Effects of temperature and dopant concentration on oxygen vacancy diffusion coefficient of yttria-stabilized zirconia

Le Thu Lam\textsuperscript{1} and Vu Van Hung\textsuperscript{2}
\textsuperscript{1}Tay Bac University, Quyet Tam, Son La, Vietnam
\textsuperscript{2}University of Education, VNU Hanoi, 182 Luong The Vinh Street, Hanoi, Vietnam
E-mail: lethulamtb@gmail.com

Abstract. Oxygen vacancy diffusion coefficient in yttria-stabilized zirconia (YSZ) is investigated by statistical moment method. Vacancy-dopant association energy, vacancy migration energy are calculated as a function of temperature and dopant concentration. Oxygen vacancy diffusion coefficient increases with the increasing temperature but decreases with the dopant concentration. This degradation of the diffusion coefficient arises from the limitation for oxygen vacancy migration across cation barriers with the increasing dopant concentration. Calculated results are in good agreement with other theoretical and experimental results.

1. Introduction

Yttria-stabilized zirconia (ZrO\textsubscript{2}) (YSZ) is one of the most popular materials in solid oxide fuel cells and oxygen sensor [1-5] due to high ionic conductivity. Hence, study of the vacancy diffusion properties in YSZ plays an important role in technological applications.

Many authors have investigated the mechanism of oxygen vacancy diffusion in YSZ system. Using first-principles theory (DFT), Eichler \textit{et al.} [6] found that the diffusion barrier in the doped material is determined by two contributions: a site-to-site diffusion barrier around 200 meV for diffusion within the \(\langle 110\rangle\) plane and the interaction energy between the dopants and the vacancies. The latter part depends strongly on the arrangement and amount of Y\textsuperscript{3+} ions in the zirconia matrix. This explains the observed dependency of the ion conductivity on Y\textsuperscript{3+} doping and temperature. A. Kushima \textit{et al.} [7] showed that the increase of the migration space and the weakening of the local oxygen–cation bonds correspond to a decrease of the migration barrier, and vice versa. In another study, F. Pietrucci \textit{et al.} [8] stated that in the case of single vacancy jump, they have observed a strong dependence of the activation barrier on the position of the other vacancies. Using Born–Mayer–Huggins interaction potential, T. Arima \textit{et al.} [9] showed that the self-diffusion coefficient of O\textsuperscript{2−} ion was much larger than those of Zr\textsuperscript{4+} and Y\textsuperscript{3+} ions, and decreased with increasing yttria content. From experimental values, M. Weller \textit{et al.} [10] observed a discontinuity in Arrhenius plots of the oxygen diffusion, which they explained as an indication for long-range ordering effects.

In this paper, we study the mechanism of oxygen vacancy diffusion in YSZ by statistical moment method (SMM). The expressions for vacancy-dopant association energy, vacancy migration energy are presented in detail. The dependences of the vacancy-dopant association energy...
energy, vacancy migration energy, vacancy activation energy on the temperature and dopant concentration will be calculated and discussed.

2. Theory approach

2.1. Free energy

From the expression determining free energy of ZrO$_2$ [10], the free energy of YSZ can be written as

$$\Psi = C_Zr,\Psi_{Zr} + C_Y\Psi_Y + C_O\Psi_O - TS_c,$$

where $S_c$ is the configurational entropy, and $C_{Ce}$, $C_Y$, $C_O$ denote concentrations of Ce$^{4+}$, Y$^{3+}$ and O$^{2-}$ ions, respectively, in YSZ system. The parameters $\Psi_{Zr}$, $\Psi_Y$, $\Psi_O$ are the total Helmholtz free energies of Zr$^{4+}$, Y$^{3+}$ and O$^{2-}$ ions, respectively, and have forms the following [11]

$$\Psi_{Zr,Y} = U_{Zr,Y}^0 + \Psi_{Zr,Y}^0 + 3N_{Zr,Y}\left\{\frac{\theta^2}{k_{Zr,Y}^e}\left[\frac{Zr,Y}{2}\coth^2 x_{Zr,Y} - \frac{\gamma_1}{3}\right]\right\},$$

$$\Psi_O = U_O^0 + \Psi_O^0 + 3N_O\left\{\frac{\theta^2}{k_O^e}\left[\frac{\gamma_2}{2}\coth^2 x_O - \frac{\gamma_1}{3}\right]\right\}$$

$$+ \frac{2\theta^2}{k_O^e}\left[\frac{4}{3}(\gamma_1^2 a_1^0) x_O \coth x_O - \frac{2\gamma_1^2 a_1^0}{3} x_O (2a_1^0 - 1)\right]$$

