Atomistic study of segregation and diffusion of yttrium and calcium cations near electrolyte surfaces in solid oxide fuel cells

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Abstract

Segregation behaviors of yttrium (Y) and calcium (Ca) cation dopant species near zirconia (111) surfaces have been investigated utilizing atomistic simulations. The results reveal that surface segregation of both species can be achieved when the density of cation and oxygen vacancies near the surface is relatively high compared to the bulk. Comparing Y with Ca, the local equilibrium concentration at the surface of Ca is estimated to be lower than that of Y; however, Ca is kinetically much easier to diffuse from bulk to the surface than Y. The analysis of in-plane cation and oxygen diffusion at Y- or Ca-rich surfaces shows that the cation diffusivity is enhanced with increasing Ca-concentration at the surface, whereas oxygen diffusivity is inhibited. This tendency is more remarkable than that of the Y-rich surface, suggesting that Ca segregation has a greater negative impact than Y segregation on

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electrolyte performance in solid oxide fuel cells.

Keywords: Solid Oxide Fuel Cells, Segregation, Surface diffusion,
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1. Introduction

Yttria-stabilized zirconia (YSZ) plays an important role as an electrolyte and anode material in energy conversion system such as solid oxide fuel cells (SOFC) due to its high ionic conductivity [1, 2, 3, 4]. It has been
5 recognized that the durability and electrochemical performance of YSZ are strongly related to diffusion properties near YSZ surfaces [5, 6, 7, 8]. For instance, mechanical creep, a typical aging phenomena observed in YSZ [9], is basically driven by the mass transport due to slow cation dynamics under low stress conditions during long-time operation. Among many experimental
10 studies of this complicated phenomenon [10, 11, 12], Laurencin et al. [5] have recently reported that the creep mechanism in Ni-YSZ cermet systems is dominated by cation diffusion at the surface rather than at grain boundaries (GB), particularly when the temperature is close to typical SOFC operating temperature (< 1100 °C). Conversely, oxygen diffusion along YSZ surfaces
15 is believed to be a part of critical process directly linked to electrochemical reactions that occur on both the anode and cathode side [13, 14]. Toward designing more efficient fuel cell systems, intensive work using a nano-scale probe has been focused on elucidating oxygen vacancy behavior near the YSZ surface [15].

20 It is well known that the chemical composition near a YSZ surface differs significantly from that of bulk material, depending on the purity of raw materials or the processing conditions [16, 17, 18, 19]. The difference between bulk and surface composition is primarily produced during the fabrication process in which YSZ experiences high-temperature calcination at approxi-
25 mately 1400 °C [8]. At this temperature, migration of various types of cation

defects, such as dopants and impurities (or additives) in the raw materials may be activated, resulting in surface segregation and change in surface chemical composition. Indeed, according to several experimental studies, after calcination a YSZ surface exhibits considerable enrichment of dopant (Y) and impurities (Ca, Si, Na, etc.), showing the strong depth dependence of the composition profile below the surface [17, 20, 21, 22, 23]. Because the properties of in-plane surface diffusion mentioned above could be strongly affected by impurity levels or the chemical composition at the surface, better understanding of the segregation physics of cation defects in YSZ is essential. However, the resolution ratio limitations and the inability to measure spatial distribution of defects accurately make it difficult to provide detailed insight on cation behavior at a micro-scale.

Atomistic simulations have been widely utilized to clarify the fundamental aspects of segregation and diffusion phenomena associated with oxide systems [24, 25, 26, 27, 28, 29]. With regard to the modeling of segregation processes in YSZ, density functional theory has been applied for accurate measurement of the segregation energy of yttrium near YSZ surfaces or GBs [30, 31]. Lee et al. [32] have successfully predicted yttrium concentrations as a function of the depth from YSZ (100) surface by developing a hybrid Monte Carlo-molecular dynamics algorithm. Besides, the effect of steps existing at the YSZ surface on segregation energetics has been revealed using a reactive force field approach [33, 34]. Yoshiya et al. [35] have examined yttrium segregation energy at various types of YSZ GBs using chemical potential concepts and an empirical potential framework to estimate the local equilibrium concentration of yttrium at GBs. Although many numerical studies have been

conducted, these simulations have relied only on the energetic aspects of the dopant segregation near the surface or GBs. More specifically, in the above studies, energetically stable dopant configurations have been explored based on the exchange algorithm between two cation sites. Although cation diffusion is known to be a thermally activated process via cation vacancy [9, 36],
 55 information about cation kinetics under the presence of cation vacancy is strikingly lacking primarily because cation diffusivity is many orders of magnitude lower than that of oxygen. Consequently, accurate tracking of cation hopping within the limited time scale of atomistic simulations becomes challenging [37, 38]. Thus, the underlying mechanisms of cation segregation are
 60 not yet fully understood.

The aim of this paper is to provide atomistic insights on the surface segregation of dopant (Y) and impurity (Ca) at the ZrO_2 (111) surface, focusing on both energetics and kinetics. We focused on (111) surface since it is the
 65 most stable one based on DFT calculations [39]. A classical pair-potential, i.e. Buckingham potential coupled with a long-term Coulomb interaction, has been used for all the atomistic simulations. A Ca ion has been selected because Ca is often employed as a potent dopant to stabilize zirconia, i.e., calcia-stabilized zirconia (CSZ) and is an intrinsic contaminant in bulk YSZ.
 70 First, using the same energetic approach as previous work [28, 35], we estimate the segregation energies and the local equilibrium concentrations for Y and Ca at the surface. Second, we report the results of nudged elastic band (NEB) analysis toward measuring cation migration barriers near the surface, emphasizing how the presence of both cation and oxygen vacancies surrounding the hopping species affects migration barriers. Finally, on the basis of
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our results, we briefly discuss the effect of dopant (or impurity) enrichment on the surface diffusion of the cation and oxygen using standard atomistic techniques, such as kinetic Monte Carlo (KMC) and molecular dynamics (MD).

80 **2. Method**

2.1. Computational Model

The atomistic model is set up as follows. First, a perfect cubic ZrO_2 crystal $2.5 \times 2.5 \times 6.8$ nm with z -axis as $[111]$ crystal orientation is produced. To simulate $\{111\}$ as the surface, the modeling cell is extended in the z direction by 50%, as shown in Fig. 1. Periodic boundary conditions are
85 imposed on the x , y and z directions. Thus, the distance between neighboring $\{111\}$ surfaces is approximately 3.4 nm.

