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Charge Transport over the Defective CeO$_2$(111) Surface
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ABSTRACT: First-principles calculations have been performed to explore the charge transport process over defective CeO$_2$(111). Charge transport can proceed either by direct migration of the oxygen anion (i.e., vacancy diffusion) or by a polaron-hopping-assisted mechanism. On the basis of DFT+U calculations, we found that the latter process is significantly more favorable than the former. The overall barrier for charge transport involving polaron migration, followed by oxygen diffusion, is determined by the barrier for polaron hopping, which amounts to 0.18 eV. This computed value is in good agreement with the experimental barrier for ceria with a low defect density. We have shown by a careful analysis of the magnetization density, the density of states, and the reaction pathway trajectory that this process is phonon induced. Our results provide valuable insights into carrier drift processes over defective metal oxide surfaces.

INTRODUCTION
The main use of ceria is as a critical component for oxygen storage in three-way catalysts for gasoline exhaust gas cleanup.$^{1−3}$ Ceria is also employed as an electrolyte in solid oxide fuel cells,$^{4−5}$ as support in catalysts for the water-gas shift reaction,$^{6,7}$ as well as a reactive material for hydrogen production and purification.$^{8,9}$ In these applications, the reducibility of the ceria surface often plays a critical role; that is, two Ce$^{4+}$ ions are reduced to Ce$^{3+}$ upon removal of a surface oxygen atom. The resulting oxygen vacancies in the ceria surface play an important role as they can act as a site for the adsorption and activation of molecular oxygen.$^{10−12}$ The Ce$^{3+}$ ions in the surface may also be involved in catalytic reactions. On surface reduction, the excess electrons are mainly localized in empty Ce 4f orbitals at low defect concentration, whereas, at higher defect concentration, they can also be localized at oxygen vacancies. These excess electrons in defective ceria give rise to n-type conductivity, which involves motion of the charge carriers in a band or by a hopping-diffusion mechanism.$^{13}$ The localization of the excess electrons in Ce 4f orbitals also gives rise to ferromagnetic behavior.$^{14,15}$ Defective ceria has also been extensively investigated as a material to drive photocatalytic reactions with the defects narrowing down the band gap into the visible light region.$^{16−21}$

In all of these processes, the Ce$^{3+}$/Ce$^{4+}$ redox couple plays an important role as does charge transport, which involves polaron hopping and oxygen migration. In the past, the stability of oxygen vacancies at the surface and the bulk of ceria and the localization of the excess electrons have been extensively investigated by density functional theory (DFT). Usually, a Hubbard-like approximation is used for accurate treatment of the electron correlation in the localized Ce 4f orbital.$^{22−27}$ A general finding is that the two electrons left after oxygen removal from the surface are preferably localized in 4f orbitals of Ce atoms in next-nearest neighbor (NNN) positions relative to the oxygen vacancy (V$_{O}$ in Kröger–Vink notation).$^{22,23}$ Surface oxygen vacancy diffusion usually involves a two-step exchange mechanism, involving migration of an O atom from the subsurface layer to the initial surface vacancy, followed by migration of an adjacent surface O atom to the subsurface position, so that effectively a surface O atom has moved into the adjacent surface vacancy. The highest barrier in this exchange mechanism is for migration of the subsurface oxygen to the surface vacancy; Hu’s group has estimated this barrier to be 0.44 eV for a defective CeO$_2$(111) surface.$^{24}$ Nakayama et al. used a relatively simple method$^{25}$ to estimate that the barrier for polaron hopping is smaller than 0.20 eV; these authors employed the nudged-elastic band (NEB) method to compute a value for the activation barrier for oxygen migration of 0.40 eV, which is quite similar to the value provided by Hu and coworkers. Sanz’s group employed the linear interpolation scheme, which is based on Marcus theory, to estimate that the barrier for polaron hopping is about 0.30 eV.$^{26}$ The barrier for migration of oxygen between Ce$^{4+}$ ions was computed to be 0.12 eV. Wang et al. investigated oxygen migration in bulk ceria and predicted a barrier of 0.43 eV.$^{27}$

Despite these relevant works, a consistent picture about charge transport in defective ceria is lacking. The debate centers around the sequence of polaron hopping and oxygen migration, that is, should polaron hopping precede oxygen migration or vice versa. Herein, we addressed this issue in a systematic way.
manner by carrying out DFT+U calculations for these two mechanisms for the defective CeO$_2$(111) surface. The CeO$_2$(111) surface was chosen as it is the most stable surface termination of ceria. We will show that charge transport proceeds by hopping of the polaron prior to oxygen migration. By carrying out a detailed analysis of the involved processes, we gain a detailed understanding about the underlying mechanism of oxygen anion migration and polaron hopping. During polaron hopping, it is found that the transferring electron is equally shared by the two Ce ions, explaining why the polaron hopping is coupled to a phonon mode of ceria.

