Oxygen Vacancy Diffusion in Bulk SrTiO₃ from Density Functional Theory Calculations

Lipeng Zhang¹, Bin Liu¹, Houlong Zhuang², P. R. C. Kent^{2,3}, Valentino R. Cooper⁴, P. Ganesh²,
Haixuan Xu^{1,*}

¹Department of Material Science and Engineering, The University of Tennessee,
Knoxville, Tennessee 37996 USA

²Center for Nanophase Materials Science, Oak Ridge National Laboratory, Bethel Valley
Road, Oak Ridge, Tennessee 37831, USA

³Computer Science and Mathematics Division, Oak Ridge National Laboratory, Bethel
Valley Road, Oak Ridge, Tennessee 37831, USA

⁴Materials Science and Technology Division, Oak Ridge National Laboratory, Bethel
Valley Road, Oak Ridge, Tennessee 37831, USA

*Email: xhx@utk.edu

Abstract

Point defects and their diffusion contribute significantly to the properties of perovskite materials. However, even for the prototypical case of oxygen vacancies in SrTiO₃ (STO), the predictions of oxygen vacancy activity vary widely. Here we present a comprehensive and systematic study of the diffusion barriers for this material. We use density functional theory (DFT) and assess the role of different supercell sizes, density functionals, and charge states. Our results show that vacancy-induced octahedral rotations, which are limited by the boundary conditions of the supercell, can significantly affect the computed oxygen vacancy diffusion energy barrier. In addition, we find that the diffusion energy barrier of a charged oxygen vacancy is lower than that of a neutral one. This difference is magnified in small supercells. We find that with increasing supercell size, the effects on the migration energy barrier of the oxygen vacancy charge state, the type of DFT exchange and correlation functional is diminishing, and all migration energy barriers of DFT prediction asymptote to a range of 0.39-0.49 eV, which is smaller than the reported experimental values. This work provides important insight and guidance that should be considered for investigations of point defect diffusion in perovskite materials and in oxide superlattices.

Keywords: DFT method, Perovskite structure, Oxygen vacancy, Diffusion energy barrier, Boundary condition

1. Introduction

Ceramics with a perovskite-type structure (general formula ABO_3) consist of a network of corner-sharing BO_6 octahedra, which form higher-coordination sites for the A -cations in a roughly cubic array. The wide variety of chemical compositions and atomic defects that can be accommodated in this structure give rise to the rich variety of phenomena observed in perovskite oxides. As a prototypical perovskite, $SrTiO_3$ (STO) attracts considerable attention due to its good insulating properties, excellent optical transparency, and high dielectric constants^{1,2}. It also has been demonstrated that STO shows potential capacitive³ and resistive switching properties^{4,5,6,7}. In addition, STO has been extensively used as a substrate for superlattices and is the parent oxide that leads to two-dimensional electron gases (2DEGs)^{8,9} in many oxide heterointerfaces.

Oxygen vacancies (V_O) are representative intrinsic defects that, in many cases, play an important role in the physical properties of STO. A V_O is generally produced during crystal growth or film deposition processes with nonstoichiometric reactants, as a result of oxygen gas release accompanying heat treatment, and in doped STO serving as a charge compensation mechanism. They form readily within STO and have been indicated to be the driving force behind STO-associated blue and green light emission^{10,11} and high n -type conductivity^{12,13,14,15}. Therefore, fully understanding the stability and diffusion of V_O is critical for tailoring the physical properties of STO for future applications. However, while the energetics and stability of oxygen vacancies and their effects on the properties of STO are understood, less is known about the energetics of V_O diffusion.