$$+ \frac{\beta_O}{6K}\left[x_O \coth x_O - 1\right] + \frac{\theta^2}{K}\left[\frac{2\gamma_1^2 a_1^0}{3K^2}\right]^{1/2} - \frac{\beta_O a_1^0}{9K^2}$$

$$+ \frac{\beta_O k_O a_1^0}{9K^3} + \frac{\beta_O}{6Kk_O}(x_O \coth x_O - 1)\right\},$$

where $\Psi_{Zr,Y}^0$, $\Psi_O^0$ denote the harmonic contributions to the total free energies of Zr$^{4+}$, Y$^{3+}$ and O$^{2-}$ ions, respectively, with the general formula as $\Psi_0 = 3N\theta[x + \ln(1 - e^{-2x})]$. The parameters $k, x, a_1, \beta, K, \gamma_1, \gamma_2$ and $\gamma$ in Eqs. (2) and (3) are given by

$$k_{Zr,Y,O} = \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{Zr,Y,O}^i}{\partial u_\beta^2}\right)_{eq}$$

$$x_{Zr,Y,O} = \hbar \sqrt{\frac{k_{Zr,Y,O}}{m}}, \quad a_{1,Zr,Y,O} = 1 + \frac{1}{2} x_{Zr,Y,O} \coth x_{Zr,Y,O},$$

$$\beta_O = \frac{1}{2} \sum_i \left(\frac{\partial^3 \varphi_{O}^i}{\partial u_\alpha \partial u_\beta \partial u_\gamma}\right)_{eq}, \quad K = k_O - \frac{\beta_O}{3\gamma},$$

$$\gamma_1_{Zr,Y,O} = \frac{1}{48} \sum_i \left(\frac{\partial^4 \varphi_{Zr,Y,O}^i}{\partial u_\beta^4}\right)_{eq}, \quad \gamma_2_{Zr,Y,O} = \frac{6}{48} \sum_i \left(\frac{\partial^4 \varphi_{Zr,Y,O}^i}{\partial u_\beta^2 \partial u_\gamma^2}\right)_{eq}.$$
\[
\gamma_{Zr,Y,O} = 4(\gamma_{1}^{Zr,Y,O} + \gamma_{2}^{Zr,Y,O}),
\]

where \(\alpha \neq \beta \neq \gamma = x, y, \) or \(z\), and \(\varphi_{i0}^{Zr,Y,O}\) is the interaction potential between the zero-th \(Zr^{4+}\) (or \(Y^{3+}\), or \(O^{2-}\)) ion and the \(i\)-th ion, and \(U_{0}^{Zr,Y}, U_{0}^{Y,O}\) represent the sum of effective pair interaction energies for \(Zr^{4+}, Y^{3+}, O^{2-}\) ions, respectively, at the equilibrium position.

2.2. The vacancy diffusion coefficient

The vacancy diffusion coefficient of YSZ can be determined as follows [12]

\[
D = D_{0}\exp\left(-\frac{E_{a}}{k_{B}T}\right),
\]

\[
D_{0} = n_{1}f\nu_{r}^{2}\exp\left(\frac{S_{l}^{f}}{k_{B}}\right)k_{B},
\]

where \(n_{1}\) is the number of \(O^{2-}\) ions at the 1NN positions with regard to the oxygen vacancy, the factor \(f\) is correlation factor which represents the deviation from randomness of the ionic jumps, \(\nu\) is the characteristic lattice frequency of the \(O^{2-}\) ions, \(r_{1}\) is the shortest distance between two lattice sites containing the \(O^{2-}\) ions, \(S_{l}^{f}\) is entropy for the formation of an oxygen vacancy.

In YSZ, the number of the mobility oxygen vacancies must be determined by the vacancy-dopant association energy. Hence, the vacancy activation energy is the sum of the vacancy-dopant association energy and the vacancy migration energy [13,14],

\[
E_{a} = E_{ass} + E_{m},
\]

a. The vacancy-dopant association energy

In YSZ, for every two \(Y^{3+}\) ions, one oxygen vacancy will be created. If yttrium concentration is \(x\) and the number of cations in the crystal lattice is \(N\), then the numbers of \(Zr^{4+}, Y^{3+}, O^{2-}\) ions and the oxygen vacancies are \(N_{Zr} = N(1 - x), N_{Y} = N_{x}, N_{O} = 2N(1 - x/4), \) and \(N_{va} = N_{x}/2\). Then, the vacancy-dopant association energy is given by the following expression