The interaction between atoms i and j is described by the Buckingham potential coupled with a long-term Coulomb potential, as shown in Eq. (1).

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

Here, r_{ij} is the distance between atom i and j . q_i is the charge of atom i . A , ρ , and C are empirical parameters that are used for the present work, as
90 shown in Table 1. All the calculations are conducted by in-house code.

By using this YSZ potential, the binding energy for Y with oxygen vacancy as nearest, second nearest and third nearest neighbor are -0.14, -0.38 and -0.19 eV, respectively. The position of second nearest neighbor is the most stable one. These results agree with DFT calculation which provided
95 the value of second nearest neighbor as -0.35 eV [42]. Meanwhile, for the

Figure 1: (a) Cubic ZrO₂(111) surface model. (b) Side view of the atomistic configuration consisting of one Y'_{Zr} at the first layer, one Y'_{Zr} and V^{••}_O at the bulk layer. Zr⁴⁺, Y³⁺, and O²⁻ ions are shown as red, yellow, and blue, respectively.

case of oxygen vacancy and Ca, three values are -0.67, -0.72 and -0.36 eV by the present Ca-O potential. Such results are in accordance with the previous study on defect structure of calcia-stabilized zirconia which declared second nearest neighbor as the most stable one as well (-0.68 eV) [43]. Hence, it is
100 deemed that the potentials for both Y and Ca are available here.

Besides, large model with size of twice the vacuum gap and lateral dimension has been used to calculate the segregation energy for defect complexes at surface layer. The results of this large model are respectively -0.78, -1.94 and -2.03 eV for Y, Ca and cation vacancy, which are similar with the values
105 of our original model. Thus, size effect would be minor and will not cause any computational inaccuracies.

Table 1: Buckingham potential parameters employed in the present calculations [40, 41].

Interaction	A [eV]	$\rho[\text{\AA}]$	$C[\text{eV}\text{\AA}^6]$
$\text{Y}^{3+} - \text{O}^{2-}$	1325.6	0.3461	0.0
$\text{Ca}^{2+} - \text{O}^{2-}$	784.38	0.36356	0.0
$\text{Zr}^{4+} - \text{O}^{2-}$	1024.6	0.376	0.0
$\text{O}^{2-} - \text{O}^{2-}$	22764.0	0.149	27.89

2.2. Segregation energy of cation defect

To investigate the surface segregation behavior of cation defects, stable atomic configurations containing the defects located layer by layer from the surface to the bulk region are computed by conjugate gradient relaxation. 110 Three types of cation defects (Y^{3+} dopant, Ca^{2+} impurity, and Zr^{4+} vacancy) are considered in this work (Table 2).

Table 2: Lists of cation defect types considered in this study. Each defect is represented by Kröger–Vink notation.

Cation defect	Type of defect	
	isolated	complexes
Y^{3+} dopant	Y'_{Zr}	$(2\text{Y}'_{\text{Zr}}, \text{V}_{\text{O}}^{\bullet\bullet})^{\times}$
Ca^{2+} impurity	Ca''_{Zr}	$(\text{Ca}''_{\text{Zr}}, \text{V}_{\text{O}}^{\bullet\bullet})^{\times}$
Zr^{4+} vacancy	$\text{V}^{4'}_{\text{Zr}}$	$(\text{V}^{4'}_{\text{Zr}}, 2\text{V}_{\text{O}}^{\bullet\bullet})^{\times}$

For a 3-valence cation dopant such as Y^{3+} , one more ion substitute Zr^{4+} at arbitrary positions in the system maintain the charge neutrality by removing the corresponding number of oxygen ions. Using Kröger-Vink notation, two

types of point defects, i.e., Y'_{Zr} as the Y^{3+} cation substituting Zr^{4+} and $V_{\text{O}}^{\bullet\bullet}$ as the oxygen vacancies, have been introduced into the system.

To discuss the effect of impurity species, a Ca^{2+} cation is considered by replacing one Zr^{4+} and removing one oxygen ion, as follows:

Because the movement of dopant or impurity is accompanied by site exchange with cation vacancy, the segregation of cation vacancy is also taken into account by removing Zr^{4+} , denoted as $V_{\text{Zr}}^{4'}$ as:

For each cation defect, several types of defect complexes are possible, depending on the positions of the oxygen vacancies. In this work, the isolated cation defect and the charge-neutralized defect complexes (Table 2) are
115 examined.

The segregation energy $E_{i,\text{seg}}$ of a cation defect at the i th layer from the surface is defined as Eq. (5)

$$E_{i,\text{seg}} = E_{i,\text{surf}} - E_{\text{bulk}} \quad (5)$$

where $E_{i,\text{surf}}$ is the relaxed energy of the configurations containing a cation defect at the i th layer from surface, and E_{bulk} is the energy of configuration with the corresponding defect at bulk (sufficiently far from the surface) [35].

120 For the case of defect complexes, the oxygen vacancies are set at the nearest

or second-nearest neighbor of the cation defect. Then, by performing energy minimization for all possible positions of oxygen vacancies, the energy of the most stable configuration is applied as $E_{i,\text{surf}}$. Fig. 1 (b) shows a typical side view of the atomistic configuration to compute $E_{1,\text{surf}}$ of Y'_{Zr} , in which one
125 Y'_{Zr} is placed at the first layer of the $\{111\}$ surface while the remaining Y'_{Zr} and $\text{V}_{\text{O}}^{\bullet\bullet}$ are positioned at the bulk.

2.3. Cation defect migration energy

The activation energy barriers of cation hopping for Y'_{Zr} , Ca''_{Zr} , and $\text{Zr}^{\times}$ are obtained with the aid of reaction pathway analysis. This analysis is
130 performed using an NEB method [44], which we have previously applied to the barrier measurement of defect nucleation in various solid systems [45, 46]. The input to the NEB method is an initial estimation of the energy pathway composed of a string of 13 images. The initial image corresponds to the energy-minimized structure in which the cation and cation vacancy
135 are introduced at the site of the i th layer and its nearest neighbor site at the j th layer, respectively. The final image is the relaxed structure after changing the positions of the corresponding cation and cation vacancy. The intermediate images are provided by connecting the two endpoints by linear interpolation. The convergence is determined when the potential force on
140 each replica vertical to the path becomes less than 1.0×10^{-5} eV/Å [45, 46]. The activation energies $E_{i \rightarrow j}$ for cation hopping from the i th layer to the j th layer have been computed for the top six layers denoted as i ($=1 \dots 6$) with three different directions denoted as $j=i-1$, i , and $i+1$ (two directions when $i=1$).

