Investigation of LiO$_2$ Adsorption on LaB$_{1-x}$B$'_x$O$_3$(001) for Li-Air Battery Applications: A Density Functional Theory Study

Hyunguk Kwon and Jeong Woo Han$^\dagger$

Department of Chemical Engineering, University of Seoul, Seoul 02504, Korea

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ABSTRACT

Li-air batteries have received much attention due to their superior theoretical energy density. However, their sluggish kinetics on the cathode side is considered the main barrier to high performance. The rational design of electrode catalysts with high activity is therefore an important challenge. To solve this issue, we performed density functional theory (DFT) calculations to analyze the adsorption behavior of the LiO$_2$ molecule, which is considered to be a key intermediate in both the Li-oxygen reduction reaction (ORR) and the evolution reaction (OER). Specifically, to use the activity descriptor approach, the LiO$_2$ adsorption energy, which has previously been demonstrated to be a reliable descriptor of the cathode reaction in Li-air batteries, was calculated on LaB$_{1-x}$B$'_x$O$_3$(001) (B$'_x$ = Mn, Fe, Co, and Ni, x = 0.0, 0.5). Our fast screening results showed that LaMnO$_y$, LaMn$_{1-x}$Fe$_x$O$_3$, or LaFeO$_3$ would be good candidate catalysts. We believe that our results will provide a way to more efficiently develop new cathode materials for Li-air batteries.

Key words : Li-air battery cathode, LaBO$_x$ perovskite, LiO$_2$ adsorption, Density functional theory

1. Introduction

The use of fossil fuels has exacerbated various environmental concerns, particularly global warming. To reduce the dependence on fossil fuels, nowadays Li-air batteries, due to their high theoretical specific energy, have attracted interest for future electric vehicles, electrical energy storage devices, and other energy applications.$^{1,3}$ However, many scientific issues such as low round-trip efficiency, short cycle life, poor rate capability, and electrolyte instability must be solved for the realization of affordable Li-air battery technology.$^{3}$ Especially, the slow kinetic rate of the oxygen reduction reaction (ORR) or the oxygen evolution reaction (OER) on the cathode side has been widely known as a main obstacle to high energy efficiency.$^{10}$ To overcome this problem, numerous attempts have been made to design new electrocatalysts with high activity for ORR or OER.$^{11}$ In the past, perovskite oxides (ABO$_3$) have been nominated as potential ORR or OER catalysts$^{12,13}$ due to their high catalytic activity, fast electronic and ionic conductivity, and low cost.$^{12,14,15}$ For these reasons, many researchers have made efforts to enhance the cathode kinetics using LaBO$_x$-type perovskite oxides such as LaSrMnO$_{3-x}$,$^{16,17}$ LaFeO$_{3-y}$, and LaSrCoO$_{3-\delta}$ in Li-air batteries. However, in spite of these constant efforts, it is still difficult to find optimal combinations of components in perovskite oxides due to changes in catalytic properties with partial or full substitution at A- and B-sites.

Previous studies have provided efficient ways to improve the catalytic properties. Introducing an activity descriptor enables us to facilitate fast screening of perovskite catalysts for Li-air batteries.$^{14,16}$ Using density functional theory (DFT) calculations, Nørskov et al.$^{20}$ suggested a method that can assess the thermochromy of the electrochemical reactions. They also verified the origin of the overpotential for oxygen reduction over Pt(111). Based on these results, Man et al.$^{21}$ derived a descriptor ($\Delta G_{Li} – \Delta G_{O}$) for oxygen reduction using different kinds of oxide materials. These results have been widely applied in various electrochemical reactions including Li-ORR and OER to introduce useful descriptors. Choi et al.$^{22}$ used the DFT calculated adsorption energy database of lithium oxide intermediates to examine the theoretical overpotentials for ORR and OER on Pd, Cu, and PdCu alloy surfaces with an ordered body centered cubic (B2-type) structure. They reported that the LiO$_2$ adsorption energy shows a good correlation with the ORR and/or OER overpotentials. Moreover, they demonstrated that controlling the LiO$_2$ adsorption energy by alloying the material with Pd and Cu can enhance the catalytic activity. A similar argument was also made by Kim et al.$^{23}$ who suggested that the overpotential of Li-OER decreases with decreasing of the strength of LiO$_2$ adsorption on Pt(111), Co(0001), and PtCo(111). These results motivated us to estimate the catalytic activity on perovskite oxides by using only a simple descriptor, the LiO$_2$ adsorption energy.

