First-Principles Study of the Diffusion and Reaction of Oxygenated Species on YSZ Surface

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Abstract: The phenomena occurred near the triple phase boundary (TPB) are key issues in solid oxide fuel cell and catalysis. In this work, we have theoretically investigated the diffusion and reaction processes on yttria stabilized zirconia (YSZ) surface, which are widely used in solid oxide fuel cell industrially. We have calculated the surface diffusion and rate coefficients of oxygen and hydroxyl ions on YSZ surface using density functional theory and transition state theory. The importance of surface diffusion and reaction of oxygenated species near TPB are also discussed using our calculated coefficients.

Keywords: Density functional theory, Diffusion coefficient, YSZ surface.

1. Introduction

Most of catalysts and electrodes have triple phase boundary (TPB) composed of gas phase, catalyst, and catalyst support or electrolyte. The performance of catalysts and fuel cells are highly dependent on physics and chemistry near TPB. Surface reactions including charge transfer at TPB are keys as we all know, but surface diffusion is also important due to the existence of concentration gradient near TPB. For example, Kohno et al. had suggested that current-voltage characteristics in solid oxide fuel cell largely depend on the yttria stabilized zirconia (YSZ) surface diffusion coefficient of oxygen ions[1]. However, it is difficult to measure the surface diffusion coefficient in experiments. Therefore, we have investigated the theoretical derivation of diffusion coefficient on YSZ surface using the density functional theory (DFT) calculations. We performed geometry optimizations and vibration analyses for the diffusion of oxygen and hydroxyl ions on YSZ surface, and derived the surface diffusion coefficient by applying transition state theory. We also calculated the rate coefficients of surface reactions on YSZ involved with oxygen and hydroxyl ions and discussed their importance.

2. Theoretical

DFT calculations were performed using CASTEP. The generalized gradient approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used. We used a $Zr_{22}O_{47}Y_2$ slab model based on a 4×2 zirconia super cell with three layers which has a vacuum thickness of 10 Å as shown in Fig.1. The lattice parameter of YSZ we used is 5.112 Å. We used Monk-horst-Pack *k*-points mesh of 2×3×1 and a cutoff energy of 489.8 eV. Model geometries were optimized by fixing relative positions of atoms in the bottom two layers. LST/QST method was used for the diffusional transition state search, where we postulated that a surface oxygen ion diffused to the position of neighbor surface oxygen vacancy. Diffusion coefficient D at each temperature was calculated by the following equation based on the transition state theory. Here, a_0 is the moving distance of an oxygen ion, N is the number of relaxing atoms in vibrational analysis, ν_n is nth vibration frequency of initial state A or transition state X obtained from vibrational analysis, and ε_0 is barrier height of the transition state.

$$D = \frac{{a_0}^2}{4} \times \frac{k_B T}{h} \frac{\prod_{n=1}^{3N} \left\{ 1 - \exp\left(-\frac{hc{\nu_n}^A}{k_B T} \right) \right\}}{\prod_{n=1}^{3N-1} \left\{ 1 - \exp\left(-\frac{hc{\nu_n}^X}{k_B T} \right) \right\}} \exp\left(-\frac{\varepsilon_0}{k_B T} \right)$$

3. Results and discussion

The energy of the YSZ slab model changes by the positions of doping yttrium and oxygen vacancy. Thus, we searched some diffusional transition states for the possible YSZ slab geometries. An example of found diffusional transition state geometries is shown in Fig.1 and part of calculated diffusion parameters are shown in Table 1. Diffusional activation energy also varies with the YSZ slab geometries, so the difference of diffusion coefficient are a few orders of magnitude at high temperature. The results show the importance of the adequate model selection to investigate the dynamics of surface diffusion. Vogler et al. were roughly estimated the D of the oxygen and hydroxyl ions on YSZ surface at 1073 K [2], which are shown together in Table 1. Our result of oxygen ion diffusion using the most stable YSZ geometry (named as ver6) agrees with the Vogler et al.'s estimated value within an order of magnitude. The details of other results including chemical reactions on YSZ in this model will be shown at the poster presentation.

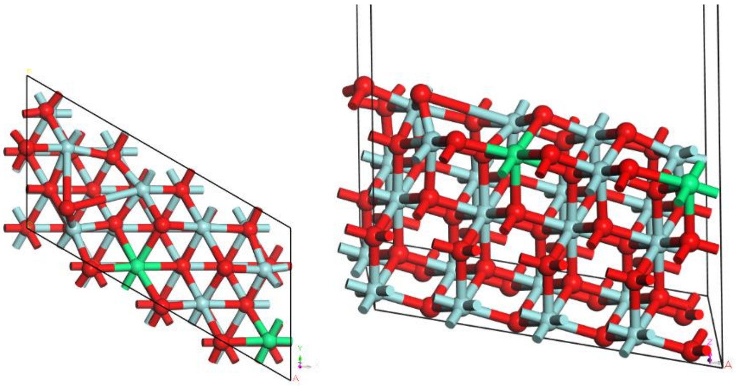

Figure 1. A transition state geometry (ver6) of an O ion diffusion on YSZ surface (Zr : light blue, O : red, Y : light green)

Table 1. Pre-exponential factor D_0, diffusional activation energy E_a in Arrhenius equation, and diffusion coefficient D at 1073 K. (re) means a reactant, (pr) means a product. (ver n) means nth model varying the position of doping yttrium and oxygen vacancy.

	D_0 (cm^2/s)	E_a (kcal/mol)
O^{2-} on ZrO_2	1.50×10^{-3}	59.50
O^{2-} on YSZ (re)(ver1)	1.73×10^{-3}	59.93
O^{2-} on YSZ (pr)(ver1)	6.60×10^{-3}	60.17
O^{2-} on YSZ (re)(ver6)	1.50×10^{-2}	39.95
O^{2-} on YSZ (pr)(ver6)	4.07×10^{-1}	20.46
O^{2-} on YSZ (ref)[2]	5.5×10^{-7}	21.50
OH^- on YSZ (re)(ver1)	1.72	40.93
OH^- on YSZ (pr)(ver1)	1.72	43.38
OH^- on YSZ (ref)[2]	1.3×10^{-2}	13.14

(T=1073K)	D (cm^2/s)
O^{2-} on ZrO_2	1.14×10^{-15}
O^{2-} on YSZ (re)(ver1)	1.07×10^{-15}
O^{2-} on YSZ (pr)(ver1)	3.66×10^{-15}
O^{2-} on YSZ (re)(ver6)	1.09×10^{-10}
O^{2-} on YSZ (pr)(ver6)	2.77×10^{-5}
O^{2-} on YSZ (ref)[2]	2.30×10^{-11}
OH^- on YSZ (re)(ver1)	7.92×10^{-9}
OH^- on YSZ (pr)(ver1)	2.51×10^{-9}
OH^- on YSZ (ref)[2]	2.74×10^{-5}

4. Conclusions

We have investigated surface diffusion and reaction of oxygenated species on YSZ surface based on the DFT and transition state theory. We successfully obtained the diffusion coefficient of oxygen and hydroxyl ions on YSZ theoretically. We found that the surface diffusion coefficient is sensitive to the positions of oxygen vacancy so adequate selection of the slab model is important to get accurate values. Our results are quite useful for the detailed kinetic simulations near TPB including surface diffusion phenomena.

References

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