

Simulation of atomic-scale defects in the clustering and oxygen jumping process of 8 mol% yttria-stabilized zirconia

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The ionic diffusion of 8 mol% yttria-stabilized zirconia (8YSZ) was investigated using atomistic simulation. The well-known inverse relation between oxygen conductivity and temperature is reproduced for a wide range of temperatures (623–1500 K). A strong defect clustering between oxygen vacancies and trivalent yttrium ions was statistically treated and explained by the simulated results, including the effect of temperature. Oxygen migration was less effective at lower temperatures, suggesting that the diffusion of oxygen was localized by jumping back-and-forth through specific lower-energy-barrier paths. Static lattice calculations further confirmed the favorable diffusion routes, of which two adjacent oxygen sites had two or more common second-nearest-neighbor yttrium atoms.

Key words: molecular dynamics, clustering, enthalpy, oxygen jumping, diffusion, ZrO₂.

Introduction

Fluorite-structured oxide ceramics, such as ZrO₂, have been utilized as the electrolyte of solid oxide fuel cells (SOFC) in the past two decades. These materials doped with trivalent or divalent cations generate charge-compensating oxygen vacancies, which also includes CeO₂, often exhibit high oxygen conductivity due to a considerable amount of oxygen vacancies. The dopant also improves the cubic-phase stability in the systems, e.g. calcium or yttrium in ZrO₂.

Among these fluorite-like oxides, yttria-stabilized zirconia (YSZ) gives acceptable ionic conductivity, phase stability, and resistance against a red-ox atmosphere. Experimental studies have reported on the electric properties of the zirconia-based system, and how the microstructure, [1, 2] dopant type, [3] and testing atmosphere [4] influence the ionic conductivity of YSZ.

Molecular dynamics (MD) simulation is a powerful tool to study diffusion processes from an atomic viewpoint, since it gives direct information of diffusion in terms of atomic motion. With MD, it is possible to understand the atomic interaction occurring dynamically in a diffusion process, which is still intractable in experiments. In the past two decades, MD simulation studies on YSZ have been performed. The conductivity anomaly (i.e. the conductivity exhibits a maximum at a certain dopant concentration, generally observed in doped ZrO₂ and CeO₂ systems) has been successfully reproduced, and the predicted maximum-

conductivity concentration of dopant was also consistent with the experimental data (at 8–10 mol% Y₂O₃) [5–9].

Experimental evidence suggested that oxygen vacancies were associated with yttrium ions at next-nearest neighbor (NNN) sites [12, 13] which have also been supported by simulation results [6, 9–11]. In addition, Arrhenius plots of the experimental conductivity-to-temperature results often exhibit an increase in activation enthalpy when the temperature is below 823 K [14, 15]. Although this phenomenon is widely regarded as the result of strong defect association, its underlying microscopic mechanisms have not been carefully studied. In this investigation, we aim to study the oxygen jumping mechanism and defect interaction at widely varied temperatures using MD simulation. 8 mol% Y₂O₃ doped ZrO₂ is studied because its electric conductivity has been widely studied, and also it is a conventional choice for an SOFC electrolyte.

Simulation Details

Molecular dynamics simulations were performed using the DL_POLY package [16]. The yttria-doped zirconia material was considered as a rigid-ion model with pairwise interatomic potentials. The potential consists of an electrostatic term for long-range interaction and a short-range term with a Buckingham form:

$$V_{ij}(r) = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} \quad (1)$$

where the first term represents the repulsive potential arising from overlap of electron clouds and the second term is the dispersion energy. The potential parameters A , ρ , and C were taken from the work of Schelling *et al.*

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[17]. The electrostatic potential was calculated using an Ewald sum, with a cutoff = 0.9 nm.

A simulation box consisting of $4 \times 4 \times 4$ unit cells of cubic ZrO_2 with periodic boundary conditions was set-up. A portion of the Zr atoms were randomly substituted with Y atoms. Meanwhile, some oxygen atoms were removed to create oxygen vacancies, with the number corresponding to the 8 mol% yttria contents. The positions of Zr to be substituted by Y and O to be removed were selected randomly. In addition, five simulations with different initial atomic configurations was performed at each temperature. Simulations were performed under constant volume-constant temperature constraint, i.e., an NVT ensemble. As a result, the lattice constants at different temperatures were determined explicitly by the following equation:

$$a(T) = a(T_0)[1 + \alpha(T - T_0)] \quad (2)$$

where a denotes the lattice constant, α represents the linear thermal expansion coefficient with a value of $1 \times 10^{-5} \text{ K}^{-1}$ for all compositions of YSZ, and $a(T_0)$ is the lattice constant at room temperature (300 K) with the value 5.136 Å [18].

