Influence of surface geometry of carbon support for migration and aggregation behavior of Pt nanoparticles during potential cycling conditions

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Abstract: The migration behavior of Pt particles supported on the outside surface of ordered mesoporous carbon powder during potential cycling measurement was studied. Monodispersion of Pt nanoparticles was successfully obtained by the arc plasma deposition technique. By use of high resolution STEM measurements, identical location observations were obtained of Pt particles supported on carbon powders before and after the potential cycling. From these measurements, we found that surface gaps formed between the carbon rod bundles of the mesoporous carbon have an important role in suppression of Pt migration and aggregation.

Keywords: PEFC, Carbon supported Pt catalyst, Migration and aggregation of Pt nanoparticles.

1. Introduction

In order to improve durability of Pt/C-based cathode catalyst used by fuel cell vehicles, suppression of migration and aggregation of Pt particles supported on carbon substrates is a crucially important issue. To overcome this obstacle, many researchers are struggling to improve properties of support materials from the viewpoints of composition, crystallinity and porosity of the support materials. Practically, Pt particles that are catalytically active are limited to those located near the outside surface of a carbon support, because the formation of a three-phase interface between Pt particles, carbon support and electrolyte is required. Considering this point, an understanding of the effect of geometrical structures on the carbon support surface for the migration behavior of Pt particles is important. In this study, the migration behavior of Pt particles supported on the outside surface of a carbon powder support with ordered surface structure was investigated.

2. Experimental

An ordered mesoporous carbon powder CMK-3 was synthesized according to the literature.[1] Pt was deposited on the carbon powder by the arc plasma deposition (APD) technique. For comparison, Pt/CB prepared by APD and a commercial Pt/CB were also tested. Potential cycling measurements were carried out using a conventional three electrode cell according to FCCJ protocol (potential step cycles between 0.6 V and 1.0 V vs. RHE, in 0.1 M $HClO_4$ solution, 65 ºC). The distribution of Pt particles at the same location of the samples before and after the electrochemical measurement was observed by high-resolution scanning transmission electron microscopy (STEM).

3. Results and discussion

As seen in Figure 1, highly dispersed Pt nanoparticles were formed on CMK-3 support surface uniformly. Figure 2 shows changes in the distribution of Pt particles before and after the potential cycling measurement for Pt/CMK-3(APD): (a, d), Pt/CB(APD) prepared by APD: (b, e) and commercial Pt/CB(COM): (c, f) observed in the secondary electron (SE) image mode using STEM. As shown in Figure 2 (a) and Table 1, nearly monodisperse Pt particles with 2.3±0.6 nm average diameter were formed on the CMK-3 support. In the case of the CB-support (b), slightly larger particles with 3.1±0.6 nm diameter were formed. As seen in Figure 2(c), the Pt/CB(COM) sample showed a wider distribution of Pt particles. After 3000 cycles of potential cycling, significant growth of Pt particles was observed for all samples. However, it is noteworthy that, in the case of the Pt/CMK-3 sample, more than 30% of the Pt particles with diameter smaller than 3 nm were still remaining even after the measurements, while in the case of Pt/CB(APD) and Pt/CB(COM), most of the fine Pt particles were diminished in number. As shown in Table 1, the remaining fraction of the fine particles (< 3 nm) for Pt/CMK, Pt/CB(APD) and Pt/CB(COM) were 32%, 6% and 12%, respectively. In the case of Pt/CB(COM), because the size distribution of Pt at the initial stage was wider, Ostwald ripening may easily take place under the potential cycling conditions. Detailed microscopic measurements revealed that fine Pt particles deposited along the gaps between the carbon rod bundles of the CMK-3 powders tended not to migrate, and particle growth was remarkably suppressed. The gap distance estimated for the geometrical structure of CMK-3 was approximately 3.5 nm, which was comparable with the size of the Pt particles. From these results, we conclude that narrow gap-like structures consisting of carbon bundles contribute significantly to the suppression of Pt migration and aggregation. In this study, effect of the gap-distance and surface group of carbon support on the migration behavior of Pt nanoparticles will be discussed deeply.

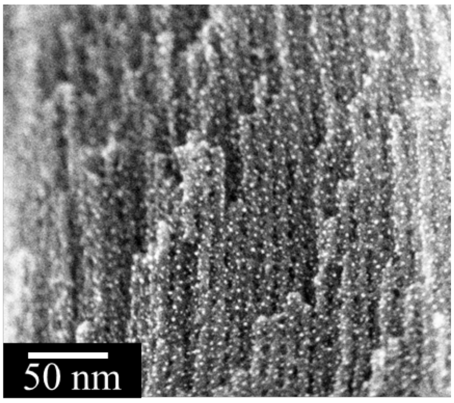

Figure 1. STEM images of fresh Pt/CMK-3 sample

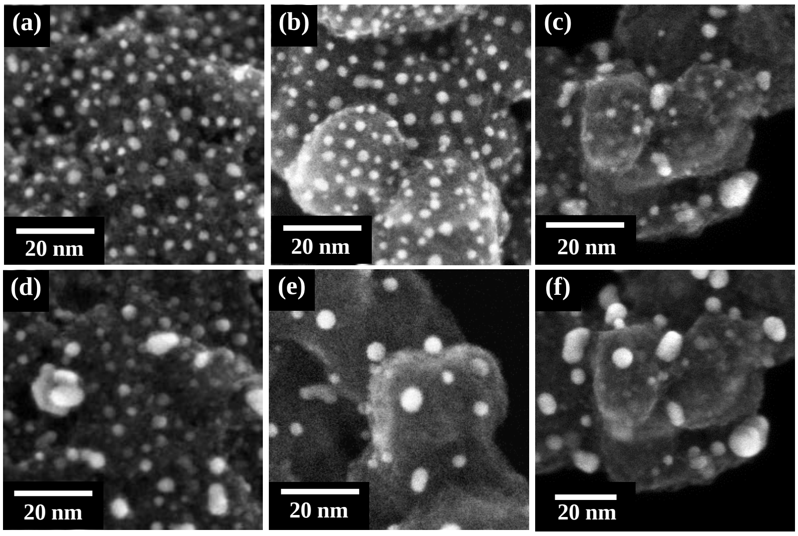

Figure 2. STEM images for Pt/carbon samples, (a, d) Pt/CMK-3(APD), (b, e) Pt/CB(APD), (c, f) Pt/CB(COM), (a, b, c) fresh, (d, e, f) after potential cycling test (65 °C, 3000 cycles).

Table 1. Changes in average diameters of Pt particles and remaining fractions of Pt particles with size smaller than 3 nm after the potential cycling test

Samples	Average diameter of Pt (nm)		Fraction of Pt particles smaller than 3 nm in diameter*, %	
	fresh	after test	fresh	after test
Pt/CMK-3(APD)	2.3±0.6	3.9±1.4	98	32
Pt/CB(APD)	3.1±0.6	4.4±1.0	76	6
Pt/CB(COM)	3.2±1.3	5.9±1.8	73	12

*Fraction of Pt particles with diameter smaller than 3 nm in all Pt particles before and after the potential cycling test

4. Conclusions

Monodisperse Pt nanoparticles were successfully deposited on CMK-3 powders by the APD technique. Identical location STEM measurements revealed that Pt particles supported on gap-like structures between carbon rod bundles were prevented from migration and aggregation under the potential cycling conditions, while most of the fine Pt particles supported on the conventional CB support were diminished in number.

References

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