In this study, we first use DFT calculations to perform a structural investigation of the LiO$_2$ adsorption on LaB$_{1-x}$B$'_x$O$_3$(001) for Li-air battery applications. We use a simple descriptor, the LiO$_2$ adsorption energy, to select the most suitable catalysts. We believe that our results will provide a way to more efficiently develop new cathode materials for Li-air batteries.

$^\dagger$Corresponding author : Jeong Woo Han
E-mail : jwhan@uos.ac.kr
Tel : +82-2-6490-2373  Fax : +82-2-6490-2364
2. Computational Methods

All periodic density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) functional, based on the generalized gradient approximation (GGA), was employed. In addition, the DFT+U method with U_{eff} = 4.0 eV (Mn), 4.0 eV (Fe), 3.3 eV (Co), and 6.4 eV (Ni) was applied to reduce the self-interaction error. All calculations included spin polarization and were performed with a cutoff of 400 eV. Geometries were optimized until the forces on each atom were below 0.03 eV Å\(^{-1}\). The optimized lattice constants were obtained using 2 × 2 × 2 supercells. An asymmetric slab structure was constructed by cleaving the bulk structure along the (001) plane. For the calculations and two fully relaxed top layers. A 15 Å vacuum layer was used to prevent interaction between the two periodic slabs. In all surface calculations, a dipole correction was applied in the perpendicular direction.

3. Results and Discussion

3.1 LiO\(_2\) adsorption on LaBO\(_x\) (001)

We first examined the adsorption phenomenon of LiO\(_2\) molecules on undoped perovskite (LaBO\(_x\)) surfaces because these surfaces have relatively simple structures. Dathar et al. previously reported that the first e\(^-\) transfer step of Li-ORR on a metal surface can be divided into associative and dissociative mechanisms depending on the activation barrier (E\(_a\)) for dissociating oxygen molecules. They suggested that a Li atom reacts with an oxygen molecule on metal surfaces with high E\(_a\) (LiO\(_2\) generation), whereas it reacts with dissociated oxygen atoms on surfaces with low E\(_a\) (O\(_2\) or LiO generation). Unlike the case of metal surfaces, the initial adsorption mechanism on LaBO\(_x\)-type perovskite surfaces is still unclear. However, the O\(_2\) dissociation reaction often shows a high activation barrier (~1 eV) on A-site undoped LaBO\(_x\)-type perovskites, which would have few oxygen vacancies due to the good balance of charge. This means that the first e\(^-\) transfer step of Li-ORR on LaBO\(_x\) perovskite surfaces may be associative adsorption. Hence, we here examined the adsorption energies and site preferences of the LiO\(_2\) molecule, not the O\(_2\) or LiO molecule.

Figure 2 shows the DFT-optimized LiO\(_2\) adsorbed LaBO\(_x\) surface structure as a representative case. The O\(_2\) part in LiO\(_2\) is adsorbed on the top layer Mn atom. This is similar to previous reports in which the adsorption site of an O\(_2\) molecule on an ABO\(_3\) perovskite structure is the B-transition metal site. The Li atom in LiO\(_2\) is adsorbed on the 4-fold site surrounded by four lattice oxygen atoms. This

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Table 1. Comparison between Calculated and Measured LiO\(_2\) Geometric Information

