

# Roles of Metal Oxides on the Activity of Fuel Cells Electrocatalysts

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(燃料電池用電極触媒の活性に対する金属酸化物の役割)

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### 論 文 内 容 の 要 旨

Fuel cells are among the potential candidates to help decrease local and global environmental impacts. Decades of research, development, demonstration, dissemination, and governmental involvement led to the commercialization of the polymer electrolyte and solid oxide fuel cells. Their limited commercialization is due to several long-standing issues. Thus several researchers have been focused on finding alternative materials for the next generation fuel cells. Among the targeted materials, metal oxides, and metal oxides-based materials showed not only promising catalytic activities but also improved stabilities. Nevertheless, in some cases, the reason behind this improvement has only been hypothesized and no conclusive results were presented. The development of new theoretical approaches formulated on a molecular level, by means of computer simulation methods are targeted as key tools to obtain sufficient knowledge of the factors determining catalytic activity, which can lead to tailoring catalysts with improved activities and selectivities. In this work, the roles of two different oxides in the catalytic activity of fuel cells electrocatalysts were studied using density functional theory method.

In Chapter 1, a concise introduction about the operating principles, components, materials, benefits, and disadvantages of solid oxide and polymer electrolyte fuel cells is given. The use of BaTiO<sub>3</sub> and Pt-nanoparticles supported on SnO<sub>2</sub> and their limitations when used as fuel cell materials are also described.

In Chapter 2, the theoretical background of the density functional theory method is presented.

In Chapter 3, the role of BaTiO<sub>3</sub> as a solid oxide fuel cell anode was studied. First, the likelihood of the sulfidation of the BaTiO<sub>3</sub>(001) surfaces was estimated via different reaction pathways. Next, the hydrogen oxidation reaction and methane sequential decomposition on pristine BaTiO<sub>3</sub>(001) were studied, and the effect of sulfur on these reactions was evaluated. For the hydrogen oxidation reaction, the presence of sulfur activated the H-H bond, led to the formation of different molecular entities; thus alternative sequences of elementary steps for the reaction to proceed came to light and promoted the formation of some intermediates such as oxygen vacancy formation. On the other hand, for the methane sequential dissociation,

methane activation and the promoted scission of some C-H bonds may be responsible for the mentioned boost in I-V characteristics.

In Chapter 4, the role of SnO<sub>2</sub> as support material for Pt-nanoparticles as polymer electrolyte fuel cell electrocatalyst was investigated based on changes in the nanoparticles' geometrical features, electronic and chemical properties, and stability. The O-atom binding energy was successfully decomposed as a linear combination of the nanoparticles' properties, and a generalized model that can describe the O-atom binding energy considering the variation of the nanoparticle size, adsorption site, and support effect was proposed. SnO<sub>2</sub> has a negative effect on the oxygen reduction reaction as it stabilizes the interaction between the Pt-nanoparticles and oxygenated species that can effectively block the active sites of the Pt-nanoparticles required for the adsorption and dissociation of O<sub>2</sub>. This strong interaction can lead to the formation and later dissolution of PtO<sub>x</sub> during the electrochemical reduction of O<sub>2</sub>. Additionally, SnO<sub>2</sub> weakened the interatomic interaction of the outer-shell atoms of small size nanoparticles, while for Pt-nanoparticles larger than 1.70 nm a slight increase in the Pt-Pt interaction was observed, which in part can explain the higher stability of Pt-nanoparticles when SnO<sub>2</sub> is used as support material.

In Chapter 5, the main results are summarized, the conclusions of this work are outlined, and the future directions are considered.