\[
E_{ass} = \left(\psi_{ZrN_{Zr}Y_{Ny},O_{NO}} + \psi_{ZrN_{Zr}+1Y_{Ny},-1O_{NO}}\right) - \left(\psi_{ZrN_{Zr}Y_{Ny},O_{NO}} + \psi_{ZrN_{Zr}+1Y_{Ny},-1O_{NO}}\right),
\]

where \(\psi_{ZrN_{Zr}Y_{Ny},O_{NO}}\), \(\psi_{ZrN_{Zr}+1Y_{Ny},-1O_{NO}}\), \(\psi_{ZrN_{Zr}Y_{Ny},O_{NO}}\), \(\psi_{ZrN_{Zr}+1Y_{Ny},-1O_{NO}}\) are the free energies of the crystal lattice in four situations: (i) the crystal lattice has \(N_{Y} Y^{3+}\) ions and \(N_{va}\) oxygen vacancies; (ii) the crystal lattice has \((N_{Y} - 1) Y^{3+}\) ions and \((N_{va} - 1)\) oxygen vacancies; (iii) the crystal lattice has \(N_{Y} Y^{3+}\) ions and \((N_{va} - 1)\) oxygen vacancies; and (iv) the crystal lattice has \((N_{Y} - 1) Y^{3+}\) ions and \(N_{va}\) oxygen vacancies.

b. The vacancy migration energy

The total free energy of the crystal lattice before the oxygen ion diffusion is denoted by \(\Psi_{1}\) and that after the oxygen ion diffusion from the lattice site A to the saddle point B is denoted by \(\Psi_{2}\) (Fig. 1). The vacancy migration energy \(E_{m}\) is given by [18]

\[
E_{m} = \Psi_{1} - \Psi_{2},
\]

In order to find \(\Psi_{1}\) and \(\Psi_{2}\), one needs to calculate the total interaction potentials of ions in two states: the diffusing oxygen ion at the lattice site A (called as initial state) and after the oxygen ion diffusion to the saddle point B (called as saddle point state). The total interaction potentials of \(Zr^{4+}, Y^{3+}\) and \(O^{2-}\) ions at the initial state are given by [19]

\[
U_{0}^{Zr} = \frac{N_{Zr}}{2} \left(\frac{N_{Zr} - 1}{N - 1}\sum_{i} a_{i}^{Zr} - Z_{r} - Z_{r} - Z_{r} - Z_{r} + \frac{N_{Y}}{N - 1} \sum_{i} b_{i}^{Zr - Y} - \varphi_{i0}^{Zr - Y}\right)
+ \frac{N_{Zr}}{2} \left(1 - \frac{N_{va}}{2N}\right) \sum_{i} b_{i}^{Zr - O} - \varphi_{i0}^{Zr - O},
\]
\[ \begin{align*}
U_Y^0 &= \frac{N_Y}{2} \left( \frac{N_R}{N-1} \sum b_i^{Y-R} \varphi_{i0}^{Y-R} + \frac{N_Y - 1}{N-1} \sum b_i^{Y-Y} \varphi_{i0}^{Y-Y} \right) \\
&+ \frac{N_Y}{2} \left( 1 - \frac{N_{va}}{2N} \right) \sum b_i^{Y-O} \varphi_{i0}^{Y-O},
\end{align*} \]
(14)

\[ U_0^O = \frac{N_O}{2} \left( \frac{N_R}{N} \sum b_i^{O-R} \varphi_{i0}^{O-R} + \frac{N_Y}{N} \sum b_i^{O-Y} \varphi_{i0}^{O-Y} + \left( 1 - \frac{N_{va}}{2N-1} \right) \sum b_i^{O-O} \varphi_{i0}^{O-O} \right), \]
(15)

where \( b_i^{X-Zr} \) (or \( b_i^{X-Y} \), or \( b_i^{X-O} \)) is the number of the \( i \)-th nearest-neighbor sites relative to \( X \) ion (\( X = \text{Zr}^{4+}, \text{Y}^{3+}, \text{O}^{2-} \)) that \( \text{Zr}^{4+} \) (or \( \text{Y}^{3+} \), or \( \text{O}^{2-} \)) ions could occupy, respectively, \( \varphi_{i0}^{X-Zr} \) (or \( \varphi_{i0}^{X-Y} \), or \( \varphi_{i0}^{X-O} \)) is the interaction potential between the \( 0 \)-th \( X \) ion and an \( \text{Zr}^{4+} \) (or \( \text{Y}^{3+} \), or \( \text{O}^{2-} \)) ion at the \( i \)-th nearest-neighbor sites of the \( X \) ion, respectively.