<table>
<thead>
<tr>
<th></th>
<th>Symmetry</th>
<th>d(O−O) (Å)</th>
<th>d(Li−O) (Å)</th>
<th>&lt; O−Li−O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT (This work)</td>
<td>C(_{2v})</td>
<td>1.367</td>
<td>1.782</td>
<td>45</td>
</tr>
<tr>
<td>Experiment(^{39}) (Previous work)</td>
<td>C(_{2v})</td>
<td>1.33±0.06</td>
<td>1.77±0.07</td>
<td>44</td>
</tr>
</tbody>
</table>
adsorption site preference of LiO$_2$ on the LaMnO$_3$ surface was almost identical for the other LaBO$_3$ perovskite surfaces examined in this study. However, the adsorption strength of LiO$_2$ shows clear differences. The trend in the adsorption energies on LaBO$_3$(001) (B = Mn, Fe, Co, and Ni) follows the order of atomic number of the B-transition metals in the periodic table (Table 2). This implies that the LiO$_2$ adsorption energy is mainly affected by the properties of transition metals in the B-site.

3.2 LiO$_2$ adsorption on LaB$_{0.5}$B’$_{0.5}$O$_3$(001)

Our results for the undoped perovskites in Section 3.1 provide useful insight into how we determined the binding site of LiO$_2$ on the B-site doped perovskite surfaces, LaB$_{0.5}$B’$_{0.5}$O$_3$(001). As can be seen in Fig. 1(b), there are two possible adsorption sites according to the two types of transition metals exposed on the surface (B and B’). Based on the results of adsorption on the undoped LaBO$_3$(001), we can reasonably assume that the O$_2$ part of LiO$_2$ is adsorbed on the top of B or B’ cations, while the Li atom in LiO$_2$ binds only on the 4-fold site surrounded by four lattice oxygen atoms. We thus calculated the adsorption energies by considering those two possible adsorption sites for all LaB$_{0.5}$B’$_{0.5}$O$_3$(001) (Fig. 3 and Table 3).

It is found that the adsorption energy and site preference of LiO$_2$ on LaB$_{0.5}$B’$_{0.5}$O$_3$ surfaces are not dependent on those characteristics of the undoped LaBO$_3$ or LaB’O$_3$ surfaces. For example, the adsorption strength of LiO$_2$ (-2.05 eV) on the Co atom of LaCoO$_3$(001) is larger than that (-1.75 eV) on the Mn atom of LaMnO$_3$(001) (Because an Li atom is always absorbed at a site surrounded by four oxygen atoms, here we only mention the adsorption sites of the O$_2$ part in LiO$_2$).

On the other hand, in LaMn$_{0.5}$Co$_{0.5}$O$_3$(001), the adsorption strength of LiO$_2$ (-2.21 eV) on the Mn atom is larger than that (-2.06 eV) on the Co atom. Furthermore, the adsorption strength on LaMn$_{0.5}$Co$_{0.5}$O$_3$(001) becomes much stronger than that on LaMnO$_3$(001) or LaCoO$_3$(001). These unpredictable tendencies of the site preferences and adsorption energies of LiO$_2$ imply that it is hard to minutely tune the adsorption energy (further, the activity) by doping considering the properties of the undoped LaBO$_3$ or LaB’O$_3$ surfaces.
or mixing of different metals in perovskite oxides. As a result, determining the fundamental origin of the characteristic adsorption phenomena must be definitively resolved and is a subject for further study.

3.3 Charge density difference analysis
Adsorption is often accompanied by charge density redistribution. Thus, to understand the adsorption phenomenon in detail, we analyzed the charge density difference using Bader charge analysis. Here, we demonstrate the results on LaMnO$_3$(001) as a representative case. Fig. 4(a) indicates that charges of -0.20 e, -0.06 e, and -0.06 e transfer from the LaMnO$_3$ surface to the O$_t$, O$_b$, and Li in the LiO$_2$ molecule, respectively (Here, O$_t$, and O$_b$ indicate the atomic oxygens located at the top and bottom, respectively, of the adsorbed LiO$_2$ molecule). Overall, -0.32 e transfers from the surface to the adsorbate (LiO$_2$). This tendency was also observed in the other perovskite surfaces we examined in this study. O$_t$ has the most negative charge state and O$_b$ and Li have relatively lower negative charge states after adsorption. Moreover, the total charge density differences of adsorbed LiO$_2$ always have negative values; these values are related to the adsorption energies of LiO$_2$.

