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Tight-Binding Quantum Chemical Study of Oxygen Adsorption and Dissociation on Strontium-Doped Lanthanum Manganites

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Theoretical study of the surface reaction resistance of oxygen ions on the cathode surface in a solid oxide electrolyte fuel cell was performed by our tight-binding quantum chemical molecular dynamics program. In the present study, we discussed the adsorption and dissociation properties of oxygen molecule on the $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) surfaces.

Key words: Solid oxide fuel cell, $La_{1-x}Sr_xMnO_{3-\delta}$, Cathode, Tight-binding quantum chemical molecular dynamics

1. INTRODUCTION

Recently, solid oxide fuel cell (SOFC) has attracted much attention as the more highly efficient energy technology [1]. Lanthanum-strontium manganite, $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) are widely used as cathode materials of SOFC because of its high electronic conductivity and high catalytic activity for the oxygen reduction [1,2]. In order to improve the efficiency of SOFC system, it is necessary to decrease the resistance of the reaction toward both the dissociation and the diffusion of the oxygen on the interface between cathode electrode and electrolyte. In this regard, the detailed information on the electronic state of the cathode surface is imperative to achieve the low reaction resistance. Quantum chemistry is one of the best methods to investigate chemical reactions on the surface, and enables us to study the detailed mechanism of the reaction on the LSM cathode. However, to the best of our knowledge, there is no theoretical study for the reaction on the LSM cathode by using quantum chemical calculations. The first-principles methods are frequently used to study both the electronic and atomic structures of perovskite such as LSM [3]. However, this method requires huge computational resources, and hence it can not be applied to the simulation of large-scale model, which reflects the realistic structure of the cathode.

Recently, we have succeeded in the development of tight-binding quantum chemical molecular dynamics program "Colors", which is based on our original tight-binding approximation. It enables us to realize 5,000 times acceleration compared to the regular first-principles molecular dynamics method [4-6]. In this study, we applied the above new program to the investigation of the detailed adsorption and dissociation properties of oxygen molecule on the realistic large-scale $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) surfaces.

2.METHOD

2.1 *Tight-binding quantum chemical molecular dynamics calculation*

Quantum chemical molecular dynamics calculations were carried out using the "Colors" program developed in our laboratory, which is based on our original tight-binding approximation [4-6]. The total energy in the system is calculated employing Eqs. (1) and (2):

$$E = \sum_{i=1}^{n} m_i v_i^2 / 2 + \sum_{k=1}^{occ} \varepsilon_k + \sum\sum_{i>j} Z_i Z_j e^2 / R_{ij} + \sum\sum_{i>j} E_{rep}(R_{ij}) \qquad (1)$$

$$E_{rep}(R_{ij}) = b_{ij} \exp\left(\frac{a_{ij} - R_{ij}}{b_{ij}}\right) \qquad (2)$$

where m_i is the atomic weight, v_i is the atomic velocity, e is the elementary electric charge, R_{ij} is the internuclear distance, and a_{ij} and b_{ij} are parameters. Z_{ij} is the atomic charge obtained by the tight-binding electronic states calculations. In Eq. (1), the first term refers to the kinetic energy of the nuclear, the second term is the summation of the eigenvalues of all occupied orbitals calculated by the tight-binding approach, and the third term represents the Coulombic interaction. The last term corresponds to the short-range exchange-repulsion energy.

2.2 *First-principles parameterization*

In a similar way to the previous tight-binding quantum chemical calculations [7], some parameters are employed for the acceleration in "Colors" program, viz., valence state ionization potential of atomic orbital i ($I_i = -H_{ii}$) and Slater exponent of atomic orbital i (ζ_i). Here, we determined all the parameters by the first-principles density functional calculations in order to realize high accuracy. Density functional theory calculation program ADF [8] was employed for the above purpose. In the ADF calculations, the triple zeta plus polarization functions (TZpp) basis sets were used, while the energies were calculated using the generalized gradient approximation (GGA) with the Perdew-Wang exchange correlation functional [9].

2.3 *Models*

After the parameterization, we performed quantum chemical calculations on various periodic LSM surface models by using our "Colors" program. Fig. 1 shows the two types of $La_{0.78}Sr_{0.22}MnO_{3-\delta}$(00-1) surface models. Model (a) is the $La_{0.78}Sr_{0.22}MnO_3$(00-1) surface and is designed as no vacancy model. Model (b) is the $La_{0.78}Sr_{0.22}MnO_{2.89}$(00-1) surface with two oxygen vacancies and is designed as two vacancies model. Model (a) contains 90 ions, and model (b) contains 88 ions. Both the LSM surface models have the dimensions of a=11.740Å, b=11.740Å, and c=5.844Å[10].