The self-diffusivity of oxygen was calculated by Einstein's relation:

$$\frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 = 6Dt + B \quad (3)$$

The left-hand side is the mean-square displacement (MSD), where r_i represents the position of atom i . The D on the right hand side is the self-diffusivity and B denotes the fluctuation term. Simulations were performed from 1500 K down to 623 K for 5–20 ns.

The static lattice calculation for oxygen jumping energy was performed by the GULP code [19]. The energy profile of the jumping species can be obtained from slowly moving an oxygen atom adjacent to the vacancy along the path to the vacant site. At each step, all atoms were relaxed and the total lattice energy was calculated. The jumping energy

is defined as the difference between the peak and the first valley encountered in the energy profile. The nearest two Zr atoms were constrained to relax on a (200) plane, as being suggested by Pornprasertsuk *et al.* [11] in each calculation.

Results and Discussion

Conductivity calculations

The MSD of oxygen at different temperatures is shown in Fig. 1. The linearity of the MSD-time relation is more apparent at 1273 K than at 623 K. At 623 K the MSD arises rapidly at the beginning, and then increases steadily but with a large fluctuation. At temperatures lower than 623 K, such a fluctuation influences the slope of the MSD so greatly that the calculated D value depends strongly on the time interval. As a result, D values at $T < 623 \text{ K}$ were thus not calculated. For similar reasons, diffusivity calculations were performed with an equilibrium time of 1 ns and a total 5 ns simulation time for those cases with temperatures above 823 K, while 4 ns and total 20 ns for those with temperatures below 823 K.

The electric conductivity can be calculated from the classical Nernst-Einstein relation:

$$\sigma_i = \frac{n_i q_i^2 D_i}{k_B T} \quad (4)$$

where σ corresponds to the dc conductivity, n the concentration of charge carriers, q and the electric charge. The subscript i denotes a specific charge carrier. The simulated Arrhenius plot is shown in Fig. 2. The calculated and experimental conductivities, and activation enthalpies are listed in Table 1. Simulation results show a slightly higher activation enthalpy at lower temperatures ($< 823 \text{ K}$). From Table 1 the similar trend for experimental data can be found, in which the temperature corresponding to the change in activation energy is often defined as the critical temperature, T_c , and in YSZ T_c is often known to occur

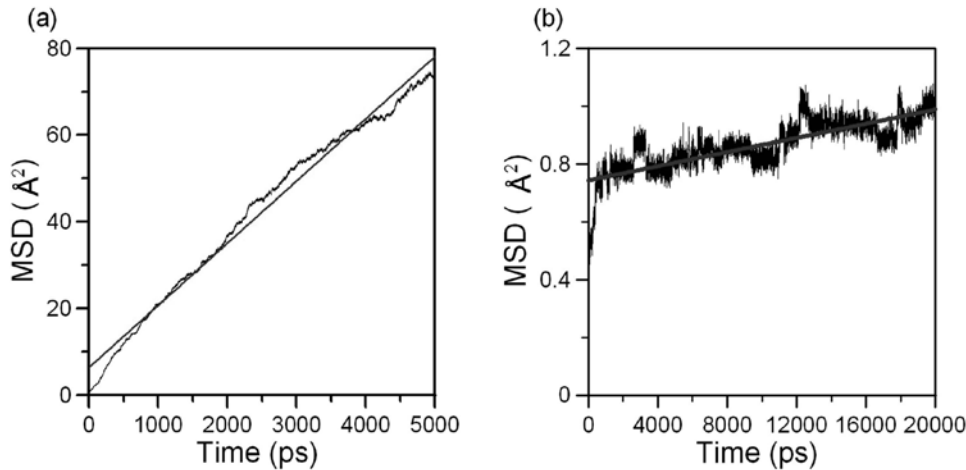


Fig. 1. (a) Mean-square displacement at 1273 K (b) Mean-square displacement at 623 K. Note that the simulation time at 623 K is 4 times longer than that at 1273 K. The straight line indicates the linear fitting curve of MSD, and the slope of the curve is directly related to the oxygen diffusivity (see eqn. 3).

