

Deterioration Behavior of Pt in a Pt/Au Nanoparticle-Loaded Carbon Black Catalyst Analyzed by an Accelerated Durability Test

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Introduction

For the reduction of Pt consumption, it is important to improve the mass activity (MA) for oxygen reduction reaction (ORR) in electrocatalyst for polymer electrolyte fuel cells. Pt-based core shell catalyst can reduce the amount of Pt used to a limit, and have high electrocatalytic activity for ORR. Recently, we have succeeded in the preparation of Au nanoparticles loaded-carbon black catalysts (Au-PVA/CB and Au-G/CB) with mean size of *ca.* 3.3 nm and *ca.* 2.5 nm by using CO as a reducing agent in KAuCl_4 aqueous solution containing polyvinyl alcohol (PVA)¹ and glutathione (GSH) as a stabilizer respectively. Those catalysts heat-treated in order to remove a stabilizer (Au-PVA/CB-HT and Au-G/CB-HT), and particle size increased slightly and was set to 3.5 ± 0.7 nm and 2.8 ± 0.5 nm, respectively. On the other hand, MA at 0.9 V vs. RHE of Pt/Au-G/CB-HT catalyst is higher than that of Pt/Au-PVA/CB-HT catalyst. Shao et al. have reported that if the particle size of Au core is prepared small, MA will improve.² Because the compressive strain of Pt monolayer become large and binding energy of Pt-O become weaker. Moreover, if small Au nanoparticle is prepared, the degradation of durability by solid solution formation of Pt and Au can be suppressed. Durability of Au-G/CB-HT has also better than that of commercial Pt/CB (Pt/CB-TKK, TEC10E50E). In this study, we evaluated the degradation factor under durability test by measuring Pt surface area, the amount of Pt dissolution, and particle size in any number of cycles of a Pt/Au-G/CB-HT catalyst.

Experimental

The Au nanoparticles was prepared by bubbling CO in KAuCl_4 aqueous solution containing GSH at 4 °C for 90 s and then Ketjen Black was added into it, followed by sonicating for 60 min. The Au-G/CB was heat-treated at 300 °C under vacuum. The content of Au in the Au-G/CB-HT was *ca.* 19 wt. %. Pt monolayer was deposited by using galvanic displacement of Cu-upd monolayer on Au nanoparticles.^{1,3,4} For Pt/Au/CB, the Au size of Pt/Au nanoparticles were evaluated by transmission electron microscope. To evaluate electrochemical properties of the Au-G/CB and Pt/Au-G/CB-HT catalysts, a Nafion-coated GC disk electrode was prepared according to the previous procedure.¹ The ORR activity for the Pt/Au/CB was evaluated in an O_2 -saturated 0.1 M HClO_4 aqueous solution at 25 °C by rotating disk electrode method. Durability against Pt dissolution of the Pt/Au/C was tested using square-wave potential cycling between 0.6 V for 3 s and 1.0 V for 3 s at 60 °C.^{1,3}

Results and Discussion

From hydrodynamic voltammograms, the current for ORR commenced to increase at *ca.* 1.0 V and reached the diffusion limiting current at *ca.* 0.6 V. From the slope of Koutecky-Levich plots, the number of electrons in ORR was evaluated to be 4, suggesting that the reduction of oxygen to water proceeded preferentially. Fig. 1 shows

the normalized surface area of Pt with potential cycling to evaluate durability against the dissolution of Pt for the Pt/Au-G/CB-HT, Pt/Au-PVA/CB-HT and Pt/CB-TKK electrodes. The normalized surface area was defined as the percentage of electrochemical surface area (ECSA) of Pt at *n*th cycle to initial cycle. The durability for the Pt/Au-G/CB-HT electrode was superior to the Pt/Au-PVA/CB-HT electrode. Fig. 2 shows the particle size for the Pt/Au-G/CB-HT electrode. The particle size did not increase between 0 and 500 cycles; however, the solid solution may have already formed, because specific surface area of Pt decreased. The particle size increased by *ca.* 0.5 nm after 2000 cycle. From 2000 to 10000 cycles, the particle size did not increase. Thus, the decrease in durability was consistent with the formation of the solid solution between 0 and 1000 cycles and the dissolution and re-precipitation of Pt from 1000 to 2000 cycles.

Acknowledgement

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) through the industrial technology research grant program (08002049-0).

References

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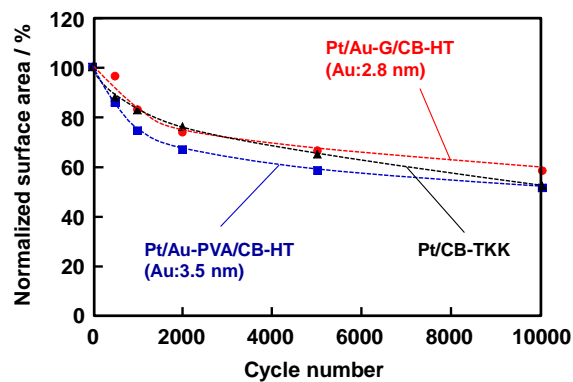


Fig. 1 Change in normalized surface area of Pt with cycle number for each electrode at 60 °C.

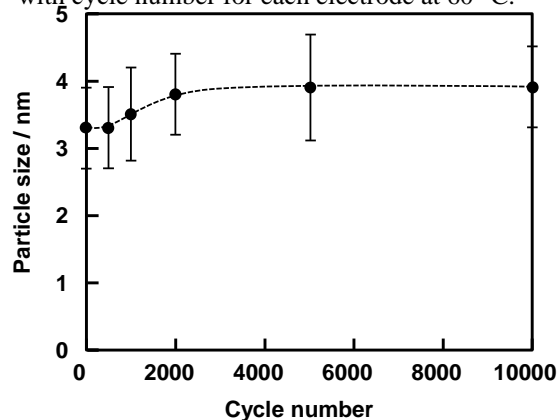


Fig. 2 Change in particle size of Pt/Au-G/CB-HT with cycle number at 60 °C.