

Improvement in Durability of Carbon Black-Supported Pt Cathode Catalysts Available Commercially for PEFC by Silica-Coating

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Abstract: To improve the durability of the commercial carbon black-supported Pt (Pt/CB) cathode catalysts for polymer electrolyte fuel cell (PEFC), the catalysts were covered with silica layers by using 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS). The activity and durability of the Pt/CB catalysts covered with silica layers (SiO₂/Pt/CB) was evaluated using membrane electrode assembly (MEA) and rotating disk electrode (RDE) in 0.1 M HClO₄ electrolyte. The SiO₂/Pt/CB showed high durability compared to the Pt/CB catalysts for the repeated potential cycling in the experiment using MEA and RDE. The silica layers which wrapped around Pt metal particles prevented the increase in Pt particle size during the operation of PEFC.

Keywords: PEFC, Pt cathode catalysts, Silica-coating

1. Introduction

The polymer electrolyte fuel cells (PEFCs) are promising alternative power devices because of low emission of pollutants, high energy efficiency and quick start-up. A lot of Pt metal have been utilized for oxygen reduction reaction (ORR) at cathode in PEFCs. The amount of expensive Pt metal at cathode should be reduced as much as possible. However, it is difficult to reduce the amount of Pt metal because of low durability of the catalysts. Pt metal particles easily migrate and aggregate on carbon supports and Pt metal is easily dissolved and redeposited (Ostwald ripening), because Pt catalysts should work under severe conditions such as low pH, high positive potential, high temperature, and oxygen atmosphere. Size of Pt metal particles thus increases during the PEFC operation¹⁻³. Increase in the Pt particle size causes a decrease of electrochemically active surface area (ECSA) of the catalyst. Therefore, high durability of the cathode catalysts are strongly required for wide spread of PEFCs.

We have prepared silica-coated Pt catalysts for the cathode of PEFCs⁴. We have used carbon nanotube support for Pt mainly because of high durability under the cathode conditions. In general, Pt metal particles with a few nanometers are densely supported on carbon black supports in commercial Pt catalysts for PEFCs. Therefore, we covered carbon black-supported Pt (Pt/CB) catalysts commercially available with silica layers to improve the catalyst durability at cathode in the present study. The silica layers prevented the increase of Pt particle size during PEFC operation, which resulted in the improvement of the catalyst durability at cathode.

2. Experimental

The coverage of Pt/CB with silica layers was performed by utilizing the hydrolysis of 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS). The catalytic activity for the ORR and the durability were evaluated with rotating disk electrode (RDE) method in 0.1 M HClO₄ electrolyte. Additionally, highly active and durable silica-coated Pt/CB was used as cathode catalysts in membrane electrode assembly (MEA) for the single cell.

3. Results and discussion

The catalytic activity of Pt/CB and SiO₂/Pt/CB for the ORR was evaluated using a conventional three electrode cell in 0.1 M HClO₄ electrolyte. Pt/CB showed high activity for the ORR in the experiment using a RDE method. The coverage of Pt/CB with silica layers of 18 wt% slightly reduced the activity for the ORR.

However, the coverage with silica layers improved the durability of Pt/CB. In the durability test, the potential of the catalysts was repeatedly changed between 0.6 and 1.0 V vs RHE in N_2 -purged 0.1 M $HClO_4$. The Pt/CB was seriously deactivated for the ORR. In contrast, the catalytic activity of the $SiO_2/Pt/CB$ for the ORR did not change significantly during the durability test. Additionally, we measured TEM images of the Pt/CB and $SiO_2/Pt/CB$ catalysts before and after the durability test. The results indicated that the increase in the size of Pt metal particles in the $SiO_2/Pt/CB$ during the durability test did not change very much, although the size of Pt metal particles in the Pt/CB significantly increased. These results indicated that the coverage with silica layers improve the durability of Pt/CB in the experiment using half-cells.

Figure 1 shows the polarization curves of the PEFC single cells with Pt/CB and $SiO_2/Pt/CB$ cathode catalysts before and after the durability test. Cell voltage of the single cells was repeatedly changed between 0.6 and 1.0 V for the durability test. The current density for the fresh $SiO_2/Pt/CB$ in the range of cell voltage of 0.85 to 0.10V was inferior to that of the fresh Pt/CB. These results suggested that silica layers which wrap around Pt metal particles work as barrier for the diffusion of oxygen and water molecules. However, the current density for the $SiO_2/Pt/CB$ around 0.85 - 0.70V maintained to high values, while the Pt/CB was seriously deactivated during the durability test. The current density at 0.7 V for the Pt/CB was reduced by 50% during the durability test, while the current density at 0.7 V for the $SiO_2/Pt/CB$ did not change appreciably during the durability test. Figure 2 shows cyclic voltammograms (CV) of Pt/CB and $SiO_2/Pt/CB$ catalysts before and after durability test. ECSA was calculated from the electric charges of hydrogen adsorption on Pt metal. ECSA of Pt/CB decreased from 60 $m^2/g-Pt$ to 24 $m^2/g-Pt$ during the durability test. In contrast, the ECSA for the $SiO_2/Pt/CB$ decreased from 45 $m^2/g-Pt$ to 27 $m^2/g-Pt$. These results indicate that the coverage with silica layers improves the durability of the Pt/CB under the cathode conditions of the single cells.

4. Conclusions

$SiO_2/Pt/CB$ catalysts showed high durability compare to commercial Pt/CB catalysts under the severe cathode conditions in PEFCs. The silica layers prevent the migration of Pt metal particles on the supports and the dissolution and redeposition of Pt metal during PEFC operations.

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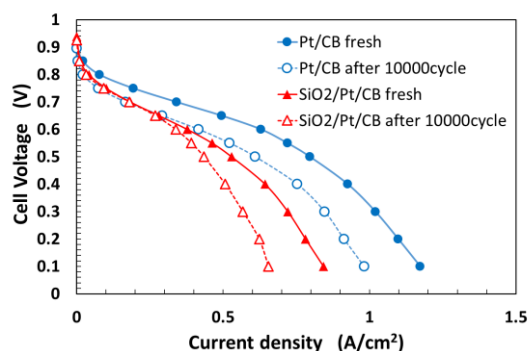


Figure 1. Polarization curves for the PEFC single cells with Pt/CB and $SiO_2/Pt/CB$ cathode catalysts during the durability test. H_2 and air were supplied to the anode and cathode, respectively at 353K

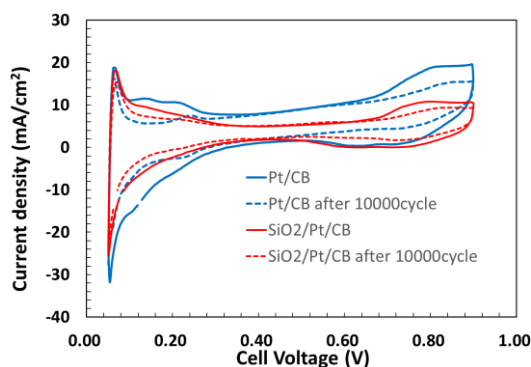


Figure 2. CVs for the Pt/CB and $SiO_2/Pt/CB$ cathode catalysts in MEAs during the durability tests.