**SIMULATION METHOD**

All calculations were performed using the Vienna *Ab initio* Simulation Package (VASP). The ion–electron interactions were represented by the projector-augmented wave (PAW) method and the electron exchange-correlation by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. We carried out spin-polarized calculations. The Kohn–Sham valence states were expanded in a plane-wave basis set with a cut-off energy of 400 eV. For Ce and O atoms, the (5s,5p,6s,4f,5d) and (2s,2p) states were treated as valence states. With a cut-off energy of 400 eV, the Ce$_4^+$ ions nearest neighbor (NN) to the oxygen vacancy create an oxygen vacancy. The two excess electrons associated with the Ce$_4^+$ ions in NNN positions. The oxygen vacancy formation energy obtained at the PBE$^+$ level is underestimated in the 3.0–5.5 eV range that provides localization of the electrons left upon oxygen removal from CeO$_2$. The reliability of this choice for $U$ has been tested for many processes involving ceria. For all surface calculations, the model was a periodic slab with a (3×3) surface unit cell, and for the Brillouin zone integration, a Monkhorst–Pack $k$-point mesh was used. The bulk equilibrium lattice constant (5.49 Å) previously calculated by PBE+U ($U = 4.5$ eV) was used. The CeO$_2$(111) slab model is four Ce-O-Ce layers thick, and the vacuum gap was set to 15 Å. The bottom layer was frozen to its bulk position, and only the three top Ce-O-Ce layers were allowed to relax.

In order to create a surface vacancy, one oxygen atom from the top layer was removed. In this way, a single oxygen vacancy was introduced in the CeO$_2$(111) surface, which corresponds to a defect concentration ($x$) of 0.028 for the given unit cell. The climbing image nudged-elastic band (CI-NEB) algorithm was used to identify the transition states for oxygen migration and polaron hopping over the defective CeO$_2$(111) surface.

**RESULTS AND DISCUSSION**

**Oxygen Anion Migration.** We removed one surface oxygen atom from the stoichiometric CeO$_2$(111) surface to create an oxygen vacancy. The two excess electrons associated with the removal of O are initially localized in the 4f orbital of the Ce$^{3+}$ ions nearest neighbor (NN) to the oxygen vacancy. The computed oxygen vacancy formation energy compared to gas-phase oxygen is 2.38 eV, in good agreement with the literature. It should be stressed that the defect formation energy obtained at the PBE+U level is underestimated by approximately 1.4 eV compared to the best experimental estimate. The initial configuration is less stable by 0.23 eV compared with the configuration with the two Ce$^{3+}$ ions in next-nearest neighbor (NNN) positions relative to the oxygen vacancy in the surface. The latter configuration is shown in Figure 1(left). The most stable configuration is obtained when the subsurface O atom migrates to fill the surface oxygen vacancy. Figure 1(right) shows this configuration, which involves an oxygen vacancy in the subsurface layer and the Ce$^{3+}$ ions in NNN positions. The oxygen vacancy formation energy for this most stable state is 2.04 eV. In order to avoid inclusion of metastable configurations, we confirmed that all configurations are local energy minima by visualizing the spin density as also done by Allen and Watson. Figure 2 depicts the spin density isosurfaces of surface oxygen vacancies with two excess electrons in NN-NN (IS1), NN-NNN (IS2), and NNN-NNN (IS3) sites, respectively. The visualization electron density isosurfaces demonstrate that excess electrons are located in similar 4f orbitals as indicated by Allen and Watson to provide the lowest electronic energy.