Numerous efforts have sought to study the diffusion of V_O in STO, producing values of V_O migration energy barriers (MEBs) that vary significantly. For instance, the activation energy of V_O diffusion was estimated to be 0.60–0.98 eV based on different experimental measurements^{16,17,18}. Even different density functional theory (DFT) calculations exhibit significant deviations between the calculated values of the oxygen vacancy diffusion barrier. The DFT estimations of the energy barrier range from 0.35–0.9 eV^{19,20,21,22,23,24,25,26}. The deviations in DFT results are considerable and the underlying cause for such deviations is unclear, as different simulation setups and parameters have been employed in the previous calculations. Carrasco et al.²² calculated neutral V_O migration energy barriers in different STO supercells containing 40 to 180 atoms with different shapes, predicting a range of values from 0.35–0.7 eV, depending on the size and shape of the supercell. Evarestov et al.²⁶ did the similar work using VASP code. They found the migration energy barrier mainly decrease with increase the supercell size, however limited by the compute cost, the maximum size of STO supercell they used containing 270 atom. Al-Hamadany et al.²³ explored charged and neutral oxygen vacancy migrations in STO using

spin-polarized DFT with the local density approximation (LDA). They employed STO supercells containing up to 320 atoms. The energy barriers in the largest cells containing 320 atoms were 0.81 and 0.77 eV for the neutral and charged (+2) oxygen vacancy, respectively. Lontsi-Fomena et al.²⁴ investigated oxygen vacancy diffusion in supercells of 40 atoms using the Perdew-Burke-Ernzerhof (PBE) functional, finding the migration energy barrier for a charged (+2) oxygen vacancy to be 0.58 eV. In order to consider the localization of *d* electrons, Cuong et al.²⁵ employed an LDA+*U* approach with *U*–*J* = 2.3 eV and supercells of 135 atoms, finding a barrier of 0.6 eV in STO supercell. These large differences emphasize the fact that calculated V_O diffusion energy barriers depend on the chosen DFT functional, supercell size, and other possibly unknown factors. As such, a comprehensive understanding of the different factors contributing to these deviations is required.

In this work, V_O formation energies and migration energy barriers in STO were calculated in a series of STO supercells with different number of unit cells, DFT exchange-correlation functionals, and vacancy charge states to systematically examine their effects on V_O diffusion. We find that the supercell size, V_O charge state and Hubbard-*U* value all affect the predicted migration energy barriers of isolated oxygen vacancies in small STO (2×2×2) supercells. However with increasing supercell size, the effect of charge state and the type of exchange-correlation functionals diminish significantly, suggesting that the deviations are dominated by finite size effects. The calculated oxygen vacancy diffusion energy barriers with different DFT methods tend towards a stable number when the STO supercell is large enough. Given that addition of a Hubbard-*U* term is thought to give a more accurate representation of the electronic states of oxygen vacancies within the STO supercell, it stands to reason that PBE+*U* and PBEsol+*U* will predict more reliable oxygen vacancy diffusion barriers. Furthermore, our calculations demonstrate that the suppression of octahedral rotations brought by artificial boundary conditions can severely alter predicted diffusion barriers. Our work provides useful guidelines for simulations of the energetics barrier of defect migration in complex oxides with electronic structure and atomistic methods.

2. Methodology

The Vienna *Ab-initio* Simulation Package²⁷ (VASP) code using the projector augmented wave (PAW) method is used in the present density functional theory (DFT) calculations²⁸. The corresponding {core}/valence configurations for each element are Sr: {[Ar]3d}/4s4p5s; Ti: {[Ne]3s}/3p3d4s; O: {[He]}/2s2p. The cutoff energy is chosen to be 550 eV based on convergence tests of 0.01 eV/atom. The Perdew-Burke-Ernzerhof (PBE)²⁹ form of the generalized gradient approximation (GGA) and the revised version for solids, PBEsol³⁰, are chosen as the exchange-correlation functionals. In addition, the rotationally invariant Hubbard-*U* term introduced by Liechtenstein et al.³¹ was also applied. We studied an isolated oxygen vacancy in 2×2×2, 3×3×3, 4×4×4, and 5×5×5 STO supercells with a cubic $Pm\bar{3}m$ perovskite

