The Oxygen Reduction Activity and Surface Structure of Co Tetraphenylporphyrin Supported on Carbon Black

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1. Introduction

Pt and its alloys have been widely used as electrocatalysts the oxygen reduction reaction in fuel cells. It has been strongly required, however, that those precious metals be replaced with non-precious materials because of their cost. Macrocyle complexes are ones of the promising candidates. When a heat-treatment is applied, the catalytic activity of macrocyle complexes are known to improve, but the mechanism of the improvement is not clearly understood. In this work, the surface structure of heat-treated Co tetraphenylporphyrin supported on carbon black (CoTPP/C) was investigated using XAFS, XPS, XRD, and TEM and its relation with the oxygen reduction activity is disccussed.

2. Experiments

CoTPP/C was prepared by drying the mixture of 0.57mg CoTPP in 200ml toluene and 490mg a carbon black substrate (Vulcan, XC-72R) at 50˚C in a rotary evaporator and at 100˚C in an oven for 24 hr. A heat treatment was performed in Ar stream at 600˚C (or 800˚C, 1000˚C) for 2 hr. Electrodes were fabricated as follows. 15uL of the aqueous dispersion containing CoTPP/C (6mg CoTPP/C in 1ml water) was deposited on a glassy carbon (GC, 0.20cm^2). Then, it was dried at 80˚C for 10 min. and 2.7uL of 0.12wt% Nafion solution was applied to the GC. Finally, it was vacuum-dried at 80˚C for 30 minutes.

The oxygen reduction activity for the prepared CoTPP/Cs was evaluated by comparing the voltammograms between in O_2-saturated 0.1M H_2SO_4 solution and in Ar-saturated one. The electrode potential was swept between 50 mVand 1000mV vs RHE at the rate of 50mV/s.

Co K-edge XAFS measurements were carried out for the prepared CoTPP/Cs using the BL16B2 beamline in Spring-8(Hyogo, Japan). CoTPP powder and Co foil were used as their references. The incident X-ray was monochromatized using a Si (111) double crystal monochromator and the harmonic content of the beam was minimized by a Rh-coated Si mirror inclined to 4.5 mrad.

3. Results and Discussion

The oxygen reduction activities for the prepared CoTPP/Cs are shown in Fig.1. All the heat-treated samples shows higher catalytic activities than the un-heat-treated one. The highest activity is obtained when the heat treatment temperature is 600˚C. The heat treatment at the higher temperatures decreases the oxygen reduction activity. These results agree well with previous studies[(1)].

In addition, a long time stability test showed that the un-heat-treated CoTPP/C loses its activity on the order of minute, but that all the heat-treated CoTPP/Cs show much stabler activities for 6 hr.

Obtained EXAFS spectra are shown in Fig. 2. The peak at 1.6Å in the spectra, which corresponds to the structure consisting of the Co atom surrounded by N atoms (Co-N_4 structure), is preserved up to 600˚C. At 800˚C or higher, however, this structure seems to start decomposing and the metallic phase of Co starts growing.

In addition, XANES spectra (not shown) indicated that the interaction between CoTPP and carbon black is strengthened by the heat treatment at 600˚C. This result suggests that the electron transfer from carbon to CoTPP becomes smoother by the heat treatment.

4. Conclusion

The results shows:

1) The Co-N_4 structure is necessary as the active site for the catalytic activity for the oxygen reduction reaction.
2) For higher activity, a strong interaction between the active site and the substrate is desiarble.

5. Reference

1) Faubert G, Lalande G, Cote R, Guay D, Dodelet J.P., Weng L.T., Bertrand P, and Denes G., Electrochim. Acta 41 (1996) 1689.

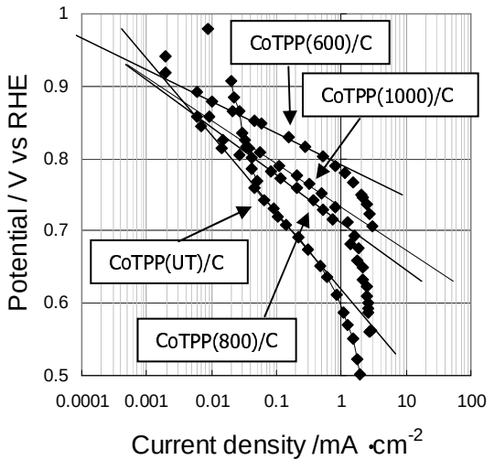

Fig.1 Tafel plot for prepared electrodes
* Quoted values stand for treatment temperature.
** "UT" stands for unheat-treated material.

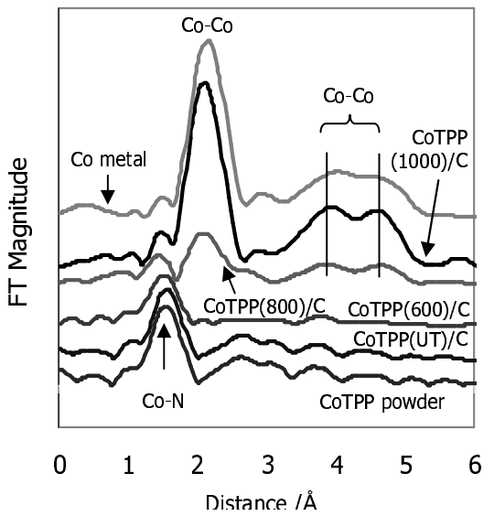

Fig.2 Co K-edge EXAFS spectra for prepared CoTPP/C catalysts