3.4 Significance of LiO$_2$ adsorption analysis for Li-air battery cathodes
As mentioned earlier, LiO$_2$ adsorption energy can be a useful descriptor for the activity because the weak adsorption strength of LiO$_2$ is closely associated with the low overpotentials of ORR or OER. To estimate the activity of electrocatalysts for Li-air batteries, we assessed the adsorption energies of LiO$_2$. Fig. 5 shows the DFT-calculated adsorption energies found in this study (reorganized from Tables 2 and 3). More red color means a weaker strength of LiO$_2$ adsorption, while more blue color indicates stronger strength. Our results suggest that among the lanthanum based perovskites LaMnO$_3$, LaMn$_{0.5}$Fe$_{0.5}$O$_3$, or LaFeO$_3$ would be good candidate materials as Li-air battery cathodes in terms of the reaction kinetics due to the weak adsorption strength of LiO$_2$. Indeed, some of these materials such as LaSrMnO$_3$ or LaFeO$_3$ have already shown high electrochemical performance in Li-air batteries.

In addition, unlike the case on metal surfaces, the adsorption phenomenon of Li-ORR or OER intermediates on perovskite surfaces have not been precisely determined at the atomic scale. Therefore, adsorption analysis of LiO$_2$, a key intermediate of Li-ORR or OER, on a wide range of per-

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**Fig. 4.** (a) Changes in the electron density upon LiO$_2$ adsorption on LaMnO$_3$(001). Yellow and cyan colors indicate decreased and increased electron densities, respectively. O$_t$ and O$_b$ indicate the atomic oxygens located at the top and bottom of the adsorbed LiO$_2$ molecule, respectively. The isosurface contour is plotted with a charge density value of 0.002 eÅ$^3$. (b) Adsorption energies as a function of the charge density differences on the LiO$_2$ adsorbed LaB$_{1-x}$B'O$_3$(001) (B, B' = Mn, Fe, Co, and Ni, x = 0.0, 0.5). Each point indicates the pure or mixed B-site cations used in this system.

**Fig. 5.** Adsorption energies of LiO$_2$ on LaB$_{1-x}$B'O$_3$ (B, B' = Mn, Fe, Co, and Ni, x = 0.0, 0.5) perovskite surfaces.
ovskite surfaces may provide useful insight into the adsorption study of the other intermediates.

4. Conclusions

In this study, we carried out structural, charge, and energetic investigations of LiO$_2$ adsorption behaviors on LaB$_{1-x}$B$_x$O$_6$ (B, B' = Mn, Fe, Co, and Ni, x = 0.0, 0.5) using DFT+U calculations. Unlike that of metal catalysts, the adsorption of lithium oxide intermediates on perovskite surfaces has hardly been examined. Our structural analysis showed that the adsorbed LiO$_2$ has a similar adsorption site preference and structure in all BO$_2$-terminated LaB$_{1-x}$B$_x$O$_6$ (001). Charge analysis demonstrated that the charge transfer from the perovskite surface to the LiO$_2$ molecule upon adsorption is a crucial factor for LiO$_2$ adsorption. LiO$_2$ adsorption energy was used as an activity descriptor to estimate the catalytic activities on LaB$_{1-x}$B$_x$O$_6$ (001). Our results showed that LaMnO$_3$, LaMn$_{0.5}$Fe$_{0.5}$O$_3$, or LaFeO$_3$ are promising candidate catalysts due to their weak LiO$_2$ adsorption, even though the cathode performance is dependent on a number of other factors. The screening results we present here also offer useful insight for experimental research into a rational design of perovskite catalysts for Li-air batteries.

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