

Durability of Cathode Catalysts under Gas Exchange Start-up Operation for Fuel Cell Vehicles

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Polymer electrolyte fuel cells directly convert chemical energy to electrical energy with high efficiency.^{1,2} In the PEFC, Pt nanoparticles dispersed on high surface area carbon black (CB) supports are used as the cathode catalyst. However, it has been found that Pt/CB cathode catalysts are degraded under PEFC operating conditions due to a combination of processes, which include loss of electrochemically active surface area (ECA) due to agglomeration or dissolution of Pt nanoparticles, and corrosion of the CB supports.³ During the start-stop cycles of fuel cell vehicles (FCVs), the cathode potential can momentarily climb to more than 1.5 V due to the so-called “reverse current mechanism”, which significantly accelerates the carbon corrosion.⁴ In order to reduce the cost of PEFCs, it is necessary to reduce the amount of Pt by improving the durability, especially for the cathode. To mitigate the corrosion of the carbon support, the use of graphitized carbon blacks (GCB), for which there is a high degree of graphitization, was found to be effective.

In this research, we focused on the start-up process of the actual FCV operation. The carbon-supported Pt catalysts were tested by the practical start-up process, i.e., the anode gas was successively cycled between air, hydrogen, and nitrogen. First, air was supplied to the anode and cathode for 90 seconds. Second, H₂ gas was introduced to the anode to start-up the fuel cell for 90 seconds. Finally, N₂ gas was supplied to the anode and cathode for 60 seconds. These three steps were defined as one cycle. The effect of the start-up process on the cell performance was evaluated using three types of catalysts (commercial 50 wt%-Pt/GCB (Pt/GCB), commercial heat-treated 50 wt%-Pt/GCB (Pt/GCB-HT) and 30 wt%-Pt/GCB prepared by the nanocapsule-method (n-Pt/GCB) supplied by Tanaka Kikinokogyo K.K.). The average Pt particle sizes of Pt/GCB, Pt/GCB-HT and n-Pt/GCB were 3.4 ± 0.7 nm, 7.0 ± 2.0 nm and 4.0 ± 0.8 nm, respectively. All of the catalysts were tested for 1000 cycles. The *I-V* performances were evaluated under O₂ and air at 65 °C with 100% RH before and after the durability test, which consisted of given numbers of start-up cycles (N). Cyclic voltammetry (CV) was also examined to estimate the ECA under N₂ at the cathode and H₂ at the anode at 65 °C and 100% RH.

Figure 1 shows the changes of ECA values for each catalyst. Pt/GCB-HT exhibited a lower decrease rate for ECA than the other catalysts. However, Pt/GCB-HT exhibited the lowest ECA values both before and after the

durability test for all cycle numbers. On the other hand, n-Pt/GCB had the highest ECA values both before and after.

Figure 2 shows the changes of the current density at 0.70 V before and after the durability test for each catalyst. Pt/GCB-HT, consistent with the changes of the ECA values, indicated a lower decrease rate of the current density, and had lower current density than the other catalysts. Pt/GCB and the n-Pt/GCB showed nearly the same initial current density. However, n-Pt/GCB exhibited a higher current density than Pt/GCB after 1000 cycles. From these electrochemical measurements, it was found that n-Pt/GCB had higher performance and higher durability compared with those for the Pt/GCB and Pt/GCB-HT catalysts.

We also investigated the catalyst layers in detail by post-analysis, in which we used Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and the glancing incidence X-ray diffraction (GIXD) method.

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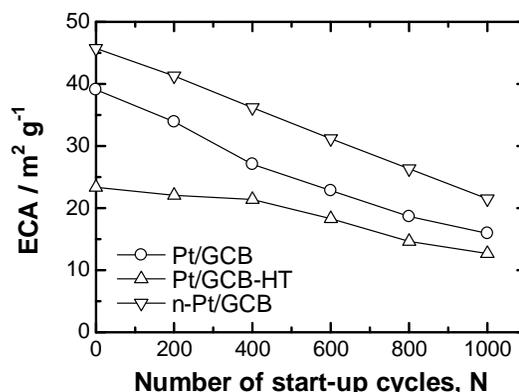


Fig. 1. Plot of the progress of ECA values for Pt/GCB, Pt/GCB-HT and n-Pt/GCB catalysts.

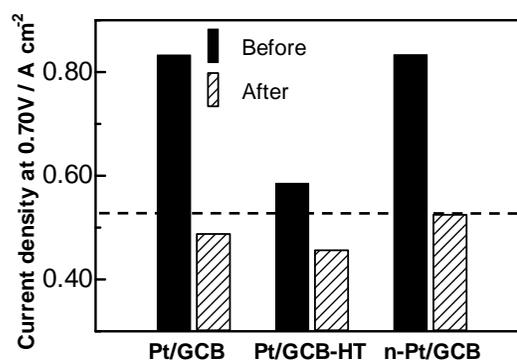


Fig. 2. Current density at 0.70 V before and after the durability test for Pt/GCB, Pt/GCB-HT and n-Pt/GCB catalysts.

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