The total interaction potentials of \( \text{Zr}^{4+}, \text{Y}^{3+}, \text{O}^{2-} \) ions at the saddle point state are given by

\[ U_{\text{Zr}Y}^{\text{zn}} = U_0^{\text{Zr}} + \varphi_{\text{O-Zr}}^B - \varphi_{\text{O-Zr}}^A, \]
(16)

\[ U_Y^{\text{zn}} = U_0^{\text{Y}} + \varphi_{\text{O-Y}}^B - \varphi_{\text{O-Y}}^A, \]
(17)

\[ U_Y^{O} = U_0^{O} + \Delta u_{\text{Zr}}^A N_{\text{Zr}} + \Delta u_{\text{Y}}^A N_{\text{Y}} + U_0^O - \Delta u_{\text{A}}^O + \Delta u_{\text{B}}^O, \]
(18)

with

\[ \Delta u_{\text{Zr}}^A = \frac{\varphi_{\text{O-Zr}}^B - \varphi_{\text{O-Zr}}^A}{N_{\text{Zr}}}, \quad \Delta u_{\text{Y}}^A = \frac{\varphi_{\text{O-Y}}^B - \varphi_{\text{O-Y}}^A}{N_{\text{Y}}}, \]
(19)

\( \varphi_{\text{O-Zr,Y}}^A \) (or \( \varphi_{\text{O-Zr,Y}}^B \)) is the interaction potential between the \( \text{O}^{2-} \) ion at the lattice site A (or B) and the surrounding \( \text{Zr}^{4+} \) and \( \text{Y}^{3+} \) ions,

\( U_0^O \) is the total interaction potential of \( (N_O + 1) \text{O}^{2-} \) ions. Here, we assume that when the \( \text{O}^{2-} \) ion is at the lattice site A, the oxygen vacancy at the site C (Fig. 1) is occupied by an \( \text{O}^{2-} \) ion from the crystal lattice outside by some way.

\( \Delta u_{\text{A}}^O \) is the total reciprocal interaction potential between two \( \text{O}^{2-} \) ions at the sites A and C and the surrounding \( \text{O}^{2-} \) ions, and \( \Delta u_{\text{B}}^O \) is the reciprocal interaction potential between \( \text{O}^{2-} \) ions at the site B and the surrounding \( \text{O}^{2-} \) ions.

Figure 1. An \( \text{O}^{2-} \) ion hops from the lattice site A, across the saddle point B and occupies an adjacent vacant site C.

A B C
\[ \square : \text{Oxygen ion} \quad \square : \text{Oxygen vacancy} \]
3. Results and Discussions
The interaction potential in YSZ is Coulomb - Buckingham potential. The Coulomb term is a long-ranged interaction which causes many difficulties in the calculation. We use the Wolf method extended by C.J. Fennell et al. [13] to replace the Coulomb interaction effectively by spherically symmetric potentials with relatively short-ranges [14]. We find the optimum values of damping parameter $\alpha$ and cutoff radius $R_c$ to be $\alpha = 0.34 \text{ Å}^{-1}, R_c = 10.911 \text{ Å}.

Figure 2. The dependences of the vacancy-dopant association energy on the temperature (a) and dopant concentration (b).

Fig. 2 shows that the vacancy-dopant association energy is calculated as function of the temperature and dopant concentration. The vacancy-dopant association energy increases nearly linearly with the increasing temperature. The higher dopant concentration can lead to create more the oxygen vacancies. The oxygen vacancy- oxygen vacancy repulsion become stronger and it influences on the associations between oxygen vacancies and dopant ions. For this reason, the vacancy-dopant association energy decreases with the increasing dopant concentration.

Figure 3. The dependences of the vacancy migration energy on the temperature (a) and dopant concentration (b).

Recently, our study [19] showed that, the oxygen vacancy also hops dominantly along the $\langle 100 \rangle$ direction. It is noted that, the vacancy diffusion pass the barrier $\text{Zr}^{4+} - \text{Zr}^{4+}$ needs the smallest energy in the three barriers, $\text{Zr}^{4+} - \text{Zr}^{4+}$, $\text{Zr}^{4+} - \text{Y}^{3+}$ and $\text{Y}^{3+} - \text{Y}^{3+}$ and the attendance of $\text{Y}^{3+}$ ions to the cation barriers restricts the hopping of the oxygen vacancy. The calculated results for the vacancy migration energy at the various temperatures and dopant concentrations...
are presented in Fig. 3. One can see that the migration energy increases with the increase of the dopant concentration. It arises from an increase in the number of available oxygen vacancies for the diffusion.