structure and used $2 \times 2 \times 2$ K-points following the Monkhorst-Pack scheme³². The K-point mesh was converged to give an energy difference of less than 0.01 eV between the $2 \times 2 \times 2$ and $4 \times 4 \times 4$ K-point meshes. The structural relaxations were performed until all the Hellmann-Feynman forces are smaller than 0.01 eV/Å. To correct for the on-site Coulomb interaction of the $3d$ orbitals, the rotationally invariant $+U$ method³⁰ is applied with $U = 5.0$ eV and $J = 0.64$ eV³³ to both exchange-correlation functionals. Although different values could be tested, these values predicted a larger band gap, which was closer to the experimental value of 3.2 eV for bulk STO³⁴. The V_O position and diffusion path are depicted in Fig. 1. Because of the symmetry of the cubic structure, there is just one unique diffusion path (Fig. 1 (b), taking the diffusion in the $3 \times 3 \times 3$ supercell as an example). The diffusion paths for neutral and charged vacancy in these supercells are indistinguishable.

The oxygen vacancy formation energy is defined as:

$$E_f(V_O^q) = E_{\text{tot}}(V_O^q) - E_{\text{tot}}(\text{Bulk}) - \sum_i n_i \mu_i + q(E_F + E_v + \Delta V) \quad (1)$$

Where $E_f(V_O^q)$ is the total energy derived from a supercell calculation with one oxygen vacancy in charge state; q , $E_{\text{tot}}(\text{Bulk})$ is the total energy for the reference perfect bulk supercell; n_i indicates the number of atoms of type i that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell when the defect is formed; and μ_i is the corresponding chemical potential of each species. E_F is the Fermi level, referenced to the valence-band maximum E_v in the bulk. ΔV is a correction term, to align the reference potential in our defect supercell with that in the bulk³⁵. In this work, the formation energy of a neutral V_O^0 and charged V_O^{+2} were calculated. The chemical potential of oxygen is chosen to be $\frac{1}{2} E_{O_2}$ (equilibrium gas state).

The migration barriers of the neutral and charged oxygen vacancy were both computed by the climbing-image nudged elastic band (CI-NEB) method³⁶. We first tested up to 5 images in a $2 \times 2 \times 2$ STO supercell and found that the calculated migration energy barrier is not sensitive to the number of images, which is attributed to the simple chemical environment along the diffusion path and success of the climbing image algorithm. For the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells we used 3 images, and 1 image for the most computationally costly $5 \times 5 \times 5$ supercell.

Fig. 1. (a) Isolated V_O in a 3×3×3 STO supercell; (b) the oxygen vacancy diffuses to the adjacent oxygen position; (c) V_O diffusion path in the 3×3×3 STO supercell. The green, red, and blue balls represent Sr, O, and Ti atoms, respectively.

3. Results and discussion

3.1 Lattice Constant

Prior to the defect study, the geometry of STO is optimized using different exchange-correlation functionals. In all these calculations, there is no distortion found in the perfect optimized STO supercells. The calculated lattice constants are summarized in Table 1. These values are comparable with other simulations^{37, 34} and experimental results (3.905 Å³⁸). Among these functionals, PBEsol³⁰ predicts a lattice constant, which is the closest to the experimental value. PBEsol+U, PBE, and PBE+U functionals overestimate the lattice parameter (< 1%). These lattice constants are used for subsequent calculations of the energetics of oxygen vacancy formation and diffusion barriers.

Table 1. Computational and experimental values of STO unit cell lattice constant

DFT functional	PBEsol	PBEsol +U	PBE	PBE + U	PBE	PW	B3LYP	LDA	Exp.
Lattice constant (a/Å)	3.898	3.939	3.940	3.969	3.940 [36]	3.950 [33]	3.940 [33]	3.860 [33]	3.905 [37]