Next, we focus on the ionic charge transport by oxygen anion mobility involving vacancies. The oxygen vacancy can diffuse by migration of subsurface and surface oxygen atoms. Figure 3 shows the two possible pathways for the migration of an oxygen atom into the surface vacancy, starting from the state IS1 obtained after removal of an O atom. The migration of a subsurface O atom into the vacancy (IS1 $\rightarrow$ IS2') involves a barrier of 0.40 eV. In the IS2' configuration, one of the excess electrons is localized on a subsurface Ce ion below the oxygen vacancy. This implies that direct oxygen migration from IS1 also involves transfer of one electron from the surface Ce$^{3+}$ ion in NN site to the subsurface Ce$^{3+}$ ion. The barrier of 0.40 eV is consistent with computed values from the literature, but much higher than the experimentally observed value for charge transport in ceria at this defect concentration. We also computed the barrier for direct oxygen migration without the electron transfer, which is much higher at 0.77 eV than the barrier for the concerted mechanism. This is due to the strong repulsion between the oxygen anion and the excess electrons localized on the two involved Ce ions. This result finding implies that concerted migration of oxygen and electron transfer does not represent well the experimental situation. The concerted oxygen migration process is then followed by polaron hopping, i.e., IS2' $\rightarrow$ IS3' (note IS3' = IS4) and IS5 $\rightarrow$ IS6 to obtain the
The alternative mechanism involves first polaron hopping, i.e., IS1 → IS2 and IS2 → IS3, followed by migration of the subsurface O atom to fill the surface O vacancy (IS4). In this configuration, the two excess electrons are localized in next-nearest-neighbor and NN sites. Further polaron hopping, involving IS4 → IS5 and IS5 → IS6, leads to the same most stable configuration as for the first mechanism. Notably, the O migration step IS3 → IS4 proceeds with a barrier of 0.15 eV, which is much lower than the barrier obtained for IS1 → IS2 O migration. The results show that oxygen migration is much more easy with the two excess electrons localized at NNN sites rather than at NN sites. We verified that the use of other values for U had only a small influence on this barrier. That is, for values of U of 3.0 and 5.0 eV, which is within the acceptable range at the GGA+U level, we found barriers of 0.14 and 0.13 eV, respectively. For a higher value of U = 6.0 eV, we find a slightly lower barrier of 0.08 eV.

The above calculations for oxygen migration were based on the ferromagnetic (FM) states of all species. If oxygen migration takes place from the antiferromagnetic (AFM) state of IS3, the energy barrier is slightly smaller at 0.11 eV. However, the AFM state of IS3 is unstable, and turns into the FM state. Several experimental works have demonstrated that reduced ceria is ferromagnetic. By employing LDA+U calculations, Lee et al. found that the FM state is more stable than the AFM state when the excess electrons are both in NN sites (IS1). In contrast, Deskins et al. reported that the AFM state is 0.01 eV more stable than the FM state in defective TiO2, when the two excess electrons are located at NN sites.

In the present study, we find that the AFM state of IS1 is 0.03 eV more stable than the FM state. On the other hand, the FM and AFM states for IS2 have the same energy, while the FM state of IS3 is 0.04 eV more stable than the AFM state. The FM state of IS6 (i.e., subsurface vacancy with two excess electrons both in NNN sites) is also more stable than the AFM state by 0.02 eV. These minor differences consistently show that the excess electrons tend to localize at NNN sites, which results in ferromagnetic behavior. We infer that electron transfer plays an important role in ferromagnetism observed in experiments with defective ceria materials.

Comparing the two charge transport mechanisms explored, we can conclude that, as far as O migration is concerned, the mechanism involving polaron hopping prior to oxygen migration is preferred. As the barrier of the O migration first mechanism is significantly higher than the experimentally observed value, we conclude that charge transport is not likely to occur in this way. Then, the barriers for the polaron hopping in the preferred mechanism should be sufficiently low to be consistent with experiment. This will be addressed in the next section.

We finally note that further charge transport will involve migration of a surface O atom into the subsurface vacancy (illustrated in Figure 4), followed by polaron transport into the most stable electron NNN localization and subsurface O migration to the surface, which gives rise to conductivity in ceria.

**Polaron Transport.** As evidently the location of the excess electrons strongly affects oxygen mobility in ceria, it is crucial to determine the barriers involved with the electron mobility. For this purpose, we studied the hopping of the two excess electrons from NN sites to NNN sites (IS1 → IS3) as illustrated in Figure 3. The overall process is exothermic by 0.23 eV. CI-NEB calculations indicate that the transition state for this process is located 0.18 eV above the initial state (Figure 5a). This applies to both polaron hopping steps. Overall, charge transport in this polaron-migration-assisted O migration mechanism involves a barrier of 0.18 eV. This value is in very good agreement with the experimental value of 0.19 eV for charge transport over ceria surfaces determined at nearly similar defect density. Our result is more accurate than the one obtained by Masanobu et al., who used a linear interpolation scheme between the initial and the final state involving 0.18 eV. However, the AFM state is 0.01 eV more stable than the FM state in defective TiO2, when the two excess electrons are located at NN sites.

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semistatic single point optimization for configurations along the reaction coordinate. The more accurate and reliable adiabatic energy barrier employing the CI-NEB algorithm involves full optimization of the ionic positions and convergence of the electron density along the reaction coordinate. Earlier attempts to describe this process of polaron hopping using the small polaron model by Holstein and Marcus–Hush theory were too simple and provided only estimates for the barrier. The successful application of the CI-NEB algorithm depended on the use of small atomic displacements per ionic iteration step to account for the relatively shallow potential energy surface. Using this method, we obtained a more accurate value for the polaron hopping barrier of 0.18 eV.