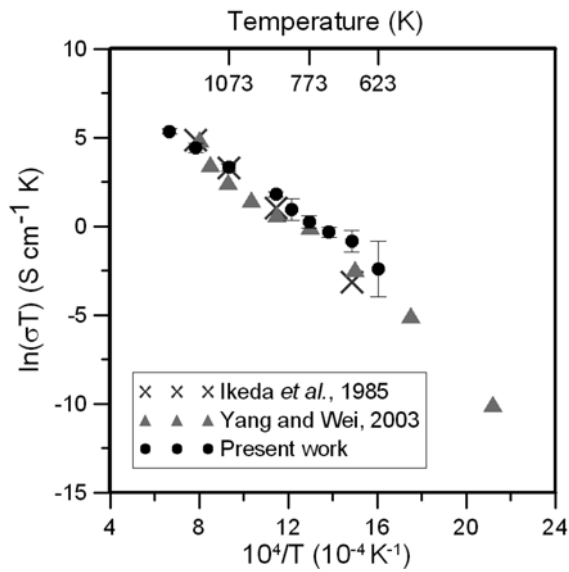


Fig. 2. Simulated Arrhenius plot, in comparison with the experimental results by Ikeda *et al.* [14] and Yang *et al.* [15].

Table 1. Calculated conductivity and activation enthalpy in comparison with the experimental results

	Present work	Ikeda <i>et al.</i> [14]	Yang <i>et al.</i> [15]
σ at 1273 K (S/cm)	0.077	~0.10	~0.067
σ at 1073 K (S/cm)	0.031	~0.025	~0.019
ΔH (eV)	0.66 eV (> 823 K) and 0.71 eV (< 823 K)	0.97 eV (> 813 K) and 1.09 eV (< 813 K)	0.97 eV (> 823 K) and 1.07 eV (< 823 K)

between 773–873 °C. Nevertheless, care must be taken when simulation results at low temperatures are interpreted. A large error bar at low temperatures is due to a greater fluctuation of the MSD-time relation as shown in Fig 1(b). A time-scale of longer than 20 ns is necessary, but laborious. Several trials and longer time scales are computationally feasible for these simulations at low temperature.

Defect association

Two types of elementary point defects, $Y_{Zr}^{\bullet}$ and $V_o^{\bullet\bullet}$, are defined in YSZ materials. The binding energies of the defect complex $(Y_{Zr}V_o)^{\bullet}$ had been calculated by an empirical potential method [9–10] and ab-initio simulation [11]. In this paper, we focus on statistical approach and the effect of temperature. Defect clustering was investigated by the probability of oxygen vacancies distributed over different types of oxygen sites, i.e. oxygen sites with different numbers of the Y atoms in the neighborhood. The term 1stNNY denotes the number of Y atoms in the first nearest-neighbor shell and SecNNY denotes the number of Y atoms in the second nearest-neighbor shell. The accumulative time that vacancies occur at sites with different environments is summarized in Fig. 3, illustrating the effect of 1stNNY and SecNNY on the probability of an oxygen site to be vacant. The sites without a 1stNNY and