3.RESULTS AND DISCUSSION

3.1 *Adsorption of O ion on the LSM surfaces*

In the present study, we investigated the adsorption properties of the oxygen on the $La_{0.78}Sr_{0.22}MnO_{3-\delta}$ surface models as shown in Fig. 1. We compared three different adsorption sites of O ion: on the topmost Mn ion of LSM, on the topmost O ion of LSM, and on the vacancy of LSM. Table I shows the adsorption energy of each model on each adsorption site at the equilibrium distance between the O ion and the surface of the LSM. Here, the adsorption energy (ΔE_{ads}) of the O ion on the LSM surface was calculated by the following Eq. (3):

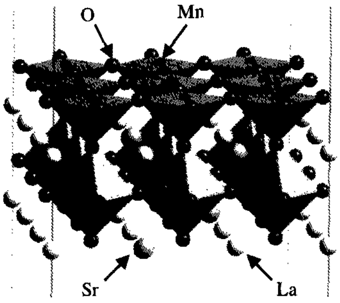
$$\Delta E_{ads} = E_{O/LSM} - (\tfrac{1}{2} E_{O_2} + E_{LSM}) \qquad (3)$$

where $E_{O/LSM}$, E_{O_2}, and E_{LSM} are the binding energies of the O ion/ LSM, the oxygen molecule, and the LSM surface, respectively.

Table I indicates that the adsorption energy on the Mn site is larger than that on the O site in both models. This result means that the adsorption of O ions take place easier on the Mn site than that on the O site. The adsorption energy of the O ion on the model (b) is larger than that on the model (a) in all sites. Especially, the adsorption energy on the vacancy site is much larger than other sites. The equilibrium distance between the adsorbed oxygen and the surface of the LSM is 0.3 Å on the vacancy site. It means that the adsorbed oxygen easily diffuses into the oxygen vacancy and there is stronger interaction between the adsorbed oxygen ion and the LSM surface than that on the other sites. These results suggest that the vacancy on the LSM surface promotes the adsorption of the O ion.

Table II shows the average atomic charges on each atom of the LSM and adsorbed O ion at the equilibrium distance between the O ion and the surface of the LSM. Atomic charges are obtained from the Mulliken population analysis[11]. The total of atomic charge on each model is neutral. O ion adsorbed on the top of O site has more negative charge than that on the top of Mn site. It indicates that the localization of electron on the adsorbed oxygen is more significant on the top of O site than that on the top of Mn site. It is the reason why the adsorption on the top of Mn site is more stable than that on the top of O site. On the other hand, the negative charge on the O ions adsorbed on the top of the vacancy is almost same as the lattice oxygen of the LSM cathode because its coordination structure is almost same as the lattice oxygen.

(a) No vacancy model



(b) Two vacancies model

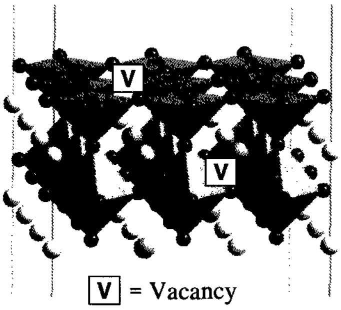


Fig. 1 $La_{0.78}Sr_{0.22}MnO_{3-\delta}$ (00-1) surface models
(a) No vacancy model, (b) Two vacancies model

Table I The adsorption energy of O ion on each adsorption site of models (a) and (b) at the equilibrium distance between the O ion and the surface of the LSM

	Adsorption site	Adsorption energy [kcal/mol]	Equilibrium distance of O-LSM [Å]
(a) No vacancy model	On the Mn	-159.28	1.9
	On the O	-93.11	2.0
(b) Two vacancies model	On the Mn	-167.58	1.8
	On the O	-94.38	2.0
	On the vacancy	-267.14	0.3

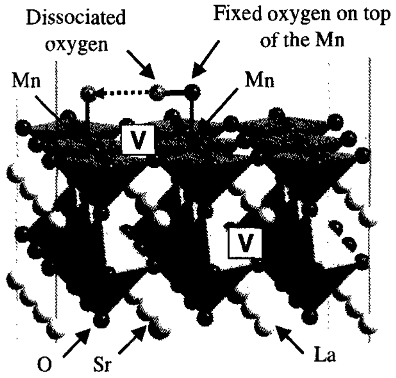
3.2 *Dissociation of the oxygen molecule on the LSM surfaces*