145 Similar to the segregation energy analysis, to investigate the effect of

oxygen vacancies on cation migration, the barriers are estimated under different local environments of oxygen vacancies $V_O^{\bullet\bullet}$ around the activated cation (Y'_{Zr} , Ca''_{Zr} , and $Zr^\times$). In this study, two systems, which we refer to as the defect-isolated and defect-complexes systems, are considered. In the defect-isolated system, all oxygen vacancies are placed far from the activated cation. In the defect-complexes system, the cation is activated under more complicated conditions. The charge-neutralized defects are combined such as $(2Y'_{Zr}, V_O^{\bullet\bullet})^\times (V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$, $(Ca''_{Zr}, V_O^{\bullet\bullet})^\times (V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$, and $Zr^\times (V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$. In the analysis of defect-complexes system, five samples are prepared, in which each has the randomly chosen $V_O^{\bullet\bullet}$ positions. Since the calculations for all the cases are computationally difficult, the mean values and standard deviation of $E_{i \rightarrow j}$ for five samples are estimated.

3. Results and discussion

3.1. Segregation Energy

Fig. 2 displays the energy of a cation defect at the surface relative to that in the bulk as a function of layer number from the surface. From Fig. 2(a) and (b), it is evident that the segregation energy values for the isolated Y'_{Zr} and Ca''_{Zr} are positive from the second layer to the bulk and that the maximum occurs at the second layer. This indicates energy-instability when an isolated defect is positioned away from the surface, which could be attributed to the reduction of binding energy involving $Y'_{Zr}-V_O^{\bullet\bullet}$ and $Ca''_{Zr}-V_O^{\bullet\bullet}$ by setting $V_O^{\bullet\bullet}$ far from Y'_{Zr} or Ca''_{Zr} . Moreover, since the effective charges of Y'_{Zr} are one more than that of Ca''_{Zr} , the interaction of $Ca''_{Zr}-V_O^{\bullet\bullet}$ is greater, leading to the higher positive value of Ca''_{Zr} . Note that values for both Y'_{Zr} (-0.08 eV) and

170 Ca_{Zr}'' (-0.31 eV) are negative at the first layer, respectively. These energy reductions could be attributed to the release of strain energy at the surface. Strain energy is accumulated in the bulk because the atomic radii of Y^{3+} (1.019 Å) and Ca^{2+} (1.120 Å) are larger than that of the host cation Zr^{4+} (0.840 Å). Indeed, the energy reduction of Ca_{Zr}'' is larger than that of Y_{Zr}' ,
 175 which is consistent with the fact that the atomic radius of Ca^{2+} is larger than that of Y^{3+} .

Segregation energy is obviously different for co-segregation with oxygen vacancies. The segregation energy values for $(2\text{Y}_{\text{Zr}}', \text{V}_{\text{O}}^{\bullet\bullet})^{\times}$ and $(\text{Ca}_{\text{Zr}}'', \text{V}_{\text{O}}^{\bullet\bullet})^{\times}$ become approximately zero from the fifth layer to the bulk. From the fourth
 180 layer to the surface, the values are negative with larger absolute values approaching the surface. The maximum occurs at the first layer $((2\text{Y}_{\text{Zr}}', \text{V}_{\text{O}}^{\bullet\bullet})^{\times} = -0.77$ eV, $(\text{Ca}_{\text{Zr}}'', \text{V}_{\text{O}}^{\bullet\bullet})^{\times} = -1.98$ eV). In the defect complexes case, the effect of binding energy becomes weaker because the oxygen vacancy is accompanied by a cation. The strain relaxation induced by vacancy and cation
 185 co-segregation is a significant component of segregation energy and leads to the negative values in the first to the fourth layers. Therefore, it can be concluded that higher concentration of oxygen vacancies at the surface than at the bulk is associated with the enrichment of both Y and Ca at the surface. These results are similar to the tendency for GB segregation for Y reported
 190 by Yoshiya *et al.* [35].

Comparison with the results of defect-isolated and defect-complexes structures shows that the values of segregation energy are significantly influenced by electrostatic interaction of oxygen vacancy. Hence, to clarify the effect of long-range electrostatic interaction, analysis on segregation energy has been

Figure 2: Segregation energy for cases in Table 2 and the situations for defect-isolated with electrostatic energy screened.

(a) Y'_{Zr} and $(2Y'_{Zr}, V_O^{\bullet\bullet})^\times$. (b) Ca''_{Zr} and $(Ca''_{Zr}, V_O^{\bullet\bullet})^\times$. (c) $V_{Zr}^{4'}$ and $(V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$.

195 performed by introducing a screened function (cut-off radius is 1 nm) [47].
 As Fig. 2, for the cases of defect-isolated structures, the segregation energy
 turns to be negative when electrostatic energy is screened. Therefore, it is
 clear that the long-range electrostatic interaction between $V_O^{\bullet\bullet}$ and dopant is
 the dominant factor of the positive segregation energy.

200 In addition, we calculated the segregation energy of $V_{Zr}^{4'}$ accompanied by
 $V_O^{\bullet\bullet}$ and far from $V_O^{\bullet\bullet}$. The results (Fig. 2(c)) show that the segregation
 of cation vacancy $V_{Zr}^{4'}$ is also enhanced by accompanying oxygen vacancies
 $V_O^{\bullet\bullet}$. Compared with the results for $(2Y'_{Zr}, V_O^{\bullet\bullet})^\times$ and $(Ca''_{Zr}, V_O^{\bullet\bullet})^\times$, the energy
 gain of $(V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$ at the first layer (-2.16 eV) is approximately the same
 205 as $(Ca''_{Zr}, V_O^{\bullet\bullet})^\times$ but much larger than that of $(2Y'_{Zr}, V_O^{\bullet\bullet})^\times$. Here, it is noted
 that the strong segregation tendency of cation vacancy, which has not been
 reported in previous theoretical works, is in good agreement with recent
 experimental findings using X-ray diffraction, i.e., the topmost YSZ (111)
 surface exhibits a high density of both cation and oxygen vacancies [22].

