



# Effect of support materials on platinum lattice strain and its oxygen reduction activity

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## ABSTRACT

The oxygen reduction activities of sputter-deposited platinum (Pt) thin films of various thicknesses on amorphous carbon (a-C), tungsten oxide (WO<sub>3</sub>), and titanium oxide (TiO<sub>2</sub>) were examined to investigate the effect of the support materials. An X-ray diffraction analysis showed that the Pt lattice constant clearly increased with decreasing Pt thickness on the a-C, while it did not change on the WO<sub>3</sub> and TiO<sub>2</sub>. The oxygen reduction activity of the catalysts was measured electrochemically in 0.5 mol/L sulfuric acid at 308 K. The measurements showed that the activity of Pt/a-C catalysts decreased with the Pt thickness. However, decrease of activity was not observed in the Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> catalysts. The correlation between catalytic activity and Pt lattice strain was obtained from these results; Pt lattice expansion, which was observed on the a-C support, resulted in the decrease of catalytic activity for an oxygen reduction reaction. The metal-oxide support, such as the WO<sub>3</sub> and TiO<sub>2</sub>, suppresses the Pt lattice expansion and maintains the Pt catalytic activity in the case of decreasing Pt thickness compared to the a-C support.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are a promising power source owing to their low pollutant emission and high energy-conversion efficiency. The performance of PEFCs has been intensively developed for decades, but improved lifetime, lower cost, and higher efficiency are still needed for extensive commercialization. One component of a PEFC, a cathode catalyst, has a great impact on the lifetime, cost, and efficiency. Platinum nanoparticles on carbon supports are generally used as the cathode catalyst for an oxygen reduction reaction. However, the catalyst performance is reduced in the operation of PEFC due to corrosion of the carbon supports in the high potential condition of the cathode [1,2]. Therefore, alternative non-carbon support material is desired to improve the catalyst durability. In addition, because an oxygen reduction reaction taking place on the cathode has slow kinetics, a large amount of platinum is required, which greatly contributes to the high cost of PEFC. Platinum–alloy catalysts with transition metals, such as iron, cobalt, nickel, chromium, and vanadium, have been extensively studied in order to increase the catalytic activity [3,4]. However, the metallic form of these transition metals is not stable in the cathode condition of PEFCs. Therefore, another method is required to increase the catalytic activity of platinum.

Metal-oxide supports such as titanium oxide (TiO<sub>2</sub>, Ti<sub>4</sub>O<sub>7</sub>) [5–9], niobium-doped titanium oxide (Nb–TiO<sub>2</sub>) [10,11], niobium oxide (NbO<sub>2</sub>) [12], tin oxide (SnO<sub>2</sub>) [9,13,14], tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) [9,15], zirconium oxide (ZrO<sub>2</sub>) [9], and tungsten oxide (WO<sub>3</sub>) [9,16,17] have recently become regarded as a promising support material. Metal-oxide supports are more stable in the high potential condition of a PEFC cathode than carbon supports. Moreover, metal oxides have been reported to enhance the catalytic activity of platinum for an oxygen reduction reaction [5,9–12,15,18,19]. The enhancement is mainly explained by reduction of the hydroxide (OH) inhibitor adsorbed on the platinum surface in the reaction. Possible reasons why the OH inhibitor is decreased by metal-oxide supports include the electronic effect between platinum and the metal oxide [5], lateral repulsion between OH and the metal-oxide surface species [12], and OH spillover to the metal-oxide surface from the platinum surface [18,19]. However, the mechanism of increase in catalytic activity caused by metal oxides is still unclear. With regard to the effect of support materials on the platinum, the metal-oxide supports produce a platinum lattice strain [20,21]. The platinum lattice strain results in changing bond strength of adsorbed species, such as the OH, to platinum surface [22]. There are few reports focusing on the platinum lattice strain caused by the metal oxides and carbon support.

In this work, we investigated the oxygen reduction activity of platinum (Pt) thin films with various thicknesses on amorphous carbon (a-C), WO<sub>3</sub>, and TiO<sub>2</sub>, focusing on the effect on the Pt lattice strain caused by the support materials. Pt/a-C, Pt/WO<sub>3</sub>, and Pt/TiO<sub>2</sub> sputtered on a silicon (Si) substrate were used as model catalysts.

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