Moreover, we investigated the dissociation of the oxygen molecule and the diffusion of the dissociated O ion on the LSM cathode. Here, oxygen is dissociated on the cathode surface and then diffused into the electrolyte in SOFC. Therefore, it is important to investigate the dissociation and diffusion process of oxygen molecule to clarify the mechanisms of the cathode reaction. Fig. 2 shows the models of the dissociation process of the oxygen molecule and the diffusion of the dissociated O ion on the model (b) as shown in Fig. 1. In the route 1, one oxygen atom of the adsorbed oxygen molecule is fixed on the Mn site near the vacancy and another oxygen atom is dissociated over the vacancy site and diffuses to the neighboring Mn site. We investigated the effect of oxygen vacancy for the dissociation of the oxygen molecule on the route 1. In the route 2, one oxygen atom of the adsorbed oxygen molecule is fixed on the Mn site far from the vacancy site and another oxygen atom is dissociated over the O site and diffused to the second neighboring Mn site over the vacancy site. We simulated the long-distance diffusion process of the dissociated O ion on the LSM surface in the route 2, in order to investigate the effect of the oxygen vacancy for the diffusion of the dissociated O ion. Fig. 2 shows only the dissociation and diffusion processes for model (b), but the same processes for model (a) are also investigated.

Fig. 3 shows the change in the adsorption energy of the oxygen molecule following the route 1. The x-axis shows the distance of the fixed O ion and the diffused O ion. The y-axis shows the adsorption energy of the oxygen molecule. In both models (a) and (b), the adsorption energy of the dissociated O around the top of the Mn site is largest. There is a shoulder of the adsorption energy around the oxygen or vacancy site, but there are no activation barriers for the dissociation of oxygen molecule along with the route 1. Similarly to the results of the adsorption of single O ion on the LSM surface as shown in Table I, the adsorption energy of the O ion on the model (b) is smaller than that on the model (a) in all the position of the dissociated oxygen.

Fig. 4 shows the change in the adsorption energy of the oxygen molecule on the route 2. The vacancy of the LSM surface stabilized the adsorption state of the dissociated oxygen molecule on the route 2 as well as on the route 1. However, there is little difference in the adsorption energy of two models in the route 2 around the O site near the initial adsorption site. The adsorption energy on the O site near the initial adsorption site in the route 2 is -212.2 kcal/mol, which is much smaller than that of the route 1 (-274.0 kcal/mol). This result shows adsorption site strongly affects the adsorption energy of

(b-1) Route 1



(b-2) Route 2

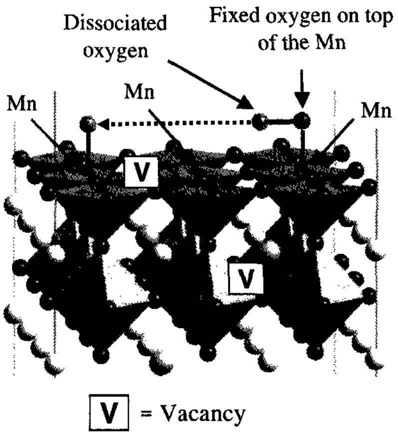


Fig. 2 The model of the dissociation process of the oxygen molecule and the diffusion process of the dissociated O ion on the two vacancies model of the $La_{0.78}Sr_{0.22}MnO_{2.89}$ surface. (b-1) One oxygen atom of the adsorbed oxygen molecule is fixed on the Mn site near the vacancy and another oxygen atom is dissociated over the vacancy site and diffuses to the neighboring Mn site. (b-2) One oxygen atom of the adsorbed oxygen molecule is fixed on the Mn site far from the vacancy site and another oxygen atom is dissociated over the O site and diffused to the second neighboring Mn site over the vacancy site.