210 Our calculations imply that both Y and Ca are likely to remain at
 $ZrO_2(111)$ surface. These results are supported by previous qualitative ex-
 periments [20, 22, 33]. However, the analysis here is focused on the dilute-
 concentration case of defects without considering defects interaction. In the
 next subsection, defect interaction is considered and segregation concentra-
 215 tions are discussed.

3.2. Equilibrium Segregation Concentrations

Based on the framework previously reported by Yoshiya *et al.*, the lo-
 cal equilibrium concentrations of a dopant at the surface (C_s^{eq}) have been
 considered as well as the interactions between defects [35, 48]. As local con-

220 concentrations of a dopant at the surface (C_s) increases, the energy change by adding a dopant would increase due to the defect interaction. Such energy change can be reflected via the chemical potential of $\mu_s(C_s)$ and $\mu_b(C_b)$, where $\mu_s(C_s)$ and $\mu_b(C_b)$ are the chemical potentials when the dopant concentration at the surface and in the bulk are C_s and C_b , respectively. At equilibrium
 225 ($C_s=C_s^{\text{eq}}$), the chemical potential at the surface should approximately equal that of bulk.

$$\mu_s(C_s^{\text{eq}}) = \mu_b(C_b) \quad (6)$$

Here, $\mu_s(C_s)$ or $\mu_b(C_b)$ under 0 K conditions can be defined as

$$\mu(n) = dE_{\text{total}}(n)/dn \quad (7)$$

where n is the number of dopant cations at the surface (or bulk) and is simply related to $C=n/n_{\text{tot}}$ using the total number of cations n_{tot} at the surface (or bulk), $E_{\text{total}}(n)$ is the whole potential energy of the relaxed configuration containing n dopant cations at the surface (or bulk). Numerically,
 230 Eq. (7) can be approximated as

$$\mu(n) = [E_{\text{total}}(n + \delta) - E_{\text{total}}(n - \delta)]/2\delta \quad (8)$$

where δ is the increment of the dopant added to the system.

In this study, the insertion of defect complexes $(2Y'_{\text{Zr}}, V_{\text{O}}^{\bullet\bullet})^\times$ or $(Ca''_{\text{Zr}}, V_{\text{O}}^{\bullet\bullet})^\times$ are considered and $\delta=4$ is used. For the computation of $\mu_s(n)$, $n/2$ number
 235 of $(2Y'_{\text{Zr}}, V_{\text{O}}^{\bullet\bullet})^\times$ or n number of $(Ca''_{\text{Zr}}, V_{\text{O}}^{\bullet\bullet})^\times$ are introduced into the surface model. The dopants are randomly exchanged with Zr at the outermost layer, and the oxygen vacancies associated with each dopants are also randomly set

at the first or second nearest positions of the dopants. Using a similar procedure, computation of $\mu_b(n)$ is also performed for a bulk ZrO_2 model ($2.5 \times 2.5 \times 6.8$ nm) containing the corresponding number of defect complexes. To reduce the statistical error [48], the relaxed energy of $E_{\text{total}}(n)$ has been estimated by averaging over 100 samples with different positions of defect complexes of $(2\text{Y}'_{\text{Zr}}, \text{V}_{\text{O}}^{\bullet\bullet})^\times$ or $(\text{Ca}''_{\text{Zr}}, \text{V}_{\text{O}}^{\bullet\bullet})^\times$, for the surface and bulk models, respectively.

The results are shown in Fig. 3. As shown in Fig. 3(a), the chemical potential of Y at bulk is initially determined to be $\mu_b(C_b) = 40.48$ eV when $C_b = 18.2$ atom%, which corresponds to the most common 10 mol% YSZ system (10YSZ, Y/Zr = 0.22). The results also show that the chemical potential at surface μ_s increases almost linearly as the dopant concentration C_s increases. These results show that local equilibrium conditions $\mu_s(C_s^{\text{eq}}) = \mu_b(C_b)$ are achieved when the dopant concentrations at the outermost layer reaches $C_s^{\text{eq}} = 46$ atom% (29.9 mol% YSZ, Y/Zr = 0.85), which gives an enrichment factor $\alpha = 3.86$. The obtained concentration is approximately twice as high as that estimated for Y segregation at ZrO_2 GBs using the same approach (~ 25 atom%) [35], indicating that dopant segregation at (111) surface is more pronounced than at GBs. Furthermore, according to recent experimental observations of a YSZ (111) surface using high-resolution X-ray photoemission spectroscopy [33], the outermost surface has approximately 45 atom% Y enrichment, which is in good agreement with our estimation and strongly supports the validity of our calculations.

As shown in Fig. 3(b), the behavior of chemical potentials at the surface of Ca is similar to that of Y. For comparison, assuming $C_b = 10.0$ atom% (10

Figure 3: Chemical potentials as a function of local dopant concentration at the outermost layer for (a) Y and (b) Ca. For comparison, the bulk values for both cations are also shown.

mol% CSZ, Ca/Zr = 0.11), which has an identical molar fraction to 10YSZ, the local equilibrium concentration at the outermost layer for Ca is estimated
 265 to be approximately $C_s^{\text{eq}} = 27 \text{ atm}\%$ (Ca/Zr = 0.37, $\alpha=3.36$). In addition, if we consider the bulk of $C_b = 18.2 \text{ atom}\%$ (18.2 mol% CSZ, Ca/Zr = 0.22), which has the same atom fraction as 10YSZ, $C_s^{\text{eq}} = 31 \text{ atm}\%$ (Ca/Zr = 0.45, $\alpha=2.05$) is obtained. Thus, we find that, for both typical cases, the local equilibrium concentration at the outermost layer C_s^{eq} and the enrichment
 270 factor α for Ca are smaller than those of Y.

It should be noted that the surface segregation at the outermost layer of $(\text{Ca}_{\text{Zr}}'', \text{V}_{\text{O}}^{\bullet\bullet})^\times$ in a dilute-concentration system is remarkably stable compared to $(2\text{Y}_{\text{Zr}}', \text{V}_{\text{O}}^{\bullet\bullet})^\times$, as shown in Fig. 2. Fig. 3(a) and (b) also illustrate that the difference in chemical potential energy between the surface and bulk ($\Delta\mu =$
 275 $\mu_s - \mu_b$) for Ca, which represents a driving force of segregation, is larger than that of Y at a lower concentration of approximately 10 atom%. However, the gradient of chemical potential with respect to the surface concentration ($\partial\mu_s/\partial C_s$) for Ca is steeper than that of Y by a factor of approximately three, which results in the quick reduction of driving force $\Delta\mu$ with increasing C_s
 280 and finally satisfies $\Delta\mu = 0$ condition at lower concentrations than Y. This gradient difference could be attributed to the following factor. The number of oxygen vacancies accommodated at the Ca-segregated surface is two times as large as that at the Y-segregated surface when the number of Ca_{Zr}'' and Y_{Zr}' is identical. The higher oxygen vacancy density will naturally lead to higher
 285 defect-defect interactions. The gradient difference could also be attributed to the ionic size mismatch between these cations and the host cation. The larger radius of Ca_{Zr}'' than Y_{Zr}' may make it relatively easier for high strain energy to

accumulate near the surface as defect defect concentration increases, which contributes to the suppression of dopant accumulation.