3.2 Defect Formation Energy (DFE)

It is known that the V_O formation energy depends on the oxygen chemical potential and electronic Fermi level³⁹. Here, the oxygen chemical potential was chosen as -4.338 eV, which is half of the chemical potential of the O_2 molecule. We applied the method of reference³⁹ to calculate the Fermi level energy, assuming the Fermi level is at the conduction band minimum. In addition, the interaction from periodic images was estimated based on the formulism in⁴⁰ and this interaction is found to be rather small (<1.2% in the $2\times 2\times 2$ STO supercell). Therefore, this correction term⁴⁰ was not included in our calculations of formation energies. The oxygen vacancy formation energies of neutral and charged (+2) states in different supercells are listed in Table 2. The relative formation energies versus supercell size obtained with the PBEsol+ U functional are plotted in Fig. 2. The oxygen vacancy formation energy in a $2\times 2\times 2$ supercell is used as a reference and is set to 0. It is observed that the DFEs decrease with increasing system size; when the supercell is larger than $4\times 4\times 4$, the DFEs is approaching to convergence, which is consistent with other studies on defect stabilities³⁵. The DFEs drop ~0.6 eV (PBEsol+ U) for the neutral oxygen vacancy when the supercell is enlarged from $2\times 2\times 2$ to $5\times 5\times 5$. For the charged oxygen vacancy, DFEs decrease by ~1.2 eV using PBEsol+ U . These decreases in DFEs are attributed to the long-ranged relaxation of atoms caused by V_O s in the supercell. The effect of electron localization in the V_O site may be more accurately described using the PBEsol+ U , because the charge density is strongly localized on the two Ti atoms adjacent to the oxygen vacancy. Buban et al.³⁵ found that the DFEs of neutral and charged (+1, +2) V_O s dropped by roughly 1.1-1.38 eV when going from a 40- to a 320-atom supercell, which is in line with our value of 1.2 eV calculated with the PBEsol+ U functional on a charged oxygen vacancy. The results of PBE with spin polarization, PBEsol, and PBE+ U show similar trends as described above.

Table 2. Oxygen vacancy formation energy (eV) in different supercells

Charge state	$2\times 2\times 2$	$3\times 3\times 3$	$4\times 4\times 4$	$5\times 5\times 5$
$V_O(0)$	6.491	6.576	6.177	6.095
$V_O(+2)$	8.767	8.145	8.119	7.783

Fig. 2. Relative formation energy of an oxygen vacancy as a function of STO supercell size. The oxygen vacancy formation energy in the 2×2×2 supercell is used as reference and is set to 0. Bold and dash lines denote data of neutral and charged vacancy, respectively.

3.3 Migration Energy Barrier

(a) Effect of supercell size on oxygen vacancy migration energy barrier

Fig. 3. Oxygen vacancy diffusion energy barriers as a function of supercell size. The dash and bond lines stand for the results calculated with + U and without + U ; black denotes the calculated values using PBE functional and red denotes the calculated values using PBEsol functional.

Figure 3 shows the migration energy barriers of a neutral vacancy obtained using different supercell sizes. Similar to DFEs, the MEBs decrease as the supercell size increases. The MEB determined using a $2\times 2\times 2$ supercell deviates considerably from those of larger supercells, indicating that this supercell size is too small to predict the MEB accurately. When the system size reaches $5\times 5\times 5$, the spread of DFT values is significantly reduced. For a single oxygen vacancy in STO, the relaxations, which appear as a long-ranged inward relaxation, extend far from the oxygen vacancy site ($\sim 16\text{\AA}$)³⁵. As the boundaries of the larger STO supercells are approached, the relaxation of these atoms far from the vacancy is very small. When the STO supercell size increases to $5\times 5\times 5$, the MEBs of oxygen vacancy is approaching to convergence, as Fig. 3 clearly illustrates. The range of convergence values, 0.39–0.49 eV, underestimates the MEB of the isolated oxygen vacancy derived from experiments and some other computations of ~ 0.60 eV^{18, 24, 25}. The underestimation as compared to other simulation work mainly comes from the large STO supercell we used (containing up to 625 atoms). In the largest supercell ($5\times 5\times 5$),