Table II The atomic charges on each atom of the LSM and adsorbed oxygen ion at the equilibrium distance between the oxygen ion and the surface of the LSM

	Adsorption site	Average charge				
		La	Sr	Mn	Lattice oxygen	Adsorbed oxygen ion
(a) No vacancy model	No oxygen	0.585	0.741	0.281	-0.300	-
	On the Mn	0.592	0.745	0.288	-0.298	-0.359
	On the O	0.571	0.731	0.252	-0.297	-0.388
(b) Two vacancies model	No oxygen	0.591	0.679	0.286	-0.292	-
	On the Mn	0.579	0.728	0.275	-0.301	-0.335
	On the O	0.580	0.727	0.273	-0.300	-0.393
	On the vacancy	0.580	0.730	0.273	-0.301	-0.303

oxygen molecule. On the contrary to the results of the that the distance between the vacancy site and the route 1, there is an activation barrier for the dissociation of oxygen molecule around the O site or vacancy site on the route 2. In the model (b), the activation barrier is 31.2 kcal/mol, which is much smaller than that of the model (a) (70.7 kcal/mol). From the comparison of the adsorption energies and the activation barriers of models (a) and (b) in both two route, it was found that the vacancies on the LSM surface not only promote the oxygen adsorption but also reduce the activation barriers for the dissociation of oxygen molecule.

Table III shows the atomic charges on each atom of the LSM and the adsorbed oxygen molecule at each site along with the route 2. The sites ① and ③ are the sites of the maximum adsorption energy of the oxygen molecule as shown in Fig. 4. The sites ② and ④ are the transition sites as shown in Fig. 4. At the transition sites for the dissociation of oxygen molecule (on the sites ② and ④), the localization of the electron is significant on the dissociated O ion compared to the most stable site (on the sites of ① and ③). On the other hand, the positive charge of Mn ion did not changed. These results suggested that covalent bonding between adsorbed oxygen and LSM surface dominates the strength of the adsorption.

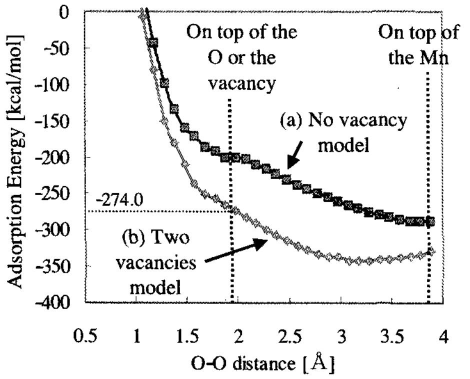


Fig.3 The change in the adsorption energy of the oxygen molecule following the route 1.

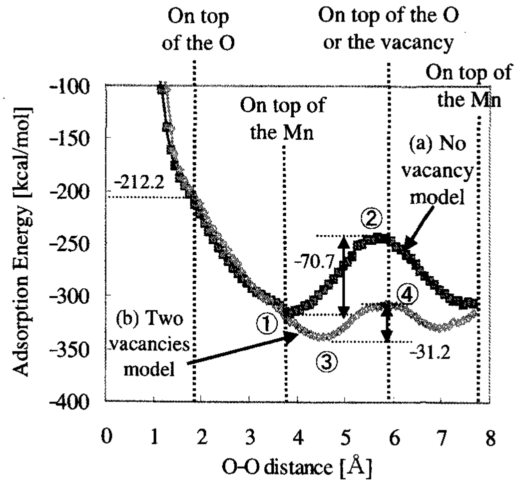


Fig.4 The change in the adsorption energy of the oxygen molecule following the route 2.

Table III The atomic charges on the adsorbed oxygen ions and the adsorption energies at each position along with the route 2.

	Site	Average charge		Adsorption energy [kcal/mol]
		Mn	adsorbed O	
(a) No vacancy	①	0.295	-0.328	-315.23
	②	0.292	-0.356	-244.44
(b) Two vacancies	③	0.283	-0.353	-338.37
	④	0.282	-0.414	-307.17

From the results of the adsorption and dissociation of oxygen, we concluded that the concentration of the vacancy on the LSM surface is very important to promote the dissociation and adsorption of O ions on the LSM cathode. Finally, we would like to stress that our tight-binding quantum chemical molecular dynamics method is very effective tool to elucidate the detailed adsorption and the dissociation properties of the oxygen on the realistic large-scale LSM cathode models.

4. CONCLUSIONS

Our original tight-binding quantum chemical molecular dynamics method with the first-principles parameterization was successfully applied to the simulation of the adsorption and the dissociation of the oxygen on the realistic large-scale LSM cathode models. Our results found that the vacancy on the LSM surface stabilized the adsorption of the O ion. Furthermore, it was suggested that the vacancies on the LSM surface not only promote the oxygen adsorption but also reduce the activation barrier. According to these results, we concluded that the concentration of the vacancy on the LSM surface is very important to promote the dissociation and adsorption of O ions in the LSM cathode.

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