In the next sections, we investigate the nature of polaron hopping by a detailed structural and electronic analysis.

Phonon–Electron Coupling. Electron–phonon coupling is known to facilitate polaron hopping in ionic crystals and polar semiconductors. Shoko et al. suggested that phonons can assist the polaron transport in reduced ceria and, accordingly, the overall charge transport. This result is reasonable as it is known that CeO₂ is a strong electron–phonon coupled system, and the observed red-shift of the absorption band in the UV region upon reduction of ceria may be the result of an interfacial polaron effect, arising from electron–phonon coupling. For the analogous TiO₂ system, a specific phonon involving asymmetric displacement of bridging O anions during polaron transfer has been identified. Figure 5b shows that the 4f orbital of the Ce³⁺ ion in the density of states (DOS) shifts from below to above the Fermi level (the positive part in Figure 5b) along the reaction coordinate, which is the phonon eigenvector. In other words, the adjacent Ce⁴⁺ ion accepts the electron initially present on Ce³⁺ (the negative part in Figure 5b). At the transition state, the DOS peaks for the two 4f orbital of these two Ce ions lie almost exactly at the Fermi level (black line in Figure 5b). This situation reflects that, in the transition state, both Ce ions share the electron. Besides, the localized 4f states are very near to the Fermi level, which implies that they are also very close to the conduction band minimum.

To further verify the localized electron distribution, we investigated and visualized the magnetization density along the reaction coordinate for polaron hopping (Figure 6). It is

Figure 4. Schematic representation of (top) direct O migration- and (bottom) polaron-assisted O migration mechanisms.

Figure 5. (a) Reaction energy diagram of the polaron transport process on the top surface involving hopping of two electrons from NN to NNN positions relative to the surface vacancy. (b) Density of states (DOS) analysis for the first hopping process (hopping I) along reaction coordinate. The positive part represents the transfer of the electron from the Ce³⁺ rendering a Ce⁴⁺ ion, the negative part the reduction of the Ce⁴⁺ ion to Ce³⁺ (the dashed arrows show the reaction coordinate).

Figure 6. Electron hopping visualization made by rendering the isosurface (yellow) of the difference of the spin-up and spin-down electron density. Magnetization density is in IS1, TS1, and IS2 states, respectively.
worthwhile to note that all interpolated optimized configurations have the same electronic spin direction and total magnetization. Indeed, in line with the DOS results, the electron completely localizes on one of the two Ce ions in IS1 and IS2 (the integrated magnetization density equals 0.952). In the transition state, the magnetization of the two involved Ce ions is 0.663 and 0.447, which implies that the shifting electron is approximately shared equally between the two Ce ions. Along the Ce$^{3+}$ → Ce$^{4+}$ electron transfer coordinate, the local lattice Ce$^{3+}$−(O)−Ce$^{4+}$ displays a subtle distortion which is a phonon mode. Despite the small difference in magnetization, the Ce−O bond lengths for both Ce ions is the same (2.37 Å) in the transition state; the initial Ce$^{3+}$−O and Ce$^{4+}$−O bond lengths are 2.46 and 2.30 Å, respectively. Thus, phonon−electron coupling plays an important role in the polaron hopping process. Dupuis and Deskins have already suggested that the phonon coupling plays an important role in the polaron hopping process.

CONCLUSIONS

DFT+U calculations are able to provide detailed insight into the mechanism of the charge transport process over the defective CeO$_2$(111) surface. Charge transport can proceed either by direct migration of the oxygen anion (i.e., vacancy diffusion) or by a polaron-hopping-assisted mechanism. The latter process is significantly more favorable than the former. After the migration of the polaron to an adjacent Ce ion in one of the NNN sites, the oxygen atom is bound less strongly and migrates with a lower barrier of only 0.15 eV as compared to a barrier of 0.40 eV found for the alternative situation with the polaron remaining in the NN site. Exploration of the polaron hopping by careful CI-NEB calculations allowed identifying a transition state in which the transferring electron is equally shared between the two Ce ions. By studying the magnetization, the density of states, and the structure (viz. the Ce−O bond lengths), we confirm that the electron transfer is linked to a lattice distortion. In other words, polaron hopping can be assisted by a phonon. The overall barrier for charge transport involving polaron migration, followed by oxygen diffusion, is determined by the barrier for polaron hopping, which amounts to 0.18 eV. This computed value is in good agreement with the experimental barrier for ceria with a low defect density. These results provide a deeper understanding into the mechanism of carrier drift in defective metal oxide semiconductors, which is important in various settings related to photocatalysis and electrocatalysis in which defective materials such as ceria and other metal oxides feature.

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