290 The current analysis clearly demonstrates that consideration of defect-defect interactions is essential for understanding surface segregation energetics. Although we assumed that surface enrichment was limited to the outermost layer, it has been reported that Y enrichment involves the second layer or even inner layers, thus reducing Y concentrations. Further analysis of the chemical potential associated inner layers could provide a more
295 quantitative connection between experimental observations and theoretical investigations.

3.3. Migration Barrier Analysis

Migration energy results for Y'_{Zr} , Ca''_{Zr} and $Zr^\times$ between the i and j th
300 layers from the surface in defect-isolated systems are listed in Tables 3–5, respectively. The migration energy in defect-complexes systems is summarized in Tables 6–8.

To investigate the boundary layer between the surface and bulk where the change of kinetic behavior is observable, we calculate the averaged values of
305 $E_{i \rightarrow i+1}$, $E_{i \rightarrow i}$ and $E_{i \rightarrow i-1}$, as follows.

$$E_{i,ave} = \frac{E_{i \rightarrow i+1} + E_{i \rightarrow i} + E_{i \rightarrow i-1}}{3} \quad (9)$$

In Fig. 4, we provide the corresponding data for $E_{i,ave}$ as a function of the layer number from the surface for both defect-isolated and defect-complexes systems. Fig. 4(a) shows that the average energy barriers remain almost constant from the third layer to the bulk ($Zr^\times(\sim 4.8 \text{ eV}) > Y'_{Zr}(\sim 4.3$

Table 3: Energy barriers when isolated Y'_{Zr} at the i th layer migrates to an isolated $V^{4'}_{Zr}$ site at the j th layer [eV].

i th layer	j th layer						$E_{i,ave}$
	1	2	3	4	5	6	
1	2.12	3.03	-	-	-	-	2.58
2	2.93	3.01	3.84	-	-	-	3.26
3	-	4.05	3.91	4.48	-	-	4.15
4	-	-	4.16	4.42	4.49	-	4.36
5	-	-	-	4.08	4.46	4.46	4.33
6	-	-	-	-	4.15	4.31	4.23

Table 4: Energy barriers when isolated Ca''_{Zr} at the i th layer migrates to an isolated $V^{4'}_{Zr}$ site at the j th layer [eV].

i th layer	j th layer						$E_{i,ave}$
	1	2	3	4	5	6	
1	0.72	2.03	-	-	-	-	1.38
2	1.72	2.16	2.33	-	-	-	2.07
3	-	2.37	2.42	2.68	-	-	2.49
4	-	-	2.49	2.50	2.62	-	2.54
5	-	-	-	2.47	2.45	2.53	2.48
6	-	-	-	-	2.29	2.50	2.40

Table 5: Energy barriers when $Zr^{\times}$ at the i th layer migrates to an isolated $V^{4'}_{Zr}$ site at the j th layer [eV].

i th layer	j th layer						$E_{i,ave}$
	1	2	3	4	5	6	
1	2.70	2.50	-	-	-	-	2.60
2	2.71	4.30	4.28	-	-	-	3.76
3	-	4.26	4.27	5.10	-	-	4.54
4	-	-	4.77	4.97	5.02	-	4.92
5	-	-	-	4.49	5.05	5.00	4.85
6	-	-	-	-	4.71	4.70	4.71

Table 6: Energy barriers when Y'_{Zr} at the i th layer migrates to a $V_{Zr}^{4'}$ site at the j th layer [eV]. Energy barriers are measured for a defect-complexes system consisting of $(2Y'_{Zr}, V_O^{\bullet\bullet})^\times$ and $(V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$. The average value and standard deviation (parentheses) for five samples are shown.

i th layer	j th layer						$E_{i,ave}$
	1	2	3	4	5	6	
1	2.58 (0.51)	2.69 (0.57)	-	-	-	-	2.64
2	3.25 (0.47)	3.52 (0.43)	3.46 (0.49)	-	-	-	3.41
3	-	4.06 (0.26)	3.74 (0.63)	3.89 (0.36)	-	-	3.90
4	-	-	3.80 (0.35)	3.82 (0.55)	3.99 (0.41)	-	3.87
5	-	-	-	3.94 (0.59)	3.67 (0.29)	3.94 (0.33)	3.85
6	-	-	-	-	3.85 (0.40)	3.77 (0.54)	3.81

Table 7: Energy barriers when Ca''_{Zr} at the i th layer migrates to a $V_{Zr}^{4'}$ site at the j th layer [eV]. Energy barriers are measured for a defect-complexes system consisting of $(Ca''_{Zr}, V_O^{\bullet\bullet})^\times$ and $(V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$. The average value and standard deviation (parentheses) for five samples are shown.

i th layer	j th layer						$E_{i,ave}$
	1	2	3	4	5	6	
1	1.53 (0.53)	1.80 (0.52)	-	-	-	-	1.67
2	1.83 (0.36)	1.99 (0.26)	1.88 (0.24)	-	-	-	1.90
3	-	2.20 (0.33)	2.27 (0.25)	2.31 (0.28)	-	-	2.26
4	-	-	2.28 (0.21)	2.56 (0.28)	2.22 (0.29)	-	2.35
5	-	-	-	2.30 (0.10)	2.46 (0.08)	2.27 (0.10)	2.34
6	-	-	-	-	2.33 (0.27)	2.32 (0.11)	2.33

Table 8: Energy barriers when $Zr^\times$ at the i th layer migrates to a $V_{Zr}^{4'}$ site at the j th layer [eV]. Energy barriers are measured for a defect-complexes system consisting of $(V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$. The average value and standard deviation (parentheses) for five samples are shown.

i th layer	j th layer						$E_{i,ave}$
	1	2	3	4	5	6	
1	2.45 (0.39)	3.14 (0.54)	-	-	-	-	2.80
2	3.24 (0.43)	3.48 (0.34)	3.77 (0.37)	-	-	-	3.50
3	-	5.04 (0.42)	4.15 (0.33)	4.42 (0.42)	-	-	4.54
4	-	-	4.19 (0.23)	4.61 (0.57)	4.99 (0.30)	-	4.60
5	-	-	-	4.44 (0.40)	4.57 (0.44)	4.75 (0.57)	4.59
6	-	-	-	-	4.88 (0.35)	4.59 (0.36)	4.74

Figure 4: Averaged migration barrier $E_{i,ave}$ for each cations (Y'_{Zr} , Ca''_{Zr} , and $Zr^{\times}$) as a function of the layer number from the top surface estimated for (a) defect-isolated and (b) defect-complexes systems.