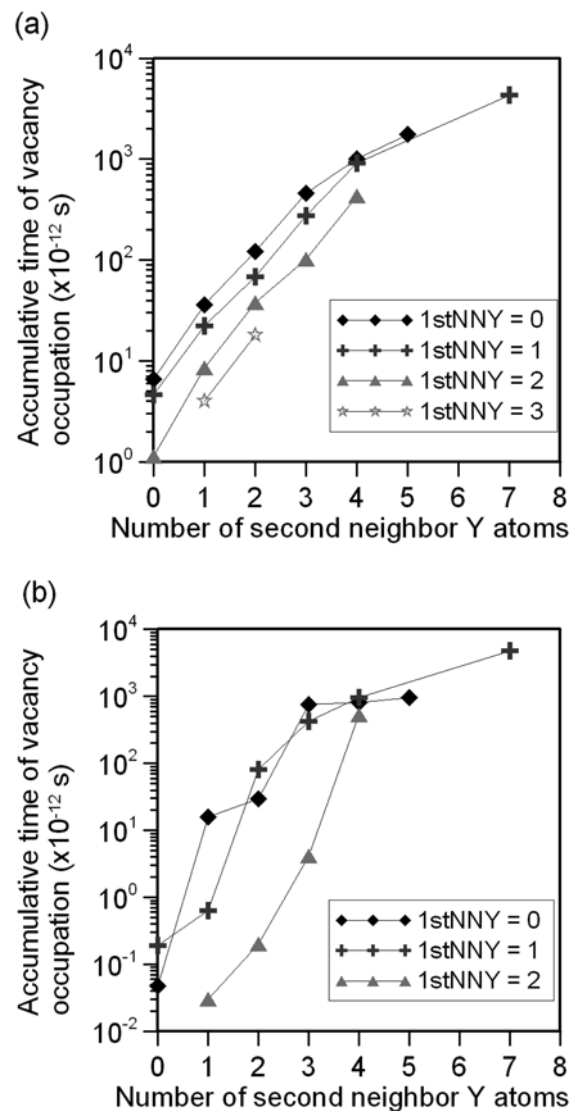


Fig. 3. The accumulative time of oxygen sites with different environments to be vacant at (a) 1273 K (b) 623 K within a total simulation time of 5 ns. Note that the accumulative time of vacancy occupation occur at a specific site is normalized by the total number of sites in the lattice. It is also worth noting that the maximum number of second neighbor Y atoms for an oxygen site is 12, while no more than 8 is observed in our system, in which the sites of Y substitution for Zr were decided randomly.

with a higher SecNNY have a higher tendency to be vacant at the temperature of 1273 K. In Fig 3(b), similar trend can also be observed, while the occurrence of vacancies at sites with 1stNNY = 2 is much lower than that with a 1stNNY < 1, and no vacancies were found at sites with 1stNNY > 2. This can probably be interpreted that the low-mobility oxygen vacancy at a lower temperature can hardly travel to an unfavorable oxygen site (i.e., sites with more 1stNNY). The observed result that oxygen vacancies favor the condition of higher 2ndNNY is consistent with the simulation work by Yamamura *et al.* [6], which emphasized the influence of the composition. While in this paper the effect of temperature is displayed.

The above result implies that an oxygen site having few 1stNNY (< 1), but a high SecNNY (> 3), is more likely to be occupied by a vacancy, especially at lower temperatures. We thus furthermore categorized all oxygen vacancies into four types:

- type 1 denotes the sites with 1stNNY = 0 and SecNNY > 0 ;
- type 2 accounts for the sites with 1stNNY = 1 and SecNNY ≥ 3 ;
- type 3 represents the sites with 1stNNY = 1 and SecNNY < 3 , or 1stNNY > 1 ;
- type 4 denotes 1stNNY = 0 and SecNNY = 0.

The probabilities of vacancy occurrence in type 1-4 sites are listed in Table 2, which shows that above 90% of vacancies prefer to occupy the sites of types 1 and 2 rather than types 3 and 4, even though the intrinsic numbers of type 3 sites are about five times greater than those of type 2. Moreover, the preference described above appears to be more apparent at lower temperatures, which implies oxygen vacancies were bound more tightly at specific sites at lower temperatures. This will be further investigated below through the analysis of oxygen jumping mechanisms.

Oxygen migration

Based on the 3-D random-walk theory, the self-diffusivity of oxygen (D_o) in zirconia can be represented as follows:

$$D_o = [V_o]D_v = [V_o]\gamma\lambda^2\nu\exp\left(\frac{\Delta S}{k}\right)\exp\left(\frac{-\Delta H}{kT}\right) \quad (5)$$

where D_v is known as the diffusivity of oxygen vacancies, $[V_o]$ is the concentration of oxygen vacancies, γ denotes the geometric factor ($\gamma = 1/6$ for a simple cubic oxygen sublattice), λ represents the jumping distance of an atom in a single jumping event, ν is the lattice vibrational frequency, ΔS and ΔH are the entropy and enthalpy changes involved in the jumping process of an oxygen vacancy, respectively and Γ corresponds to the frequency of jumping of an oxygen vacancy. Herein, we are reporting the analysis on the dependence of Γ on temperature.

