

Effect of Agglomeration of Pt/C Catalyst on Hydrogen Peroxide Formation

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A long life over 90,000 hours (= 10 years) is required for polymer electrolyte fuel cell (PEFC) stacks in the small-scale cogeneration systems; however, sufficient durability to meet this demand has not been established. Hydrogen peroxide formation, which is formed electrochemically or chemically during operation, is one of the potential deteriorating factors of PEFCs.¹⁾ Oxygen reduction reaction (ORR) on clean bulk Pt surface has been thoroughly studied for decades, and it is widely believed that oxygen is reduced predominantly to water through direct 4-electron reduction. We recently found that a large amount of H₂O₂ is formed on Pt/C catalysts when they are highly dispersed on GC. Here we report the effect of agglomeration of Pt/C on H₂O₂ formation by using the rotating ring-disk electrode (RRDE) technique.

The RRDE (Nikko Keisoku) consisted of a glassy carbon (GC) disk and a platinum ring. Various amounts of 20 wt.% Pt/C catalysts (56.7–5.7 μg_{carbon} cm⁻²) were loaded on glassy carbon (GC) disk electrode. Fig. 1 shows optical micrographs of 20 wt.% Pt/C catalysts dispersed on GC with different amounts. The catalysts loaded with 56.7 μg_{carbon} cm⁻² were highly agglomerated, and formed a thick layer on GC (Fig. 1a and e). The agglomeration decreased with a decrease in the loading amount of Pt/C. The catalysts loaded with 5.7 μg_{carbon} cm⁻² seemed highly dispersed at a low magnification (x 50); however, agglomerates of about 10 μm were still observed at a high magnification (x 500).

Cyclic voltammograms at GC loaded with various amounts of Pt/C are compared in Fig. 2. The currents per mass of Pt for characteristic peaks of Pt increased with decreasing Pt/C loading, which indicates that mass activity increased with decreasing Pt/C loading. This is reasonable, because agglomeration of the Pt/C catalysts was enhanced with an increase in Pt/C loading as shown in Fig. 1. Fig. 3 shows current-potential relations for O₂ reduction at Pt/C with different loadings. The onset of cathodic O₂ reduction current (*I_D*) shifted positively with an increase in Pt/C loading on GC. This is due to an increase in the total amount of platinum. On the other hand, the ring current (*I_R*), which is oxidation current of H₂O₂ formed at the disk electrode, was detected at potentials more negative than 0.8 V, and increased with lowering the disk potential. *I_R* increased with a decrease in Pt/C loading on GC, which indicates that the ratio of H₂O₂ formation increases with a decrease in agglomeration of Pt/C. For each electrode, a significant increase in *I_R* was observed in the H_{upd} region (< 0.20 V), which is generally attributed to the blocking effect of the adsorbed hydrogen atoms on the dissociative adsorption of oxygen molecules.³⁾ Here H₂O₂ formation increased with a decrease in agglomeration of Pt/C.

From these results, it is concluded that the formation of H₂O₂ is enhanced with a decrease in agglomeration of Pt/C and series 2-electron reduction pathway, which is negligible on clean bulk Pt surface, does exist on Pt particles supported on carbon. However, in agglomerated state, water is predominantly formed through apparent 4-

electron reduction, which results from the series 4-electron reduction or catalytic decomposition of H₂O₂ at nearby Pt/C catalysts in the agglomerates. The facts obtained in the present study would be a key to clarify the mechanism for H₂O₂ formation in the MEAs and the resulting deterioration of the MEAs of PEFCs.

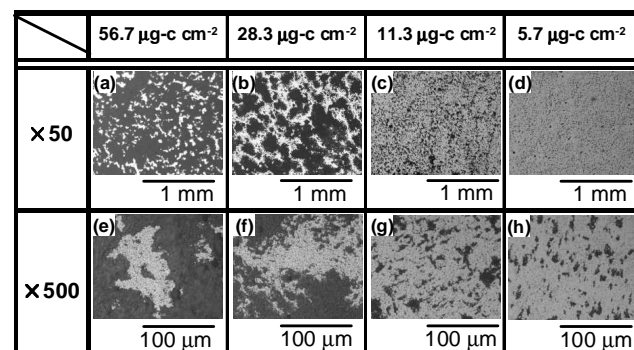


Fig. 1. Optical micrographs of 20 wt.% Pt/C dispersed on GC. Pt/C loadings: (a, e) 56.7, (b, f) 28.3, (c, g) 11.3, and (d, h) 5.7 μg cm⁻²

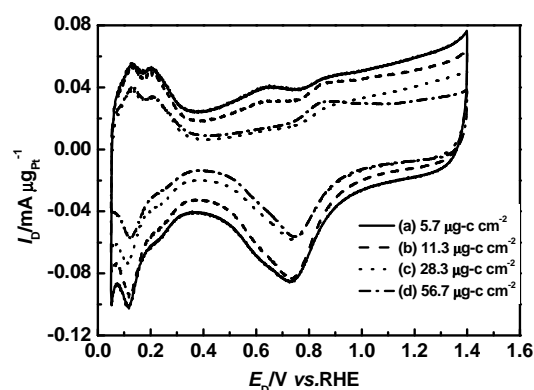


Fig. 2. Cyclic voltammograms at 20 wt.% Pt/C loaded with different amounts on GC in 1 M HClO₄ under argon atmosphere.

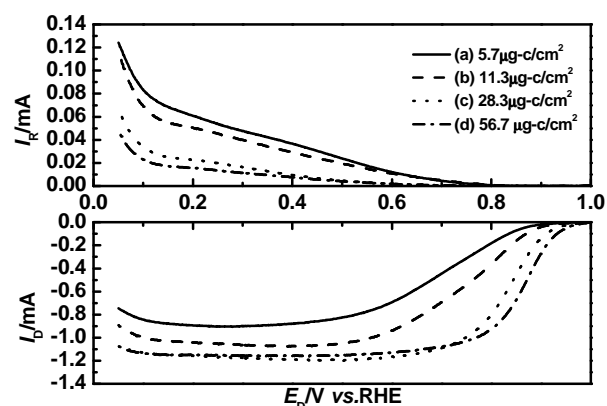


Fig. 3. Hydrodynamic voltammograms for oxygen reduction in 1 M HClO₄. Disk electrodes: 20 wt.% Pt/C loaded with different amounts on GC, Ring electrode: Pt. Rotating rate: 900 rpm.

Reference

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