310 eV) $>$ Ca''_{Zr} (~ 2.5 eV)). The obtained activation energy for bulk is sufficiently comparable to the experimental value for Zr diffusion in 10 mol% YSZ (4.6 eV [49]) estimated using secondary ion mass spectroscopy. Clearly, the barriers involving the first and second layers are much lower than those of the bulk. The values at the first layer are found to be approximately 60% that of

315 bulk for the three species. Similar values are found for $Zr^{\times}$ and Y'_{Zr} (2.6

eV) and an even lower values is found for Ca_{Zr}'' (1.4 eV). The results for the defect-complexes case (Fig.4(b)) display a coincident tendency with the defect-isolated case. The barriers below the third layer for $\text{Zr}^\times$, Y_{Zr}' , and Ca_{Zr}'' are approximately 4.6, 3.9, and 2.3 eV, which are slightly lower than the defect-isolated case. Slightly higher barriers for the first layer are obtained, i.e., 2.8, 2.6, and 1.7 eV, respectively. Thus, for both the surface and bulk, independent of the defect type, the migration barrier of Ca is significantly lower (approximately 50%) than that of Zr.

To further consider the effects of oxygen vacancy on migration kinetics, we evaluate the energy barrier difference, E_{diff} , as a function of layer position (denoted by the midpoint), where a defect jumps between the i th and $(i+1)$ th layer.

$$E_{\text{diff}}\left(\frac{2i+1}{2}\right) = E_{i \rightarrow i+1} - E_{i+1 \rightarrow i} \quad (10)$$

Barrier difference E_{diff} corresponds to the total energy difference associated with the configuration before and after cation hopping, shown schematically in Fig. 5. Thus, the positive value of E_{diff} (Fig. 5(a)) indicates that the probability of a cation jump from bulk to surface $P_{i+1 \rightarrow i}$ is higher than that for the opposite direction ($P_{i \rightarrow i+1}$).

In Fig. 6, we show the results of E_{diff} with respect to the layer number from the surface for both Y_{Zr}' and Ca_{Zr}'' movements, focusing on the comparison between the defect-isolated and defect-complexes systems. It is found that E_{diff} of Y_{Zr}' for both systems are nearly constant and positive at the bulk region (below the third layer), displaying higher values for the defect-isolated system than for the defect-complexes system. However, the obvious

Figure 5: Schematic illustrations of the energy profile associated with the cation jump between the i th and the $(i+1)$ th layer, where $E_{i \rightarrow i+1}$ is the energy hopping barrier from the i th layer to the $(i+1)$ th layer, $E_{i+1 \rightarrow i}$ is the energy hopping barrier for the opposite direction, and E_{diff} corresponds to the energy difference between two metastable states; (a) $E_{\text{diff}} > 0$, (b) $E_{\text{diff}} < 0$.

drop of E_{diff} values can be detected between the second and third layers
 340 where the averaged migration energy $E_{i,\text{ave}}$ exhibits transition (Fig. 4). In
 particular, the E_{diff} for Y'_{Zr} in the defect-complexes system decreases to a
 larger negative value (-0.6 eV) between the second and third layers than
 in the defect-isolated system and maintains similar at the surface layer. For
 instance, at a typical firing temperature for the fabrication of dense YSZ
 345 (~ 1400 °C), a E_{diff} of -0.6 eV can yield a forward transition rate ratio of
 approximately 0.015, i.e., $P_{i+1 \rightarrow i}/P_{i \rightarrow i+1} \sim 0.015$. Thus, forward jumping is
 unlikely when the jump species is subjected to a local environment with a
 high density of $\text{V}_{\text{O}}^{\bullet\bullet}$. Compared to other defect complexes, this energy differ-
 ence would be caused by the stronger energy gain when the defect complexes

350 of $(V_{Zr}^{4'}, 2V_O^{\bullet\bullet})^\times$ are positioned at the first and second layers, as shown in
 Fig. 2. Therefore, at a quasi-equilibrium state when the detailed balance
 is satisfied, the concentration of cation vacancies $V_{Zr}^{4'}$ at layer (i) should be
 sufficiently higher than that at layer $(i+1)$ to compensate for the difference
 in jump probability $P_{i+1 \rightarrow i}/P_{i \rightarrow i+1}$. A recent experimental report in which
 355 the Y-enriched YSZ (111) surface is accompanied by a high cation and oxy-
 gen vacancy density [22] supports our findings. Comparing Ca with Y, the
 overall behavior of Ca for E_{diff} (Fig. 6(b)) is similar to that of Y; however,
 the values of E_{diff} at the first and second layers are smaller than that of Y
 because the segregation at the surface layer of $(Ca_{Zr}^{''}, V_O^{\bullet\bullet})^\times$ is energetically
 360 more stable than $(2Y_{Zr}', V_O^{\bullet\bullet})^\times$, as shown in Fig. 2.

De Ridder *et al.* experimentally found that Ca segregation was more
 pronounced than Y segregation when the raw powder intrinsically included
 both elements as dopant and impurity. After calcination, the YSZ surface
 exhibited Ca enrichment at the outermost layer while Y was abundant at
 365 the second layer [7, 8]. Recent scanning transmission electron microscope
 observations also showed the formation of Ca-rich layers on a YSZ electrolyte
 surface [50]. Although our energetic analysis suggest that both Y_{Zr}' and $Ca_{Zr}^{''}$
 cations have a potential to cover the outermost layer at a higher ratio, the
 kinetic analysis indicates that the mobility of Ca is much higher than that
 370 of Y. Hence, the diffusion flux density of Ca from bulk to the surface is
 more notable than that of Y when the raw material is calcinated at high
 temperatures, which could lead to the complexes depth profile of the chemical
 composition near YSZ surfaces, as shown in the previous experiments.