The Γ calculated was found to be influenced by temperature only, and almost remains constant within the ensemble simulation. However, to further explore the mechanism of diffusion, it is necessary to know the percentage of the forward jumps among the observed jumps. A forward jumping is defined as a jumping process which does not reverse its previous jumping process,

Table 2. The probability of vacancy occurrence in type 1-4 sites (as defined in the section on defect association), and the corresponding probability calculated based on a random-walk model

Temperature (K)	1273	623	Random-walk model
Percentage of type 1 vacancy (%)	68.5	75.9	45.0
Percentage of type 2 vacancy (%)	23.4	21.6	9.4
Percentage of type 3 vacancy (%)	7.92	2.51	37.9
Percentage of type 4 vacancy (%)	0.182	5.79×10^{-3}	7.7

while a backward jumping is defined as the opposite meaning of forward jumping. Both jumping processes are defined as successful jumpings when an oxygen atom actually jumps into the site being originally vacant. The calculated frequency of jumping and the percentage of forward jumps are listed in Table 3. The backward jumping tends to be more dominant at lower temperatures. The temperature dependence of diffusivity D and jumping frequency Γ is shown in Fig. 4. The calculated activation enthalpies from $D(\Delta H^D)$ and $\Gamma(\Delta H^\Gamma)$ are listed in Table 4. The results show that the slope obtained from D and Γ (i.e., ΔH^D and ΔH^Γ) are incommensurate. It should be emphasized that from eqn. 5, which is based on the random-walk theory, should be equal to ΔH^Γ . Generally in the knowledge of oxygen conduction in acceptor doped zirconia, the mechanism for oxygen transport at $T > T_c$ (as defined in the section on conductivity calculation) corresponds to the extrinsic defect dissociation region with $\Delta H^D = \Delta H_M$, where ΔH_M is the enthalpy for the thermally activated motion of an oxygen vacancy, and that at $T < T_c$ correspond to the extrinsic defect association region with $\Delta H^D = \Delta H_M + \Delta H_A$, where ΔH_A represents the additional enthalpy related to the

Table 3. The frequency of jumpings per oxygen vacancy and the percentage of forward jumping

Temperature (K)	Frequency of jumpings (s ⁻¹)	Percentage of forward jumping (%)
673	1.60×10^{11}	0.8
873	2.15×10^{11}	3.4
1273	6.16×10^{11}	16.3

Table 4. Calculated activation enthalpies from various simulated results (in eV)

	$\Delta H (> 823 \text{ K})$	$\Delta H (< 823 \text{ K})$
From $D (\Delta H^D)$	0.67	0.71
From $\Gamma (\Delta H^\Gamma)$	0.22	0.13

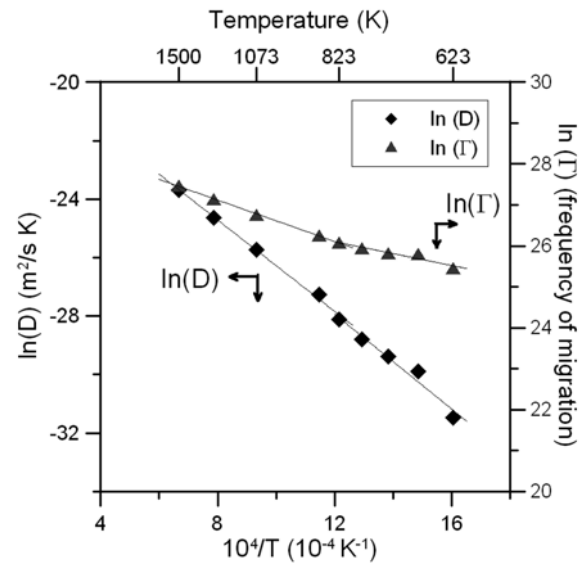


Fig. 4. Arrhenius plot of diffusivity (D) and jumping frequency (Γ).