the interaction between two adjacent oxygen vacancies is lower than the smaller supercells (up to 320 atoms)^{23, 24, 25}. The interactions between oxygen vacancies have been shown to enhance migration energy barriers²⁵. So the migration energy barriers presented here are lower than earlier simulation works. The reason for this underestimate comparing with experimental result ~ 0.6 eV may be due to the limit of the standard DFT method we employed in our calculations or the interactions of single oxygen vacancy with complex defects in experimental sample. The hybrid functional such as B3PW *xc*-functional was demonstrated could predict more accurate optical gap (3.65 eV) of STO bulk⁴¹. However it is still a huge challenge of computation cost to predict the vacancy migration energy barrier in very large STO supercell in which the vacancy concentration can reach the comparable value compared with the experimental ones.

When PBEsol or PBEsol+*U* are employed, the energy barriers calculated in the $3 \times 3 \times 3$ STO supercell are lower than that of the $4 \times 4 \times 4$ supercell. We found that this comes from the difference of the distortion model of the local atomistic environment around the oxygen diffusion path in $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercell. Due to the absence of one oxygen atom in STO bulk, oxygen octahedral rotations are introduced into the system¹¹. This local configuration change is limited by the boundary condition of the supercell, leading to two different situations as observed in $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercell. One situation makes the distances between the diffusing oxygen atom and its nearest oxygen neighbor longer, while the other shortens it, resulting in substantially different MEBs.

Fig. 4. (a) Oxygen octahedral rotation induced by oxygen vacancy in $4\times4\times4$ STO supercell; (b) oxygen octahedral rotation characteristic parameters and the distance between diffusion oxygen and its neighboring atoms in STO supercell; oxygen vacancy diffusion plane (010) in initial states of $3\times3\times3$ (c), $4\times4\times4$ (e) and transition states of $3\times3\times3$ (d), $4\times4\times4$ (f) STO supercells. The blue and red balls represent titanium and oxygen atoms, respectively. $D(O_A-O_B)$, $D(O_A-Ti_2)$ represents the distance between diffusion oxygen atom A and oxygen atom B or titanium atom 2 in Fig. 4 (d) or (f).

The initial and transition point configurations of the $3\times3\times3$ and $4\times4\times4$ STO supercells are shown in Fig. 4. An oxygen octahedral rotation ($a^-b^-c^0$) pattern (following Glazer pattern⁴²) is found when an oxygen vacancy is introduced into the system (shown as Fig. 4 (a), in a $4\times4\times4$ supercell). Here we use the bond angle of $O_B-Ti_1-O_C$, which is near the oxygen vacancy (shown as Fig. 4(c), (e)) to characterize the oxygen octahedral rotation magnitude in different sizes of STO supercells. The magnitudes of this angle in the initial state (IS) and transition state (TS) are shown in Fig. 4 (b), where it is evident that boundary conditions control the rotation characters. For the initial states, when the number of unit cells in a particular direction is even, bond angles of $O_B-Ti_1-O_C$ are smaller with values of 86.46° , 87.42° in $2\times2\times2$ and $4\times4\times4$, respectively. On the other hand, for an odd number of unit cells, these bond angles are larger with values of 88.24° , 88.08° in $3\times3\times3$ and $5\times5\times5$, respectively. Similar observations are found for the transition states, where the $O_B-Ti_1-O_C$ bond angles are again smaller with values of 88.15° , 93.43° in even-numbered supercells (2, 4, respectively) and larger, i.e., 95.76° , 96.47° , in odd-numbered supercells (3, 5, respectively). In the $2\times2\times2$ supercell, this angle is much lower than those in other supercells, because the corresponding oxygen rotations are pinned by a periodic boundary.

