COMPUTATIONAL APPROACH TO SOLID-GAS INTERACTIONS IN SOFCs

Y. M. Choi, Harry Abernathy, Robert Williams Jr., and Meilin Liu
Center for Innovative Fuel Cell and Battery Technologies
School of Materials Science & Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245, USA

ABSTRACT

Hybrid density functional theory (DFT) has been used for a computational study of oxygen reduction in solid oxide fuel cells (SOFCs). A simplified cluster model of Mn(OH)$_4$O$_2$ was employed to represent a cathode material, La$_{1-x}$Sr$_x$MnO$_3$ (LSM), for study of the molecular oxygen reduction processes. The energy barriers to oxygen adsorption, dissociation, and reduction processes were calculated using hybrid B3LYP DFT with the 6-311+G(d) basis set. Predicted vibrational frequencies of surface oxygen species are in good agreement with available experimental results, suggesting that advanced computation could be a powerful approach to elucidating oxygen reduction mechanisms on the cathode surfaces in an SOFC.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have great potential to be the cleanest and most efficient chemical-to-electrical energy conversion system. One of the key technical challenges for the SOFC technology is to reduce the operating temperature to below 700°C (1,2). Understanding the detailed mechanisms for oxygen reduction on the cathode of an SOFC is a critical step toward this goal. A fundamental understanding of the mechanistic details of gas-surface interactions is vital to rational design of more efficient SOFC electrode materials. For this purpose, in-situ surface vibrational spectroscopic techniques such as Fourier Transform Infrared (FTIR) and Raman scattering have been used to study the mechanisms of solid-gas interactions in SOFCs (3-5). While experimental methods can offer important insight to the understanding of the gas-surface interactions, there are still many unknown factors that cannot be probed by experimental tools, due either to inherent inaccessibility of the processes or to the complexity of the electrocatalytic reactions. A complementary and powerful approach is advanced computational modeling that provides electronic structures and molecular parameters of electrode materials and intermediate species (6-11). Because of the rapid advances in computation and quantum-mechanical methodology, it is possible to deal with the SOFC system at a sub-atomic level to understand the reaction mechanisms on the electrode surfaces. The computational methods optimize the geometries of various intermediates and transition states on the surfaces, as well as predict their energetics and vibrational frequencies. Favorable reaction pathways can be suggested based on the construction of potential energy surfaces. As a result, the computational approach could help to establish proper
mechanistic models to guide effective design of more efficient electrocatalysts (9). The goal of this study is two fold: to predict the most probable reaction mechanisms and to compare the predicted vibrational frequencies of surface oxygen species with available experimental data.

**COMPUTATIONAL APPROACH**

**Elementary Reaction Steps**

Oxygen reduction on SOFC cathode can be generally described as follows (4,12-14):

\[
\frac{1}{2} O_{2(g)} \xrightarrow{ads} \frac{1}{2} O_{2(ad)} \xrightarrow{+e^{-}} O_{(ad)}^{-} \xleftarrow{rec} O_{(ad)}^{+} \xrightarrow{+e^{-}} O_{O_x}^{2-} \xleftarrow{-V_{O}} \xrightarrow{+v_i} O_{O_x}^{2-} \xrightarrow{-(V_{O}+\varepsilon)} \]

Electrocatalytic reaction mechanisms occurring on the electrode surfaces are difficult to elucidate due to the existence of multiple complex reaction zones, i.e., various double and triple phase boundaries (TPBs). Under the normal operating conditions of an SOFC, oxygen from the ambient air initially approaches the cathode surface and physisorsbs as either a superoxide or peroxide species -- as schematically shown in Figure 1 (15).

![Figure 1. Schematics showing adsorption/desorption and dissociation/recombination of oxygen species on the cathode surface.](image)

The highly exothermic nature of the dissociation of free O₂ molecule (493.7 kJ mol⁻¹) might explain the reason for the higher temperature to activate the oxygen molecule on the surface (13). Subsequent dissociation of the adsorbed oxygen species produces oxygen atoms that strongly react with neighboring surface atoms and form a chemical bond (16). Figure 2 represents the charge transfer from the surface to the adsorbed atomic and molecular oxygen species, producing oxygen anions. Thermodynamics predicts that the binding energy between an adsorbed O²⁻ anion and a metal cation on the surface is larger than those in the lattice -- a prediction confirmed by our quantum-chemical calculations of vibrational frequencies of the corresponding bonds.
The $O_2^-$ anion can diffuse into an oxygen vacancy of the lattice and combine with the vacancy to enter the lattice. At the same time, surface diffusion of these species may occur as illustrated in Figure 3. For example, the adsorbed species may have to diffuse to an electrochemically active site such as a triple phase boundary (TPB) to be reduced or oxidized. Similarly, oxygen ions (or vacancies) may have to move to the vicinity of an oxygen vacancy (or ion) to be incorporated into the lattice.

