Effects of Strain on Oxygen Reduction Kinetics in AO- and BO_2-terminated Perovskite Surfaces

Hyunguk Kwon[1], Jeong Woo Han[1,*]
[1]*University of Seoul, Seoul, Republic of Korea*

*E-mail: jwhan@uos.ac.kr

The slow electrochemical reduction of oxygen on the perovskite cathode results in significant efficiency loss, which is a critical limiting factor for development of high performance solid oxide fuel cells (SOFCs). Therefore, improving surface reactivity of perovskite oxides has become an important issue to increase the performance of fuel cell.

Although the surfaces of ABO_3 perovskite materials are composed of two types (AO- and BO_2-terminated), many theoretical studies only have focused on oxygen reduction reactions on BO_2-terminated surfaces because it is expected to have relatively higher catalytic activity due to the B-site cations (transition metals) at topmost layer. Recently, however, Druce et al. reported that transition metals were not experimentally detected at the outmost surface layer in SOFC operating conditions [1]. In addition, it was proved that BO_2-terminated surface as well as AO-terminated surface would participate in oxygen reduction reaction (ORR) [2]. These results imply that both surfaces should be considered to understand cathode reactions in details.

In this study, we thus investigated surface termination-dependent reaction mechanism in $Sr(Ti,Fe)O_3$ (STF) perovskite oxide using density functional theory (DFT) calculations. STF perovskite was selected as a model material for SOFC cathode. According to our previous paper, planar tensile strain reduces migration barrier of oxygen vacancy on the surface of $LaCoO_3$ perovskite oxide, and thus enables to enhance the oxygen reduction reaction (ORR) kinetics [3]. Therefore, the role of strain on the surface reaction depending on the surface termination was studied to suggest useful design principles for improving surface reactivity. Our DFT results showed that surface oxygen vacancy may play an important role for O_2 incorporation in both AO- and BO_2-terminated surfaces. Moreover, migration of oxygen vacancy and adsorbed atomic oxygen were revealed as the key reaction steps. Accordingly, the effects of strain on the two elementary reaction steps were quantitatively assessed. It turns out that lattice tensile strain contributed to reduce migration barrier of oxygen vacancy in both terminated surfaces (Figure 1). However, the responses of the migration barrier on lattice strain were different between the surfaces: the lattice strain has more influence on the migration barrier in BO_2-terminated surface than AO-terminated one. We expect that these results will be useful to specifically understand ORR mechanism at SOFC cathode.

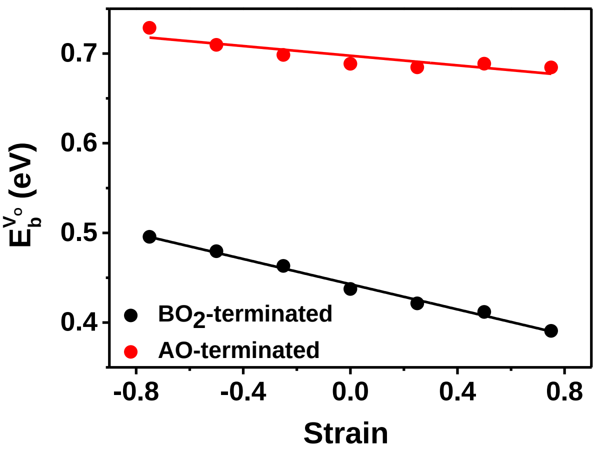

Fig.1 Migration barrier of oxygen vacancy as a function of strain in AO- and BO_2-terminated surfaces.

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