

Evaluation of Oxygen Electroreduction on Metal Oxide-supported Platinum Catalysts

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Introduction

Pt catalysts were dispersed as small particles on high-surface-area carbon powders to get a better utilization of Pt. However, many papers have reported that the specific activity decreased with the decrease in Pt particle size on Pt/C (~3nm).¹ On the other hand, Pt alloys with transition metals (Co, Cr, Ni, Fe, etc.)^{2,3} or Pt with metal oxide (WO₃, etc.)^{4,5} have shown the enhanced electrocatalytic activity for ORR with respect to pure Pt. Thus, transition metal or metal oxides might have some effect to Pt characteristics.

In this work, we have investigated the effect of metal oxide supports as base materials to the catalytic activity of Pt cathode. Because of large contact resistance and electric resistance of oxide, it is difficult to evaluate the activity of Pt when the oxide layer is thick. We prepared very thin layer of metal oxides support on glassy carbon rod by RF sputtering and evaluate the catalytic activity of Pt on it using a solid-state cell.⁶

Experimental

The metal oxide supports were deposited onto a glassy carbon rod substrate by RF sputtering. The sintered metal oxide targets (WO₃, V₂O₅, SnO₂, Cr₂O₃) were used in Ar atmosphere. Pt catalyst was deposited onto the metal oxide supports or glassy carbon rod by the RF sputtering. The sputtering pressure in the chamber was 1×10^{-1} Pa. Deposition thickness and Pt loading was measured by the quartz crystal microbalance. The average thickness of a metal oxide was 1nm. Pt loadings were changed from 0.6 to $2.1 \mu\text{g cm}^{-2}$.

The characteristics and the electrocatalytic activity of the ORR were investigated by electrochemical measurements. The electrochemical measurements were carried out in the solid-state cell using Nafion[®]117 at 30 °C.⁶ The sputter-deposited Pt/metal oxide or Pt/glassy carbon (GC) sample was placed at the working electrode position. The electrolyte membrane was sandwiched between the working electrode on the upper side and the counter electrode on the lower side. The counter electrode was platinum foil with Pt black. The reference electrode was the reversible hydrogen electrode (RHE). The contact pressure of the working electrode on the polymer electrolyte was measured with a strain gauge and controlled by a strain control screw. Oxygen or nitrogen gas fed into the cell. They were humidified by passing through a bubbler at 50 °C in order to attain a saturated humidity.

The ORR current density was obtained from the difference in O₂ atmosphere and N₂ atmosphere through the slow sweep voltammetry at 5mV s⁻¹.

Results and discussion

Figs. 1 and 2 show the specific activity i_s and the mass activity i_M , respectively. They were obtained from

the ORR current density of the cathodic sweep at 0.9V vs. RHE on Pt/Metal oxide and Pt/GC catalyst. The real surface area of Pt particle was obtained from H adsorption charges between 0.05 and 0.4V vs. RHE in N₂ atmosphere. For comparison, the activity at Pt loading $21 \mu\text{g cm}^{-2}$ was shown in the same figure.

The specific activity of Pt/V₂O₅ at $2.1 \mu\text{g cm}^{-2}$ showed the highest of all catalysts and is even higher than that of Pt/GC at $21 \mu\text{g cm}^{-2}$. The activity of each specimen do not show the significant change at the loading of $1 \sim 2 \mu\text{g cm}^{-2}$. However, the activity decreases when the loading is less than $1 \mu\text{g cm}^{-2}$ in most case. Further results will be shown to compare the effect of metal oxide supports.

References

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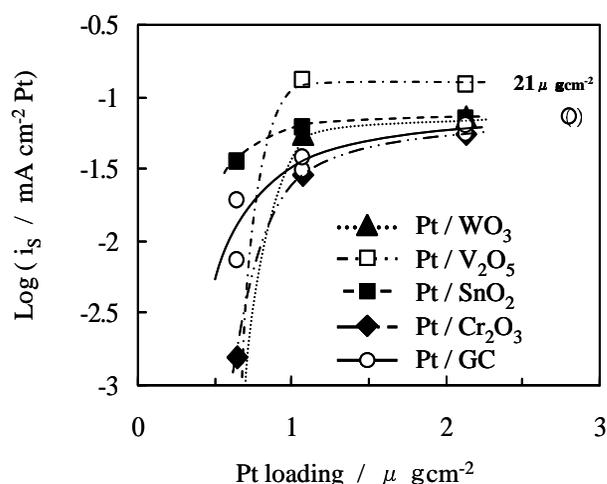


Fig. 1. Relationship between Pt loading and specific activity calculated from the cathodic sweep ORR density at 0.9V (vs. RHE) for on Pt/Metal oxide and Pt/GC electrodes at Nafion[®]117, 5mV s⁻¹, 30°C.

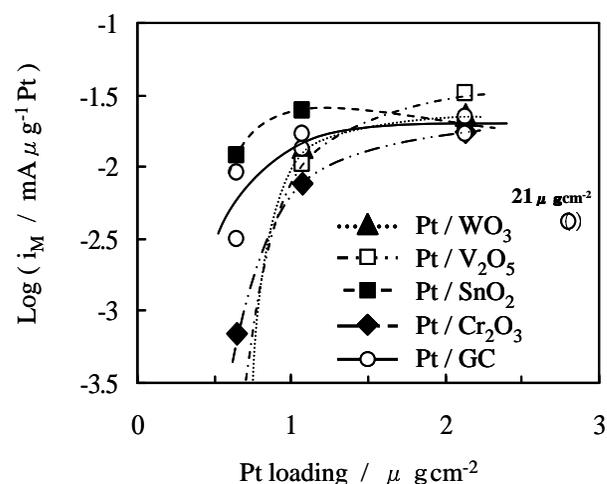


Fig. 2. Relationship between Pt loading and mass activity calculated from the cathodic sweep ORR density at 0.9V (vs. RHE) for on Pt/Metal oxide and Pt/GC electrodes at Nafion[®]117, 5mV s⁻¹, 30°C.