The distances between the diffusing oxygen atom A and its first nearest oxygen atom B or C at the transition state are shown in Fig. 4 (d), (f). These distances are smaller in even-number-size supercells ($2.84 \text{ \AA}$ in $2\times2\times2$ and $2.89 \text{ \AA}$ in $4\times4\times4$), and larger in odd-number-size supercells ($2.94 \text{ \AA}$ in $3\times3\times3$ and $2.95 \text{ \AA}$ in $5\times5\times5$). Therefore, one can infer that the repulsive Coulomb interaction between the diffusing oxygen atom and its nearest oxygen atom in a $3\times3\times3$ supercell is lower than that in $4\times4\times4$ supercell. As such, this weaker repulsive interaction would enhance the oxygen diffusion rates by lowering diffusion barriers. This difference in the local atomistic environment in different supercells, due to the artificial boundary conditions, is considered to be the cause of the observed anomaly and explains why the MEB in a $3\times3\times3$ supercell is lower than that in the $4\times4\times4$ supercell.

(b) The Effect of Charge States of the Oxygen Vacancy

We further examine the effect of charge states of the oxygen vacancy on the MEB. Results using PBEsol are shown in Fig. 5. The MEB of a neutral oxygen vacancy is found to be higher than that of charged vacancy, which is consistent with the previous study carried out by Hamadany et

al.²³. The MEB difference between the neutral and charged vacancies is substantial (as high as 0.35 eV) in small supercells ($2\times 2\times 2$); however, this energy difference decreases quickly to less than 0.05 eV upon increasing supercell size.

Fig. 5. Diffusion energy barrier of neutral and charged oxygen vacancy corresponding to STO supercell size calculated with PBEsol functional.

To further elucidate the effects of charge states on oxygen vacancies, the charge density differences of the saddle point configurations between charged and neutral states are analyzed, as shown in Fig. 6. For consistency, charge density difference calculations employ the atomic positions of the relaxed neutral configurations as a reference structure for obtaining both the neutral and charged vacancy charge densities. We observe that with increasing supercell size, the excess charge ($2e^-$) becomes more delocalized, reducing the total charge density on titanium and oxygen atoms, thereby diminishing the effect of the extra charge on MEBs. This is indeed more

pronounced in larger supercells ($n \times n \times n$, $n > 3$) where there is a relatively smaller difference in the MEBs for neutral and charged vacancies.

Fig. 6. Charge density difference of saddle point structure between containing charged oxygen vacancy and neutral vacancy in $3 \times 3 \times 3$ (a), $4 \times 4 \times 4$ (b), and $5 \times 5 \times 5$ (c) STO supercells. In these figures, green, red, and blue balls represent strontium, oxygen and titanium atoms; the isosurface value is 0.00018 e/Bohr^3 , the negative and positive values are shown in light blue and yellow. The primitive unit cell containing the vacancy is indicated by dashed red box.

(c) The Effect of $+U$

As mentioned above, the charge density should be strongly localized around the Ti atoms adjacent to the oxygen vacancy. The GGA+ U method adds a Hubbard-type term to the density functional that penalizes partial occupancies in correlated orbitals and subsequently increases electron localization. Figure 7 shows the migration energy barrier of (a) a neutral oxygen vacancy and (b) a charged oxygen vacancy calculated using either the PBEsol or PBEsol+ U functional. In general, we find the inclusion of a Hubbard- U type term results in higher MEBs for neutral vacancies (the exception being the $2 \times 2 \times 2$ case). For a charged oxygen vacancy in the large $5 \times 5 \times 5$ supercell, we obtain a MEB of 0.40 eV, 0.48 eV, 0.33 eV, and 0.27 eV using PBEsol+ U , PBE+ U , PBEsol, and PBE, respectively.