thermally-activated dissociation of a defect complex. However, there is no related research which has suggested that in the defect dissociation region the diffusion of an oxygen vacancy corresponds to a random-walk process, i.e. $\Delta H^D = \Delta H_M = \Delta H^F$, and ΔH^F is also hard to measure in an experiment. In our results, it is now suggested that even at $T > T_c$, ΔH^F is substantially smaller than ΔH^D , implying a large deviation from a random-walk process. This analysis result on defect association also support this inference, as can be found from Table 2, a still-prevailing defect association phenomenon at as high as 1273 K. It is becoming unreasonable to use the conventional notation of activation enthalpies in this paper, for we had actually separated the enthalpy related to oxygen hopping, ΔH^F from ΔH^D . As a result the term is defined as an effective binding energy, indicating the actual deviation of the oxygen diffusion process from a random-walk process. It is quite interesting to see from Table 4 and Fig. 4 that, for the data points below 823 K, the ΔH^F is lower than the value calculated from points above 823 K, while the ΔH_b , which becomes 0.45 as $T > 823$ K and 0.58 as $T < 823$ K, displays an opposite trend. The trend for jumping frequency is reasonable because the jump of an oxygen vacancy through different paths is considered a parallel processes. Therefore, oxygen hopping through low-energy-barrier paths is preferred over that via high-energy-barrier paths at lower temperatures. The energy, 0.13 eV at lower temperatures, should indicate that oxygen hopping (not diffusion) is becoming easier than at higher temperature. However, the higher ΔH_b indicates that oxygen atoms are relatively less mobile although a lower activation energy for oxygen-vacancy jumping is observed at lower temperatures.

Low-energy-barrier paths in the YSZ lattice

Atomic configurations that constitute these paths were studied. Firstly, four nearest-neighbor Zr ions are around every oxygen, but two of them in a pair will block the jumping path. These two Zr ions constitute a shared “edge” of an OZr_4 tetrahedron, and located at the midpoint of two neighboring oxygen sites, as shown in Fig. 5. We use the terms “Zr-Zr path”, “Zr-Y path” and “Y-Y path” to represent different paths in distinction of the type of ions on the edge. The oxygen-vacancy jumping energy has been evaluated by first-principles [11, 20] and static lattice calculations. [9] The reported value for oxygen migration energies in the literature varies in value but appears with a common tendency, which can be summarized as below. The activation energy of jumping along the Y-Y path is much higher than that of the others, and that of the Zr-Zr path is the lowest. Additionally, the activation energy of jumping along of the Zr-Zr path is the lowest. Therefore, the jump through the Zr-Zr edge is expected to be the most dominant route over the others, as had also been suggested by Kilo *et al.* [8].

We also repeated this investigation on the fraction of the three jumping paths at different temperatures, and reported in Fig. 6. The fraction of jumpings via the Zr-Zr path is much

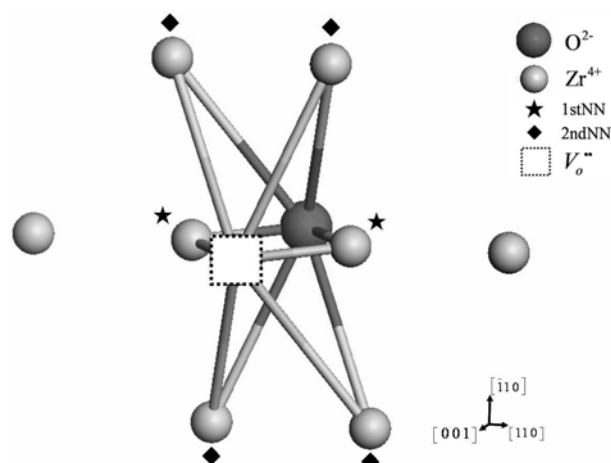


Fig. 5. Graphical illustration of common first- and second-nearest cations of an [001] $\text{O}^{2-} - V_o$ pair (jumping path). Note that all the cations (Zr^{4+}) shown lie on the (002) plane.

