

# Formation of Pt-free Fuel Cell Catalyst with Highly Developed Nano-space by Carbonizing Catalase

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Utmost reduction of platinum used as a catalyst for electrodes in a polymer electrolyte fuel cell is required to make the technology feasible. In the present study, the formation of a platinum-free catalyst from a natural organic compound, catalase, was achieved.

Recently, Lai et al. found that an iron enzyme, catalase, immobilized on glassy carbon (GC) electrodes had the activity for O<sub>2</sub> reduction in 0.1 mol dm<sup>-3</sup> potassium phosphate buffer at pH 8.0.<sup>1</sup> Catalase consists of four equal subunits (molecular weight: 57000) containing Fe(III) porphyrin. However, the enzyme would be hydrolyzed in the superacidic atmosphere of the polymer electrolyte.

The idea occurred to us that carbonization of catalase would produce a stable and active catalyst for O<sub>2</sub> reduction with the active site homogeneously dispersed in a carbon matrix, due to inherent inclusion of the Fe(III) porphyrin. Probability of absence of the moiety on the surface of the carbonized material was the problem of this idea, but it would be overcome by just developing pores inside the material (activation) to expose the moiety to the pore surface. Slow transfer of O<sub>2</sub> and H<sup>+</sup> in the pores might cause another problem; however, it would also be overcome by CF<sub>3</sub>SO<sub>3</sub>H adsorption in the pores, since we recently revealed that effective utilization of the nano-spaces in activated carbon loaded with Pt, achieved by the CF<sub>3</sub>SO<sub>3</sub>H adsorption that enabled fast mass-transfer, produced a highly active catalyst for O<sub>2</sub> reduction in PEFC.<sup>2</sup>

The carbonisation was carried out in 0.1 dm<sup>3</sup> min<sup>-1</sup> of Ar flow at 700, 750, 800, 850, 900, and 1000 °C for 2 h after raising temperature at 5 °C min<sup>-1</sup>. For convenience, the catalase carbonised at 700 °C is hereafter called CC700 and the others in a similar manner. The pore structure of CC700, CC750, CC800, and CC850 was characterized by N<sub>2</sub> adsorption isotherms at -196 °C. The heat-treatment at above 900 °C shrank the carbonized material to result in hardening it and destroying the porous structure. The specific surface areas and the mean pore diameters determined by the isotherm data were: CC700, 290 m<sup>2</sup> g<sup>-1</sup>, 2.04 nm; CC750, 449 m<sup>2</sup> g<sup>-1</sup>, 2.04 nm; CC800, 790 m<sup>2</sup> g<sup>-1</sup>, 2.22 nm; CC850, 975 m<sup>2</sup> g<sup>-1</sup>, 3.53 nm. The 50 °C difference in temperature caused the great difference in the pore structure. The surface areas of CC800 and CC850 were as large as that of commercial activated carbon. In addition to these values of specific surface area and mean pore diameter, differential pore-volume distributions of CC700, CC750, CC800, and CC850 (Fig. 1) confirmed significant development of nano-space in the carbonized material, which was formed in a single step simply by carbonization; the activation step was unnecessary.

An aliquot of 100 mg of finely ground carbonized material and 10 mg of carbon black as an electron-conductive agent were added to 1 ml of the Nafion<sup>®</sup> solution to give a catalyst paste after ultrasonic dispersion. CC850 could not be used since strength of CC850 was low. One microliter of the paste was pipetted onto the surface of a rotation glassy carbon disk electrode

(diameter, 3 mm) to form a catalyst layer. A catalyst layer was also formed from CC800 with CF<sub>3</sub>SO<sub>3</sub>H adsorbed in the pore. A catalyst layer without the carbonized material was formed similarly from 10 mg of the carbon black and 1 ml of the Nafion<sup>®</sup> solution for comparison. A conventional catalyst layer was also formed from 10 mg of Pt/C and 1 ml of the Nafion<sup>®</sup> solution. Oxygen reduction currents at the catalyst layers were measured in O<sub>2</sub>-saturated 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub> at various angular frequency of rotation ( $\omega$ ). The activities of the catalyst layers for O<sub>2</sub> reduction were evaluated using the reduction current free of the influence of mass transfer in the solution ( $I_K$ ) determined as the current at  $\omega \rightarrow \infty$ .

The relationships between electrode potential and  $\log(-I_K/A)$  (Tafel plots) was shown in Fig. 2. The activity for O<sub>2</sub> reduction at the catalyst layers formed from the carbonized material was significantly larger than that at the layer without it, formed only from carbon black, and increased with increase in the heat-treatment temperature. The increase in the number of the active sites caused by the development of micropore could essentially yield the increase in  $-I_K$ . In addition, the heat-treatment at 800 °C would produce the catalyst of maximum activity, according to the previous studies. The combination of these two effects substantially changed  $-I_K$  with only 50 °C change in the heat-treatment temperature. Adsorption of CF<sub>3</sub>SO<sub>3</sub>H in the pore of CC800 achieved further increase in  $-I_K$ , attributed to the fast mass-transfer in the pore. The activity was inferior to the conventional Pt/C catalyst layer containing Pt whose weight was nearly equal to that of Fe in the CF<sub>3</sub>SO<sub>3</sub>H-adsorbed CC800 layer, except the low potential region. The activity will be further improved by optimization of the carbonization condition including atmosphere and heat-raising speed, and of the method for the catalyst layer formation, such as particle size and composition.

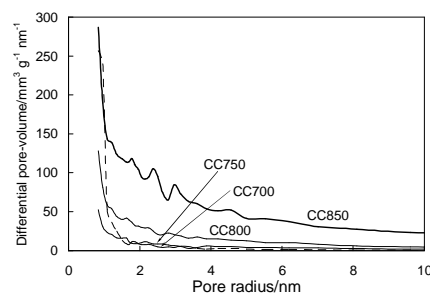


Fig. 1. Differential pore-volume distributions of CC700 (broken line), CC750 (thin line), CC800 (thick line), and CC850 (very thick line).

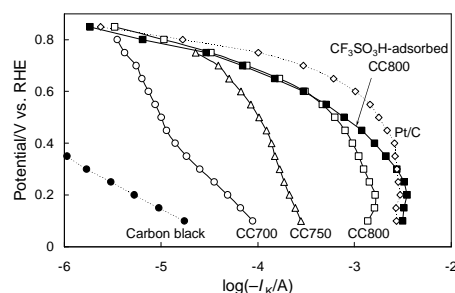


Fig. 2. Relationships between electrode potential and  $\log(-I_K/A)$  for catalyst layers formed from CC700 (○), CC750 (△), CC800 (□), and CF<sub>3</sub>SO<sub>3</sub>H-adsorbed CC800 (■). Relationships for catalyst layers formed from carbon black (●) and that formed from Pt/C (◇) were also shown for comparison.

1. M. E.Lai, A. Bergel, *J. Electroanal. Chem.* **494**, 30, (2000).
2. J.Maruyama, I. Abe, *J. Electrochem. Soc.* **151**, A447, (2004).