Applying Hubbard-type terms in DFT calculations can significantly affect the charge density distribution of the STO supercells. Figure S1 (supplementary material) shows the charge density difference between PBEsol+ U and PBEsol for saddle points in different STO supercells containing a neutral oxygen vacancy. We observe that the charge density difference is localized

to regions surrounding the Ti atoms due to Hubbard-type term in DFT making the electronic Ti *d*-orbitals more localized. Because of the charge interaction effect between titanium and its neighboring oxygen atoms, the orbitals of the neighboring oxygen atoms also become localized. An oxygen vacancy in an STO supercell significantly changes the electronic states of atoms near the vacancy site. It is well established that localized states can be more adequately described with the application of a Hubbard-*U* term, thus implying that the DFT+*U* calculations may predict more reliable MEBs for an oxygen vacancy in STO supercells. In addition, density of states (DOS) for 3×3×3 supercell is calculated using PBEsol+*U* and PBEsol functionals. The valence band maximum (VBM) and conduction band minimum (CBM) gap calculated by PBEsol+*U* is closer to the experimental value, seeing supplementary material. This also indicates that adding a Hubbard-type term can more accurately describe the electronic states of STO supercell and further predict a more reliable vacancy migration energy barriers.

(a)

(b)

Fig. 7. Migration energy barrier of neutral oxygen vacancy (a) and charged oxygen vacancy (b) calculated with PBEsol and PBEsol+*U* functionals.

Table 3. Diffusion Energy barrier of isolated oxygen vacancy in STO supercells calculated by different DFT methods.

DFT method	Vacancy charge state	Energy barrier/eV			
		2×2×2	3×3×3	4×4×4	5×5×5
SP_PBE	V ⁰	0.81	0.34	0.32	0.30
	V ⁺²	0.44	0.33	0.30	0.27
PBE+ <i>U</i>	V ⁰	1.62	0.82	0.61	0.49
	V ⁺²	0.65	0.54	0.58	0.48
PBEsol	V ⁰	0.90	0.43	0.47	0.39
	V ⁺²	0.55	0.41	0.43	0.34
SP_PBEsol	V ⁰	0.89	0.42	0.46	0.38
	V ⁺²	0.54	0.40	0.43	0.33
PBEsol+ <i>U</i>	V ⁰	0.82	0.50	0.64	0.39
	V ⁺²	0.69	0.55	0.64	0.40

Note: SP=spin polarized

4. Conclusion

The migration energy barrier of an isolated oxygen vacancy was systematically examined using DFT. Our results indicate that artificial boundary conditions, which are limited by finite supercell size, are important causes of deviations in the calculations—typically resulting in dramatic overestimations of migration energy barriers in small supercells. Increasing the size of the supercell employed in the simulations leads to decreased values of the energy barrier. When a sufficiently large supercell is employed, different simulation approaches result in similar values, between 0.39–0.49 eV. Limited by supercell boundary conditions, the octahedral rotation induced by oxygen vacancy generates two different results. One outcome makes the distance between diffusing oxygen atom and its nearest oxygen longer (3×3×3 or 5×5×5 supercells) and the other makes it shorter (2×2×2 or 4×4×4 supercells), which affect the oxygen vacancy migration energy barrier in different size supercells. On the other hand, the computed MEBs of neutral and charged oxygen vacancy indicate that a charged vacancy has a lower MEB than the neutral vacancy and that the effects of different DFT functionals and vacancy charge states are substantial in small 2×2×2 supercells and diminishing as supercell size increases. Finally, a comparison of the energy barriers and induced charge density distributions calculated with and

without the addition of a Hubbard- U term suggests that PBEsol+ U and PBE+ U methods can more accurately describe the electronic state of STO supercells and thus would be preferable for studying vacancy migration within this material. We note that our predicted values lie below the experimental value of ~ 0.60 eV, probably due to the limitation of DFT functional chosen and the complex defect interactions in experimental samples. However, our work provides a deep analysis of DFT simulations of oxygen vacancy MEBs in STO supercells. These results provide fundamental insights on oxygen vacancy diffusion in STO, which can be extended to all perovskite structure materials.

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Author Contributions

LZ and HX directed the study, analyzed results and wrote the manuscript. BL and PK did part of the calculations, analyzed the results. HZ, VRC, PG analyzed the results. All authors made contributions to write the manuscript.

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Oxygen Vacancy Diffusion in Bulk SrTiO₃ from Density Functional Theory Calculations

Graphical abstract: