



Linking diffusion kinetics to defect electronic structure in metal oxides: Charge-dependent vacancy diffusion in alumina

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We study the diffusion of charged vacancies in α -Al₂O₃ crystal using the first-principles calculation method. We predict that the migration energy for vacancy diffusion strongly depends on the charge state of the vacancy involved. Importantly, we reveal that this charge-dependent vacancy diffusion is directly related to the electron occupancy and energy level change of the defect states of the charged vacancy in alumina. Hence, our study establishes a direct link between the diffusion kinetics and electronic structure of metal oxides.
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Understanding the static and dynamic behavior of point defects in metal oxides is essential for optimization of electrical, optical, and mechanical functions of these materials [1,2]. In this letter, we used the first-principles density functional theory (DFT) calculation method to unveil the physical origin of the charge-dependent atom/vacancy diffusion in alumina (α -Al₂O₃). The dependence of atom/vacancy mobility on its electric charge state has direct implication for the growth kinetics of protective alumina scales on high-temperature alloys [3] and the functional performance of alumina in a resistive random-access-memory (ReRAM) device [4].

In this study, the formation energy and migration energy of charged vacancies in alumina were calculated using the DFT calculations with the projector augmented wave method [5] and the Perdew–Burke–Ernzerhof exchange–correlation functional [6], as implemented in the Vienna Ab initio Simulation Package (VASP) [7,8]. In all these DFT calculations, we used a kinetic energy cutoff of 500 eV. The α -Al₂O₃ bulk crystal was modeled with a $2 \times 2 \times 1$ supercell of a conventional hexagonal cell lattice (shown in Fig. 1(a)). Without vacancy defects, there are in total 48 Al atoms and 72 O atoms in our simulation cell. We used a $3 \times 3 \times 2$ Monkhorst–Pack k -point mesh [9] for k -space integration in our DFT calculations. A charged vacancy in α -Al₂O₃ was generated by removing an atom from the supercell and changing the total number of electrons in the supercell as required. In this work, we investigated the formation energy and mobility of the O vacancy with a charge of 0 (V_{O}^0), +1 (V_{O}^{1+}), or +2 (V_{O}^{2+}) and the Al

vacancy with a charge of 0 (V_{Al}^0), −1 (V_{Al}^{1-}), −2 (V_{Al}^{2-}), or −3 (V_{Al}^{3-}). All the crystal structures were optimized under constant-volume restriction until the Hellman–Feynman force exerted on each ion is less than 0.01 eV/Å.

The formation energy (ΔE_f) of a vacancy with a charge of q in alumina can be calculated as follows [10]:

$$\Delta E_f = E^{\text{def},q} - E^{\text{perf}} + \mu_i + q\mu_e \quad (1)$$

where $E^{\text{def},q}$ is the energy of the relaxed simulation cell containing the charged vacancy whereas E^{perf} is the energy of the perfect crystal; μ_i is the chemical potential of the Al or O atom removed from the alumina crystal; In this study, μ_i was calculated following the scheme suggested in Ref. [10] and using the DFT results and experimental data [11] as inputs; μ_e is the chemical potential of an electron in alumina. When calculating $E^{\text{def},q}$, we have corrected the finite size error introduced by periodic charges following the established schemes [12]. The electron chemical potential μ_e has been calculated as a summation of the valence-band maximum (E_{VBM}) of the perfect crystal and a Fermi level ε_F (whose value is zero at VBM). In this study, E_{VBM} was taken as an energy difference between the bulk alumina with 0 and 1+ charge and ε_F was calculated by enforcing the requirement of charge neutrality in the crystal [13].

It was noted that the Fermi level ε_F of the alumina crystal affects the stability of charged vacancies and can be tuned by changing the concentration of aliovalent dopants. We found from our DFT calculations that V_{O}^0 would be the most stable O vacancy when ε_F is greater than 2.58 eV whereas V_{O}^{2+} would be the most stable O vacancy when ε_F is below 2.58 eV. Regarding various charged Al vacancies, our DFT results predicted that the stable region of ε_F for

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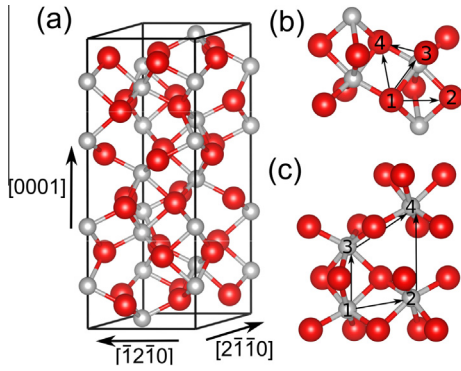


Figure 1. (a) Conventional hexagonal unit cell of the crystal structure of α - Al_2O_3 . Schematics of various paths (delineated with black arrows) for (b) O vacancy and (c) Al vacancy to diffuse through the alumina bulk crystal. In the figure, the red balls represent O atoms and the gray balls represent Al atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

V_{Al}^0 , V_{Al}^{1-} , V_{Al}^{2-} , and V_{Al}^{3-} was from 0.0 eV (i.e., E_{VBM}) to 0.25 eV, from 0.25 eV to 0.82 eV, from 0.82 eV to 1.49 eV, and greater than 1.49 eV, respectively. Our predictions agree with the previous results attained by Hine et al. [10]. It should be pointed out that the self-interaction error of DFT could lead to underestimation of the formation energy of V_{O}^0 and V_{O}^{1+} [10]. Consequently, our DFT predictions on the stability of various O vacancies are in a qualitative (not quantitative) nature. At an example condition of $T = 1300$ K and $p_{\text{O}_2} = 0.2$ atm, ε_F was calculated to be 1.93 eV in an un-doped alumina crystal. Thus, the stable vacancies are predicted to be V_{O}^{2+} for O vacancy and V_{Al}^{3-} for Al vacancy in intrinsic Al_2O_3 crystal at such a condition. Introducing n-type dopants to alumina crystal leads to an increase in ε_F , which could make V_{O}^0 more likely to occur. In contrast, increasing p-type doping level might increase the concentration of V_{Al}^{2-} , V_{Al}^{1-} , and V_{Al}^0 of Al vacancies in α - Al_2O_3 .

Inside the bulk alumina crystal (shown in Fig. 1(a)), we have identified four distinct elementary paths for O atom-vacancy exchange (shown in Fig. 1(b)) as well as four distinct elementary paths for Al atom-vacancy exchange (shown in Fig. 1(c)) [14]. For each of these diffusive jumps, we determined the minimum energy path (MEP) of the migrating vacancy with different charge states using the

climbing image nudged elastic band method [15] and further verified the transition state (which should have only one imaginary vibrational mode) with vibrational frequency calculations. Moreover, we calculated the migration energy for each diffusive jump and presented our calculation results in Table 1. We find that the MEP of the jumps Al_2 - Al_4 and Al_3 - Al_4 contains a locally minimum-energy configuration and thus could be further divided into two diffusive segments. It is worth pointing out that our calculated value of 3.57 eV for the migration barrier of V_{O}^0 along the O_1 - O_2 path is in good agreement with previous DFT calculation of 3.70 eV for the same path [16]. Importantly, our DFT results in Table 1 revealed that the vacancy diffusion in the alumina crystal strongly depends on the charge state of the vacancy involved.

In order to understand this charge-dependent vacancy diffusion, we have analyzed the electronic structure of the migrating charged vacancies in the alumina crystal. As discussed in previous electronic structure calculations [17], the valence band of perfect alumina is just the O 2p band near the valence-band maximum whereas the conduction band is mainly composed of Al 3s and 3p bands. Moreover, extra defect states could be observed inside the band gap if there are vacancies in the alumina crystal. In this study, we found in α - Al_2O_3 that the defect state associated to the O vacancy was located at 2.41 eV above E_{VBM} and composed of the 3s and 3p orbitals from the nearest-neighbor Al atoms (illustrated in Fig. 2(a and b)). The defect states associated to the Al vacancy were found to posit at 0.58 eV above E_{VBM} and are composed of the 2p orbitals from the nearest-neighbor O atoms (illustrated in Fig. 3(a and b)). Comparing the electronic structures of the O vacancy at its relaxed state (Fig. 2(a and b)) and its transition state of jump O_1 - O_2 (Fig. 2(c and d)), we noticed that the energy level of the defect state shifted up by 1.51 eV at the transition state accompanying to the spreading of defect electron density from one local Al tetrahedron to the two neighboring Al tetrahedrons. Examination of the other O vacancy diffusion paths yields similar results. It is apparent that the O vacancy diffusion through the alumina crystal involves an upshift of the energy level of the defect state (composed of Al 3s and 3p bands) toward the conduction band of the crystal. Regarding to the Al vacancy diffusion in α - Al_2O_3 , Figure 3 shows that the energy level of the defect states (composed of O 2p band) actually shifts down toward the valence band of the crystal at the transition state in which the defect electron density is evenly distributed between the two neighboring O octahedrons.

Table 1. Calculated migration energy for charged O and Al vacancy diffusion in the α - Al_2O_3 lattice. For the Al_2 - Al_4 and Al_3 - Al_4 diffusion paths, we present the migration energies for both the two separate diffusion segments. Zero point energy correction is included in the migration energy by calculating the vibrational frequencies of the vacancies and their transition states.

O vacancies	O_1 - O_2	O_1 - O_3	O_1 - O_4	O_3 - O_4		
V_{O}^0	3.57	4.07	4.70	5.02		
V_{O}^{1+}	2.06	2.78	3.09	3.64		
V_{O}^{2+}	0.91	1.79	1.75	2.65		
Al vacancies	Al_1 - Al_2	Al_1 - Al_3	Al_2 - Al_4		Al_3 - Al_4	
			Step 1	Step 2	Step 1	Step 2
V_{Al}^0	1.78	2.07	1.53	1.64	1.91	0.32
V_{Al}^{1-}	1.73	2.07	1.48	1.64	1.87	0.31
V_{Al}^{2-}	1.66	1.98	1.29	1.67	1.74	0.27
V_{Al}^{3-}	1.55	1.79	1.01	1.78	1.56	0.25

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