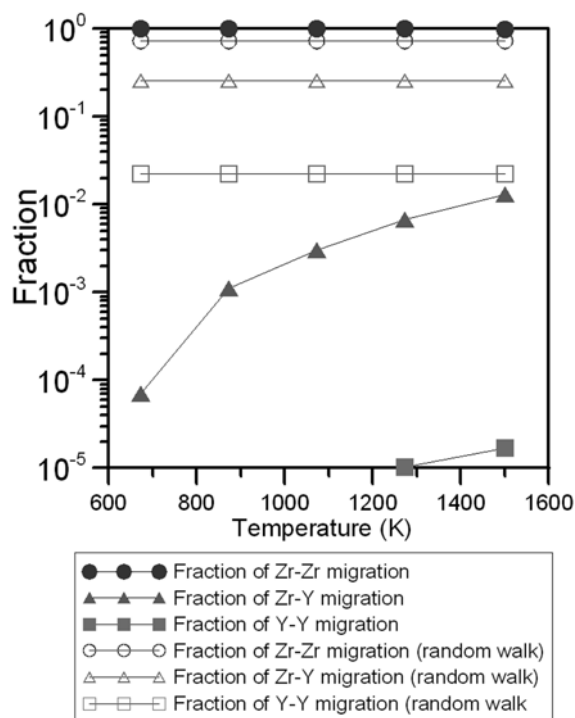


Fig. 6. The fractions of Zr-Zr edged, Zr-Y edged and Y-Y edged jumpings in response to temperatures. The closed and open symbols represent the observed fraction from simulation and the evaluated fraction based on a random-walk diffusion process, respectively.

higher than that of the others, considering either random-walk or effective jumping. Furthermore, the fraction of the jumpings via the Zr-Y and Y-Y paths increase as the temperature, which is consistent with our expectation that three jumping routes are thermally activated independently.

As mentioned in the section on defect association that the oxygen sites with a Y ion at a second-neighbor are preferentially “vacancy binding sites,” in which vacancies are preferentially trapped in these sites at lower temperatures. Furthermore, the vast majority of oxygen jumpings

(Table 3) at lower temperatures can be noted to be “backward jumpings”, indicating a poor efficiency of oxygen migration. If the migration relates to the energy barrier especially at lower temperatures, the atomic configurations constituting different symmetries (for both back and forth directions) should be considered. For this reason, we postulate that two adjacent vacancy-binding sites (i.e. oxygen sites types 1 and 2, discussed in the section on defect association) with one or more SecNNY atoms may influence the activation energy for oxygen-vacancy jumping. Fig. 5 illustrates that two nearby oxygen sites (one is vacant) share 4 common SecNN cations. Thus there is a total of six possible arrangements of neighboring cations, which include 0–4 common SecNN Y atoms.

An investigation was made into the fraction of oxygen-vacancy exchanges with different numbers of surrounding common SecNNY (second neighbor Y ions shared by an oxygen-vacancy pair) at different temperatures. In the following text, we denote the number of common SecNNY of a oxygen-vacancy pair as #_SecNNY. The results are shown in Fig. 7. The fraction of 0_SecNNY exchange is lower than the cases of 1_SecNNY and 2_SecNNY. This is consistent with the fact that vacancies are trapped more frequently at the sites with second-nearest-neighbor Y atoms, resulting in a greater probability for the ion exchange on 1_SecNNY and 2_SecNNY cases. Fig. 7 also shows that the fraction of the 2_SecNNY case increases when the temperature decreases, but the fraction of the 0_SecNNY case shows the opposite trend. Such a characteristic might account for the change in jumping enthalpy at different temperatures.

In order to explore the actual activation energies for the oxygen-vacancy exchange with 0–4_SecNNY, we performed static lattice calculations to get the energy profile when an oxygen atom moved into a vacant site. Different numbers of SecNN Y atoms were placed surrounding the paths. The graphical illustration and results are shown in Fig. 8. The configuration of Fig. 8(a) corresponds to the 0_SecNNY case. Fig. 8(b) to 1_SecNNY, Fig. 8(c)–(e) to 2_SecNNY, and Fig. 8(f) to 3_SecNNY, respectively. One can find that the configurations in Fig. 8(d)–(f) exhibit lower jumping energies than in Fig. 8(a). Therefore, the cases with 2_SecNNY and 3_SecNNY jumpings experience lower energy barriers than 0_SecNNY jumping. The range that the calculated oxygen jumping energies varied in Fig. 8 (0.168–0.27 eV) seems commensurate with the value obtained from the slope on the Arrhenius plot of frequency of jumping in Table 4 (0.13–0.22 eV). However, a slight discrepancy resulted from the underlying difference between the static lattice and MD approaches: the effect of temperature is not considered in the static lattice method.

