, leading to a 2.0 eV activation barrier. At the TS1, the Ce³⁺ in the subsurface is oxidized to Ce⁴⁺, which is followed by the oxidation of second Ce³⁺ in the top surface to form the Ce-H. For the reaction along path I over the overly hydroxylated GDC, the barrier is 2.5 eV, where the O-H bond of TS1 is broken but the total magnetization remains unchanged (i.e., no Ce³⁺ or Gd³⁺ is oxidized). The higher barrier in GDC system arises from the higher stability of the overly hydroxylated GDC as discussed in the part of E_H (presented in Figure 2). However, the HER proceeds easily along Path II, having a 0.7 eV and 0.05 eV barrier on the overly hydroxylated ceria and GDC, respectively. By comparing Path I and Path II, it is noticed that breaking the O-H bond in the subsurface in Path I is the most difficult step. This indicates that if the formation of Me-H moiety becomes more favorable by adding a substitutional dopant, the reaction along Path I can proceed with a lower activation barrier for H₂ formation.

Figure 5. Energy diagrams for hydroxyl decomposition into H_2 on the overly hydroxylated CeO_2 (7H) surface (a) and on the overly hydroxylated GDC (7H) surface (b). (c) Side views of the optimized structures for each intermediates and transition states (the top views are given in Figure S10 in the supporting information). The bond lengths of the O-H, Ce-H and Gd-H involved in the reactions are labeled. In addition, the magnetization (μ_B) of the each reaction states are marked with pink.

The reaction pathways for hydrogen production at reduced GDC and ceria.

Based on the previous discussions on the configurations of the reduced surface and the kinetic barriers of each reaction steps at the reduced surface, the free energy of the intermediates at each reaction steps during the WSR is calculated. Because of the operation for electrochemical

reactions over GDC is at temperatures 773-1073 K,^{19,20} the free energy diagram at 800 K is investigated and a higher temperature (1200 K) is investigated for comparison. The simplified free energy diagram of HER on the ceria and GDC are shown in Figure 6. To calculate the relative free energy of the reduced surfaces at each reaction step, the surface without any vacancies or hydroxyl groups in ceria and GDC is chosen as reference surfaces. The reduced surfaces are formed via the reaction between vacancies, oxygen and water at the reference surface. On the basis of this reaction, the free energies for each reduced surface are calculated (see more details at page S11 and S12 in the supporting information). The formation of the fully hydroxylated (covered by 6H) GDC and ceria is more favorable than the other H coverage at $400\text{ K} < T < 1200\text{ K}$, as presented in Figure S11. Besides, it is easier to form the overly hydroxylated (7H) GDC than ceria at $400\text{ K} < T < 1200\text{ K}$.

At 800 K, a 3.20 and 2.60 eV enthalpy barrier is required for the hydrogen formation over the partially hydroxylated ceria and GDC surface, respectively as shown in Figure 6. Here, the transition state occurs with the first O-H bond breaking in hydroxyl coupled with electron transfer from Ce^{3+} as discussed in the part of “Barriers for hydroxyl decomposition”. Compared to the partially hydroxylated pathways, the HER proceeds more efficiently via the Ce-H and Gd-H intermediates on the overly hydroxylated ceria and GDC surfaces, respectively, where we find a 1.60 and 2.20 eV kinetic barriers for the H_2 formation, respectively. However, the reaction energy required to form the Ce-H intermediate on fully hydroxylated ceria is 1.31 eV, while only 0.46 eV is required for the formation of the Gd-H on the fully hydroxylated GDC because of the stabilization of the reduced states by the incorporation of Gd. Thus, it is more difficult to form overly hydroxylated ceria and overall free energy barrier for the HER on the overly hydroxylated ceria surface is 2.91 eV. By contrast, 2.67 eV is required for the hydrogen production on the

overly hydroxylated GDC. These results indicate the reaction activity of the HER on ceria is significantly improved by the incorporation of gadolinium. In addition, if the formation of the 7H is favorable and the Metal-H is stabilized by adding a substitutional dopant in ceria, the total free energy for the H_2 formation will decrease.

Figure 6. Top panel: Free energy of the intermediates during the hydrogen evolution reaction on the partially (2H) and overly (7H) hydroxylated GDC and CeO₂, at 800 and 1200 K, respectively. Bottom panel: Atomic configurations of reaction intermediates over the four different surfaces. The color for each kinds of atoms is used the same as in Figure 4. The dashed circle stands for an oxygen vacancy.

As temperature increases to 1200 K, the free energies of all intermediates increase mainly due to the loss of gas phase entropy upon adsorption.¹⁷ A significant increase is found for the reaction free energy to form the overly hydroxylated surfaces, which increases to 1.60 and 0.75 eV in ceria and GDC, respectively. The formation of the overly reduced ceria competes heavily

with the water adsorption/desorption at high temperature (Figure S12), which prevents the formation the highly reduced states. However, the hydroxyl decomposition remains to be the rate-determining step, which can be seen from the full reaction pathways in Figure S12 in the supporting information. At 1200 K, the lowest energy cost reaction remains to proceed via the Gd-H intermediate on the overly hydroxylated GDC. The operating temperature for the HER on GDC should be higher than 800 K to reach the same rate as on Pt at 400 K (Figure S13 in the supporting information). The predicted operating temperature is consistent with the experimental operating temperature range (773-1073 K).^{19,20} However, temperatures higher than 900 K are required for the HER on ceria. Therefore, the HER is allowed to proceed at lower temperature on GDC than on un-doped ceria. The reactivity of the WSR on ceria is improved by the incorporation of gadolinium.

Conclusions

Using the DFT+U method, we have studied configurations of reduced ceria and reduced GDC via creating vacancies and forming hydroxyls. We find that Gd can distribute freely between the top surface or subsurface of the $\text{Gd}_2\text{Ce}_{16}\text{O}_{35}$ (111) surface at 11% Gd concentration. The vacancy and hydroxyl formation energy in GDC was more negative than in pure ceria. Thus, it is much easier to form highly reduced GDC than to form highly reduced ceria via creating vacancies and forming hydroxyls. Then, the mechanism of water splitting on the GDC surface compared to pure ceria was revealed by the kinetic investigations. We observed that one vacancy diffusion in the GDC surface was faster than in the ceria surface. The following step for the water dissociation on both GDC and ceria surface was facile even at very high hydrogen coverage. However, there is a large barrier for hydroxyl decomposition on the partially hydroxylated ceria and GDC. The reaction activity for the HER was improved significantly via the Gd-H

intermediate on the overly hydroxylated GDC surface under the operating temperature (800 and 1200 K), which is attributed to the much favorable formation of the Gd-H than Ce-H intermediate.

In conclusion, the incorporation of Gd plays an important role in stabilizing the intermediates and transition states for hydroxyl decomposition and further enhancing performance of ceria for water splitting. Therefore, a dopant that stabilizes the reduced ceria surface and has strong binding to hydrogen is capable of effectively improving the reaction activity of ceria for renewable hydrogen production in SOEC. Our findings give insight in the mechanism of water splitting in GDC and ceria, which help for the design of ceria-based electrocatalyst for renewable hydrogen production via water splitting reaction.

ASSOCIATED CONTENT

Supporting Information

Figures containing the configurations of the $\text{Ce}_{18}\text{O}_{36}$ (111) surface, reduced ceria and GDC surface via forming one oxygen vacancy or hydroxyl and also the most stable configurations of water adsorption, overly hydroxylated surface and hydrogen desorption on ceria and GDC. Barriers for hydroxyl decomposition into H_2 and V_O formation energy as a function of the U correction on Ce 4f states. The pathway for vacancy diffusion in a two-vacancy system of GDC. Free energy of the H covered ceria and GDC as a function of hydroxyl coverage. Free energy diagrams for water splitting at 800 and 1200 K. Views of the optimized structures for each intermediates and transition states during the hydroxyl decomposition into H_2 . Discussions of the relative stability of $\text{V}_\text{O}^{\text{subsurface}}$ and $\text{V}_\text{O}^{\text{surface}}$ in the ceria with and without Gd doping at different hydroxyl coverages. Tables of DFT energies for vacancy formation, vacancy diffusion, and water

adsorption and dissociation. Details of methods for calculating free energies of the reduced surface.

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