Figure 4. The dependences of the vacancy activation energy on the temperature (a) and dopant concentration (b).

The dependences of the activation energy on the temperature and dopant concentration are presented in Fig. 4. When the temperature increases, the ions vibrate more strongly to restrict the movement of the oxygen vacancies which leads to an increase of the migration energy. Because the migration energy increases quickly with the increasing dopant concentration, the activation energy also increases with the dopant concentration. The calculated activation energies are in good agreement with the experimental results at temperature 1250 K [23].

The SMM vacancy diffusion coefficients at the various temperature and dopant concentration are presented in Fig. 5. The high temperature promotes the mobility of oxygen vacancies and it is reason for an increase of the vacancy diffusion coefficient. Further, the increasing activation energy due to the influence of temperature decreases the diffusion coefficient. Our calculations are in good agreement with results using MD at the various temperatures and dopant concentrations [24].

Figure 5. The dependences of the vacancy migration energy on the temperature (a) at $x = 0.1$ and dopant concentration at $T = 1273$ K (b).
4. CONCLUSIONS
The oxygen vacancy diffusion coefficient of YSZ is calculated by the SMM using the Coulomb-Buckingham potential. The expressions of the vacancy-dopant association energy and vacancy migration energy are performed. The vacancy activation energy and vacancy diffusion coefficient depend strongly on the temperature and dopant concentration. Note, the vacancy diffusion coefficient decreases with an increase of dopant concentration. It arises from the limitation for the oxygen vacancy migration across the cation barriers at high dopant concentration. Our results are in good agreement with other simulation results.

References
[1] Zhang L, Zhu L, Virkar A V 2016 Journal of Power Sources 302 98
[2] Krishnamurthy R, Yoon Y-G, Srolovitz D J, Car R 2004 J. Am. Ceram. Soc. 87 1821
[3] Xia X 2010 Thesis submitted for the degree of Doctor of Philosophy - University College London
[4] Kilo M, Jackson R A 2005 Diffusion Fundamentals 2 23
[5] Broxmann U, Knoner G, Schaefer H-E, Wurschum R 2004 Rev. Adv. Mater. Sci. 6 7
[6] Eichler A 2011 Physical Review B 64 174103
[7] Kushima A, Yildiz B 2010 J. Mater. Chem. 20 4809
[8] Pietrucci F, Bernasconi M, Laio A, Parrinello M 2008 Physical Review B 78 094301
[9] Arima T, Fukuyo K, Idenitsu K, Inagaki Y 2004 Journal of Molecular Liquids 113 67
[10] Hung V V, Thanh L T M 2010 Journal of science of HNUE 55 17
[11] Hung V V, Lee J and Masuda-Jindo K 2006 J. Phys. Chem. Solids 67 682
[12] Hung V V, Tich H V, Masuda-Jindo K 2000 Journal of the Physical Society of Japan 69 2691
[13] Kang Y J, Park H J, Choi G M 2008 Solid State Ionics 179 1602
[14] Zhang C, Li C-J, Zhang G, Ning X-J, Li C-X, Liao H, Coddet C 2007 Materials Science and Engineering B 137 24
[15] Krishnamurthy R, Yoon Y-G, Srolovitz D J, Car R 2004 J. Am. Ceram. Soc. 87 1821
[16] Ye F, Mori T, Ou D R, Cormack A N 2009 Solid State Ionics 180 1127
[17] Nakayama M, Martin M 2009 Phys. Chem. Chem. Phys. 11 3241
[18] Matsushita M, Sato K, Yoshiie T, Xu Q 2007 Materials Transactions 48 2362
[19] Hung V V, Lam L T 2018 HNUE Journal of Science 63 34
[20] Hung V V, Thanh L T M, Masuda-Jindo K 2010 Computational Materials Science 49 S355
[21] Schelling P K, Phillpot S R 2001 J. Am. Ceram. Soc. 84 2997
[22] Fennell C J, Gezelter J D 2006 J. Chem. Phys. 124 234104
[23] Pornprasertsuk R, Ramanarayanan P, Musgrave C B, Prinz F B 2005 Journal of Applied Physics 98 103513
[24] Devanathan R, Weber W J, Singhal S C, Gale J D 2006 Solid State Ionics 177 1251