Conclusions

The diffusivity of oxygen in yttrium-stabilized zirconia was simulated in the temperature range from 623 K to 1500 K, and the calculated electrical conductivities are essentially

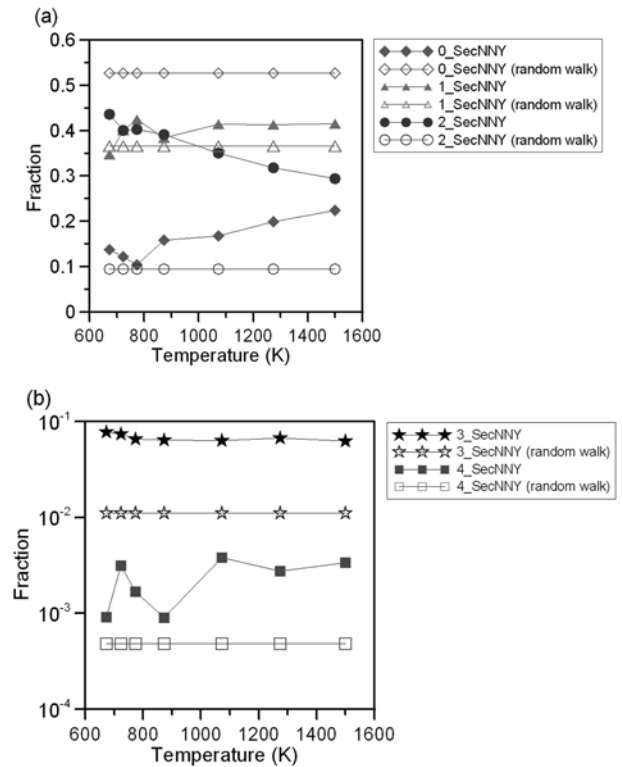


Fig. 7. The fractions of jumpings via paths with different numbers of second-nearest Y atoms surrounded as a function of temperature and the estimated value from a random-walk model. (a) Fractions of jumpings through 0–2SecNNY paths (b) Fractions of jumpings through 3–4SecNNY paths.

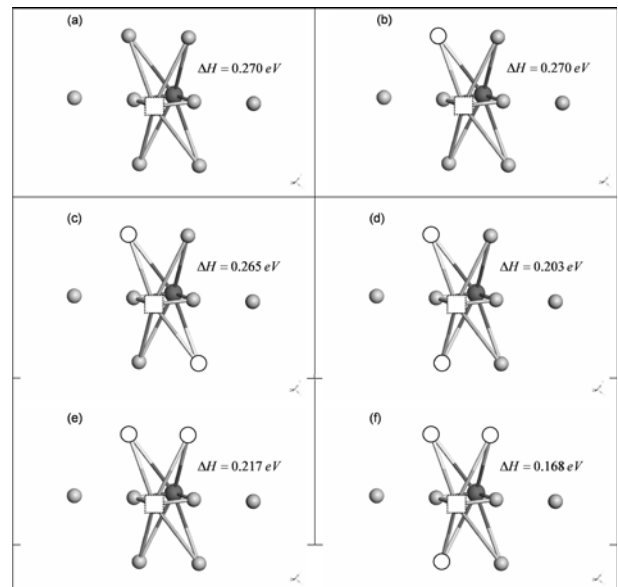


Fig. 8. Calculated jumping energies with different configurations of surrounding second-nearest-neighbor cations. The open circles correspond to yttrium ions, other ions are represented in the same way as in Fig. 5. Note the atomic configuration for (a)–(f) only differ in the geometry of cations surrounding the jumping path.

consistent with previous experimental results. Therefore, the above simulations were analyzed in statistical and geometrical points-of-view, and can be summarized as below.

1. Defect analysis shows that oxygen vacancies are trapped when they are in the sites surrounded with 2nd-nearest neighbor Y atoms. Furthermore, this tendency is more apparent at lower temperatures, which is consistent with the experimental observations that the activation enthalpy slightly increases when the temperature is lower than 823 K.

2. In the oxygen jumping analysis, the frequency of the jumping exhibits a lower dependency to the temperature than the oxygen self-diffusivity. At lower temperatures, slow oxygen migration prevails due to "backward jumping", which does not contribute to the diffusion process.

3. A lower enthalpy of the jumping frequency (ΔH^f), a low fraction of forward (effective) jumping, and a strong vacancy bonding effect at lower temperatures suggest that the diffusion of oxygen does occur via low-energy-barrier paths. The paths with two to three surrounding second-nearest-neighbor Y atoms exhibit a much higher fraction of effective exchange of oxygen with vacancies than that predicted by random-walk diffusion. Some atomic configurations constituting 2_SecNNY paths have lower energy barriers than that via the paths with 0_SecNNY and 1_SecNNY.

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