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**Computational Methods**

The electrode materials in SOFCs can be described as an infinite number of atoms from the viewpoint of the molecular level as depicted in Figure 4. Therefore, molecular-level studies are of great significance to fully understand the reaction mechanism of oxygen reduction. Cluster (17) and periodic slab models (18) are commonly used in electronic structure calculations to explore gas-surface interaction. In this preliminary work, a cluster model has been applied to predict reaction barrier and vibrational frequency due to its less demanding computational times, even though the cluster approach has boundary effects. More advanced calculations with a periodic slab model are in progress. The quantum-chemical calculations were carried out using the hybrid B3LYP density functional theory (DFT) (19) with the 6-311+G(d) basis set (20) implemented in the Gaussian03 package (21). The geometries were optimized according to the Berny algorithm. The energetics were calculated according to the following equation.

\[
\Delta E = \Sigma E_{\text{products}} - \Sigma E_{\text{reactants}} = E_{\text{adsorbate + cluster}} - E_{\text{gas-phase $O_2$ molecule}} - E_{\text{cluster}}
\]
In this study, we focused on the perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) as the cathode material to study $\text{O}_2$ dissociative adsorption; however, for computational convenience, a Mn $(\text{OH})_4\text{O}_2$ cluster model, as depicted in Figure 5, was used to approximate the interactions of the cathode material LSM with $\text{O}_2$.

**RESULTS AND DISCUSSION**

To test the validity of the computational methods, we first calculated the vibrational frequencies and bond lengths for oxygen species using two different DFT methods: B3LYP and BPW91. The same 6-311+G(d) basis set was used for both methods. As summarized in Table 1, the B3LYP method is in better agreement with existing experimental data. In addition, isotope frequencies, $\nu(\text{O}^{16}\text{O}^{18})$ and $\nu(\text{O}^{18}\text{O}^{18})$ have been predicted, which are yet to be confirmed experimentally.

Shown in Figure 6 are some of initial results for our DFT study of a Mn$(\text{OH})_4\text{O}_2$ cluster model with oxygen molecule to estimate the energetics and vibrational frequency for oxygen dissociation on a cathode material LSM. The energy of the oxygen molecule adsorbed to the Mn$(\text{OH})_4\text{O}_2$ cluster relative to the individual energies of the oxygen molecule and Mn$(\text{OH})_4\text{O}_2$ cluster is plotted as a function of the distance between O1 and O3. For fast computation, the dihedral angle of $\angle\text{O1-O2-O3-O4}$ was kept at 180°. At the asymptotic region (> 4.0 Å), the bond length of the oxygen molecule has the gas-
phase one of 1.206 Å. As the O₂ molecule approaches the O₃ and O₄ O²⁻ anions of the cluster, the total energy increases, as shown in Figure 6(b). After overcoming the reaction barrier of ~5 kcal mol⁻¹ in which the O₁-O₂ bond breaks, the new O₁-O₃ and O₂-O₄ bonds are formed. The computed IR frequency of the O-O stretching with the 1.201 Å is 1100 cm⁻¹. Comparing with experimental bands using FTIR, it may be assigned to be superoxide ion (O₂⁻).

Table 1. Molecular parameters for O₂, O₂⁻ and O₂²⁻. Bond lengths and vibrational frequencies are in Å and cm⁻¹, respectively.

| Computational method | O₂  | O₂⁻  | O₂²⁻  |
|----------------------|-----|------|-------|
|                      |    |      |       |
| Rₑ                  | 1.206 | 1.221 | 1.346 |
| Rₑ, exptl.          | 1.208 | 1.350 | 1.490 |
| ν(O₁=O₁₆)           | 1633 | 1541 | 1165  |
| ν(O₁=O₁₆), exptl.    | 1580°| 1165 | 1097  |
| ν(O₁=O₁₈)           | 1587 | 1498 | 1132  |
| ν(O₁=O₁₈)           | 1539 | 1453 | 1098  |

a, b. B3LYP/6-311+G(d) and BPW91/6-311+G(d), respectively. c, d. Ref. (22) and ref. (23), respectively.

Figure 6. (a) Geometrical features and (b) schematic energy profile for the dissociation of oxygen on a Mn(OH)₄O₂ cluster model at the B3LYP/6-311+G(d) level of theory. r(O-O) represents the distance of O₁-O₃.

CONCLUSIONS

Preliminary computational studies on oxygen reduction in SOFCs have been carried out with a Mn(OH)₄O₂ cluster model at the B3LYP/6-311+G(d) level of theory. The close agreement of the predicted vibrational frequencies with available experimental values is very encouraging. More detailed computational modeling with a periodic slab model to compute reaction barrier heights and possible intermediates for oxygen reduction on various cathode materials is in progress. We also plan to predict rate constants for the elementary steps involved in oxygen reduction on different cathode materials, which could be used for phenomenological modeling of cathode performance.
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