3.4. Surface Diffusion Analysis

375

This section describes how the enrichment of a dopant or impurity at the surface affects the in-plane surface diffusivity for both cation and oxygen. Since cation self-diffusion, which involves a relatively high energy barrier, is uncommon in an MD framework with a limited time scale, we employed

Figure 6: Energy barrier difference E_{diff} between $E_{i \rightarrow i+1}$ and $E_{i+1 \rightarrow i}$ with respect to the layer number from top surface for (a) Y'_{Zr} and (b) Ca''_{Zr} cations, where $E_{i \rightarrow i+1}$ corresponds to the activation hopping barrier from the i th layer to the j th layer. Results for defect-isolated and defect-complexes systems for both cations are shown.

a standard KMC technique, which is a useful tool for exploring long-time
 380 dynamics consisting of diffusive jump events at an atomic level [51]. This
 method requires input of the event catalogs and the corresponding rate of
 each event. These data were supplied by utilizing the NEB results. For
 oxygen self-diffusion with relatively low jump barriers, previous studies have
 reported successful use of common MD techniques to analyze it in various
 385 oxide systems [29, 52, 53]. Thus, this work also utilized an MD to measure
 oxygen self-diffusivity at a segregated surface.

3.4.1. Cation diffusion at the surface

The KMC simulations are performed with a rigid lattice model in which
 only cation sites are considered. The basic configuration of the cation sites
 390 are the same as those used in the $\text{ZrO}_2(111)$ surface model (Fig. 1); however,
 the surface area is scaled-up to 10.9×10.0 nm in both x and y directions.
 In this model, both the first and second layers are treated as surface layers
 based on a previous experiment [33] and our results. Initially, for a given
 local concentration of dopant (or impurity) at surface C_s , the corresponding
 395 number of Y'_{Zr} or Ca''_{Zr} are replaced randomly to a zirconium site within the
 surface layers. In addition, cation vacancies $\text{V}^{4\prime}_{\text{Zr}}$ (10^{-3} concentration) are ran-
 domly introduced into surface layers by removing the corresponding number
 of zirconium sites. The concentration of $\text{V}^{4\prime}_{\text{Zr}}$ is assumed to be constant and
 independent of temperature T .

400 In this KMC model, the event catalog is constructed based on all possi-
 ble cation movements between layers i and j via cation vacancies. Within
 approximations from harmonic transition theory, each hopping rate can be
 simply described as $P_{i \rightarrow j} = P_0 \exp(-E_{i \rightarrow j}/k_{\text{B}}T)$, where P_0 is a typical attempt

frequency of 10^{13} (1/s) and k_B is Boltzmann constant. Here, the NEB re-
405 sults deduce from the defect-complexes systems (listed in Tables 6–8 for Y,
Ca, and Zr cations, respectively) are used as $E_{i \rightarrow j}$ input, as long as the $E_{i \rightarrow j}$
values are independent of the local concentration of dopant. The system con-
figurations are evolved using a basic KMC algorithm [51] during 10^7 steps
under the given C_s (10~90 atom%) and T (600~1000 °C) conditions. For
410 each run, the self-diffusion coefficients of cations at surface D_s^{cat} are extracted
from the relationship between the mean square displacement (MSD) and the
time t ($\text{MSD}=4D_s^{\text{cat}}t$). Then, the Arrhenius slope is plotted to estimate the
apparent activation energy of in-plane cation diffusion at surface $E_{\text{act}}^{\text{cat}}$.

The obtained $E_{\text{act}}^{\text{cat}}$ are shown in Fig. 7(a) as a function of C_s . In addi-
415 tion, the self-diffusion coefficients of Y and Ca at $T=1000$ °C, normalized
by the coefficients of Zr ($D_s^{\text{Y}}/D_s^{\text{Zr}}$ and $D_s^{\text{Ca}}/D_s^{\text{Zr}}$) are shown in Fig. 7(b) for
the same segregation level range. It is found that the activation energy of
cations at the Y-segregated surface do not exhibit clear dependence on chem-
ical composition of Y at the surface because the migration barriers ($E_{1 \rightarrow 1}$)
420 for Y and Zr are similar values, i.e., 2.58 and 2.45 eV, respectively. More-
over, these values are well matched with the estimated activation energy $E_{\text{act}}^{\text{cat}}$
(approximately 2.5 eV), which indicates that the in-plane surface diffusion is
primarily governed at the outermost layer. Similarly, $D_s^{\text{Y}}/D_s^{\text{Zr}}$ is nearly con-
stant (~ 0.3), independent of the dopant segregation level. Conversely, the
425 strong dependence of the activation energy of cation $E_{\text{act}}^{\text{cat}}$ on the segregation
level appears in the case of the Ca-segregated surface. The activation energy
 $E_{\text{act}}^{\text{cat}}$ decreases nonlinearly with increasing C_s ; $E_{\text{act}}^{\text{cat}}$ shows the maximum drop
at approximately $C_s=30\%$, hereafter followed by a slow decrease. At high

C_s near full coverage, the $E_{\text{act}}^{\text{cat}}$ approaches 1.5 eV, which is identical to the
 430 migration energy of $E_{1 \rightarrow 1}$ for Ca (1.53 eV). Fig. 7(b) clearly shows that the
 Ca diffusivity can be significantly enhanced as the impurity level increases.
 Assuming the case of an extremely enriched Ca surface ($C_s \sim 90\%$), it is pos-
 sible to attain $D_s^{\text{Ca}}/D_s^{\text{Zr}}$ of approximately 10^3 . Thereby, the in-plane mass
 transport ability of a Ca-segregated surface, showing strong dependence on
 435 the chemical composition, is significantly higher than that of a Y-segregated
 surface.

Several experimental studies have revealed that the activation energy as-
 sociated with the creep deformation of YSZ or Ni-YSZ at a temperature
 approximating that of SOFC operation (< 1100 °C) was found to be in the
 440 range of 1.0 to 2.0 eV [5, 54, 55]. Laurencin *et al.* suggested that these
 barriers characterized the surface diffusion of a cation, which was also con-
 sistent with our KMC simulations. Furthermore, our results suggest that
 wide range of experimentally measured values may arise from the surface
 segregation level of impurities. In other words, controlling and reducing the
 445 amount of surface segregation will make it possible to improve the durability
 of YSZ electrolytes.

