Evaluation of MEAs prepared by Pt/C catalysts with improved durability through the heat treatment

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Introduction

Polymer electrolyte fuel cells (PEFCs) are attractive power devices for both stationary and automobile application. Nevertheless, durability is still one of major obstacles to develop next generation PEFCs for further improvement. Platinum catalyst degradation due to the electrochemical oxidation (corrosion) of carbon supports is known to be one of the most serious problems for traditional PEFCs. Objective of our research is to develop electrocatalysts with high durability by designing the nanostructure of carbon supports through the systematic heat treatment of commercially available carbon black materials.

In this research, we have synthesized eight different Pt/C catalysts through the heat treatment of carbon supports at different temperatures and examined their durability in both half-cell and full-cell.

Experimental

Two kinds of commercially available state-of-the art carbon materials, Vulcan XC-72 (VC) and Ketjen Black EC600-JD (KB) were selected for the carbon sources in this study. With the aim of graphitizing the surface of carbon materials, they were heat treated at 1100°C, 1600°C and 2000°C, respectively. Then, platinum was deposited using platinum (II) acetylacetonate as a precursor[1]. The amount of platinum on carbon was controlled at about 20 wt%.

Electrochemical analyses were carried out for each catalyst by using the three electrode half-cell setup. Durability was evaluated in terms of electrochemically active surface (ECA) of platinum and oxygen reduction reaction (ORR) activity. For durability analysis, the potential cycle test demonstrating start/stop cycles of FC vehicles was applied using the protocol recommended by Fuel Cell Commercialization Conference of Japan (FCCJ) in 2011[2]. Nanostructures of Pt/C catalysts were also characterized by using transmission electron microscopy (TEM).

For MEAs, small cells with the electrode area of 0.5 cm^2 were prepared (Fig.1). Pt amount was kept as 0.3 mg/cm^2 on each electrode side. Current-voltage characteristics along with their durability were evaluated.

Results and discussion

According to physical properties of obtained carbon materials, BET surface area had a tendency to decrease more with higher heat treatment. This is associated with the increase in more crystallized surface as a consequence of the removal of amorphous surface by the heat treatment. The crystallized carbon surface, graphite-like layers, was also confirmed by carefully comparing TEM images of Pt/VC and Pt/GVC1600 (carbon heat-treated at 1600°C) catalysts (Fig.2). Even though BET surface was somewhat lost by the heat treatment, platinum particles were adequately dispersed on the carbon even though agglomeration started seen for samples heat treated at 2000°C. The size of platinum was within the range of 2 to 3 nm for all samples.

After the potential cycle test (up to 60000 cycles), all Pt/C catalysts showed the tendency to lose their ECAs and ORR activity. However, Pt/GVC1600 showed the highest retention of them, resulting in highest durability. Although carbon treated at 2000°C had highest graphitization degree, the durability was rather lower. This can be explained by the fact that the interaction between platinum nanoparticles and carbon is weakened owing to the smoothened carbon surface, where platinum agglomeration and detachment easily occur. TEM observation also supported obtained electrochemical results. The same tendency was also observed for KB samples.

We have found that too graphitized carbon surface rather results in lowering the durability of electrocatalysts. Therefore, the heat treatment at an adequate temperature is necessary to have graphitized carbon surface and good interaction of platinum and carbon at the same time. In our case, we have found graphitization at 1600°C is an optimum condition to develop highest durability for Pt/C catalysts[3].

For our next step, we have started to develop and evaluate MEAs using our electrocatalysts with high durability. The graphitized carbon surface, resulting in more hydrophobic characteristic, has led to improving a flooding problem. Details of the durability of MEAs will be also discussed.

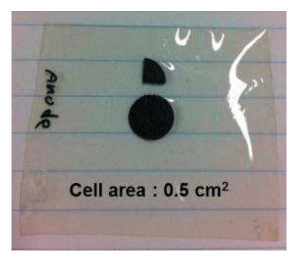

Fig.1 Photograph of MEA used in this study.

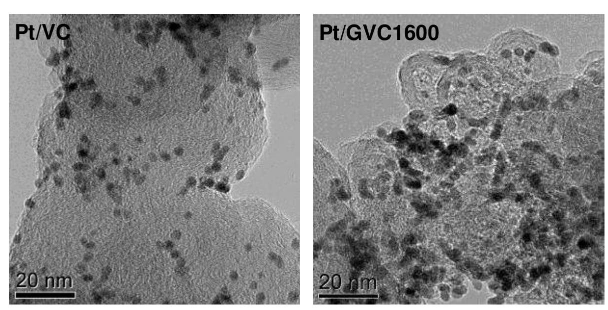

Fig.2 TEM images of Pt/VC and Pt/GVC1600.

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