3.4.2. Oxygen diffusion at surface

Here, the MD models are the same as the model shown in Fig. 1. The
 first and second layers are enriched by Y or Ca for given concentrations
 450 of C_s and the layers below third layer are assumed to be a 10 mol% YSZ
 system. The corresponding number of oxygen vacancies was introduced into
 the systems, followed by initial equilibration at 1000 °C for 10 ps. Then, the
 MSD of the surface layers is calculated during a 500 ps run under the given C_s

Figure 7: KMC simulation results for in-plane surface diffusion of cations; (a) apparent activation energy for cation diffusion as a function of Y or Ca concentrations at surface (b) surface diffusion coefficients for Y or Ca measured at 1000 °C as a function of Y or Ca concentration at the surface. The values are normalized by Zr value.

(18.2~75.0 atom%) and T (1000~2227 °C) conditions. For each condition,
 455 three samples starting from different initial velocities are examined to reduce
 the statistical error. Finally, the self-diffusion coefficients of oxygen D_s^{oxy}
 (averaged over three samples) and the related activation energy $E_{\text{act}}^{\text{oxy}}$ are
 obtained in a manner similar to that of the KMC simulations.

The results for activation energy $E_{\text{act}}^{\text{oxy}}$ as a function of the concentra-
 460 tion C_s are shown in Fig. 8(a). The relationship between the self-diffusion
 coefficients D_s^{oxy} at $T=1000$ °C (normalized by that for 10 mol%YSZ, i.e.,
 $D_{s,18.2}^{\text{oxy}}$: 18.2 atom% Y at the surface) and the concentration C_s are shown
 in Fig. 8(b). Our simulations indicate that the activation energy $E_{\text{act}}^{\text{oxy}}$ in-
 creases linearly from 0.57 to 1.01 eV as the concentration of Y increases
 465 from 20 to 75 atom%. As shown in Fig. 8(a), this linear dependence is
 consistent with the MD simulation results for oxygen diffusion in bulk YSZ
 (10~25YSZ) reported by Devanathan *et al.* [53]. However, the main differ-
 ence between the surface and bulk is that the activation barrier at the surface
 is lower than that of bulk for equal concentration. In addition, sensitivity to
 470 concentration is reduced. Oxygen diffusion coefficients at the Y-segregated
 surface decreases monotonically as the concentration increases, as shown in
 Fig. 8(b). It is also found that the dependence of diffusion coefficients at
 the surface on the concentration is less sensitive than that of bulk D_b^{oxy} . As
 estimated in this study, the local equilibrium concentration of Y at the sur-
 475 face is approximately $C_s^{\text{eq}}=46\%$ when the concentration of bulk is assumed
 to be $C_b=18.2\%$ (10YSZ). Under this equilibrium condition, our MD results
 predict that the oxygen diffusion coefficients at 46 atom% Y-segregated sur-
 face ($D_{s,46}^{\text{oxy}}$) is approximately equal to that at 18.2 atom% YSZ bulk ($D_{b,18.2}^{\text{oxy}}$).

In addition, as shown in Fig. 8, the trend of oxygen diffusion properties for
 480 the Ca-segregated surface with respect to the concentration is basically similar
 to that of the Y-segregated surface. However, even though the oxygen
 concentration of the Ca-segregated surface is greater than the Y-segregated
 surface by a factor of two, the corresponding activation energy (or diffusion
 coefficients) for the Ca-segregated surface is higher (or lower) than that of
 485 the Y-segregated surface, which would be mainly attributed to the higher
 binding energy of $\text{Ca}_{\text{Zr}}''\text{-V}_{\text{O}}^{\bullet\bullet}$ compared with $\text{Y}_{\text{Zr}}'\text{-V}_{\text{O}}^{\bullet\bullet}$.

According to our study, the in-plane cation diffusivity accelerates with
 increasing Ca-concentration at the surface and the in-plane oxygen diffusivity
 decelerates simultaneously. This effect is more striking than the Y-enriched
 490 surface. To improve YSZ electrolyte performance in SOFC systems, it is
 desirable to suppress durability behavior and promote the electrochemical
 reaction. This would require lowering the mass transfer ability and enhancing
 the oxygen transfer ability at the YSZ surface. Our analysis suggests that
 controlling the chemical composition at the surface, particularly reducing
 495 impurities such as Ca, is effective for the improvement of electrochemical
 properties in a YSZ electrolyte.

4. Conclusions

We have performed an energy minimization and reaction pathway analysis
 at an atomistic scale to investigate the segregation behavior of a dopant
 500 or impurity near the surface of YSZ (111). The segregation energy results
 indicate that both Y and Ca as well as cation vacancies become more stable
 near the surface, especially when co-segregated with oxygen vacancies. At a

Figure 8: MD simulations results for in-plane surface diffusion of oxygen. (a) Apparent activation energy for oxygen diffusion as a function of Y or Ca concentrations at the surface. Dotted line indicates barrier data for YSZ bulk obtained using the MD reported in Ref. [53]. (b) Surface diffusion coefficients for oxygen measured at 1000 °C as a function of Y or Ca. Values are normalized by that estimated for 10 mol% YSZ (18.2 Y atom%).

dilute limit condition, Ca is more energetically stable than Y at the surface; however, increased Ca concentrations at the surface is accompanied by a more
505 rapid increase in chemical potential than Y, which results in the enrichment of Y rather than Ca at 0 K equilibrium condition. We have provided an activation energy for cation migration between neighboring layers near the surface and show that the Ca barrier is approximately half that of Y for both bulk and surface regions. The kinetic analysis also reveals that the
510 migration energies near the surface are more complex compared to bulk, because the stability of cation and oxygen vacancies near the surface becomes pronounced.

In addition, we have examined the influence of the enrichment of a dopant or impurity with the in-plane surface diffusivity for both cations and oxy-
515 gen using KMC and MD simulations, respectively. The results indicate that increasing the surface concentration of Ca leads to suppression of the oxygen transport ability, which could enhance the mass transport ability. This trend is found to be insignificant in the case of a Y enriched surface. Our analysis demonstrates that controlling dopant or impurity enrichment at the
520 surface can improve both durability and electrochemical properties of an YSZ electrolyte in SOFC systems.

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