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CATALYTIC ACTIVITY OF HEAT-TREATED Co(II)-TETRAPHENYLPORPHYRIN FOR CATHODIC REDUCTION OF OXYGEN

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Heat treatment effect of Co(II)-tetraphenylporphyrin (Co-TPP) on the catalytic activity for cathodic reduction of oxygen was studied. The improved catalytic activity of Co-TPP heat-treated at temperatures between 500 and 700°C was found to be due to a remarkable increase in the conductivity and the variation of the electronic states of the central metal ion, resulting from an extension of π-electron system by polymerization.

Carbon-supported metal complexes of porphyrins and phthalocyanines,1-3) prepared by the heat treatment in an inert atmosphere, have been found to be promising O_2 reduction catalysts in fuel cells because of their improved catalytic activities and stabilities. The cause of the above improvements, however, seem to have not yet been fully clarified. In this work, the relations between the change in bulk properties by the heat treatment and the improvement of the catalytic activity for cathodic reduction of oxygen were studied using Co-TPP.

Co-TPP used as the catalyst was prepared from commercial TPP (Aldrich) and cobalt (II) acetate by the chloroform-acetic acid method.4) The Co-TPP was heat-treated in an atmosphere of Ar at a given temperature for 10 minutes. The heat-treated Co-TPP samples were subjected to the evaluation of bulk properties. For the cathodic polarization measurements, however, pellet-type electrodes were prepared in the following way; A mixture of 5 wt% heat-treated Co-TPP as catalyst, 5 wt% Teflon powder as binder and 90 wt% natural graphite (ACP, Nippon Kokuen Co.,Ltd) as conductor was pressed at 1.7 t/cm^2 to a dense pellet and then heated at 300°C for 30 minutes in Ar to sinter the binder. The measurements were carried out in O_2-saturated 0.05 M H_2SO_4 solution at room temperatures. The counter and the reference electrodes used in this study were a Pt net and a KCl saturated calomel electrode, respectively.

Figure 1 shows the data of thermogravimetry (TG) and differential thermal analysis (DTA) with respect to Co-TPP. This compound was stable up to about 400°C, but showed a first exothermic peak at 450°C and a second one at 740°C. The first exothermic reaction is considered to be attributable to a release of the side-chain phenyl groups from the porphyrin ring.3) In this reaction, metal-N bonds and the porphyrin skeleton would be maintained. Since metallic cobalt species was detected in Co-TPP heat-treated above 800°C from the X-ray analysis, the second exothermic reaction is presumed to be due to a cleavage of the porphyrin ring. Table 1 summarizes the molecular weight of the porphyrin unit per cobalt ion with Co-TPP obtained by the heat treatment at different temperatures. The molecular weight was obtained by determining cobalt ion with the EDTA titration method.[5] It is evident from Table 1 that heat-treated Co-TPP up to 400°C is present as a monomer, because the molecular weight was almost the same as that of non-heated Co-TPP, 672. On the other hand, Co-TPP heat-treated above 500°C showed a lowering in the molecular weight, which suggests a polymerization due to a release of phenyl groups. In fact, the molecular weight at 700°C, 357 is very close to that for the structure lost four phenyl groups, 364. In the infrared spectra, the absorption peaks due to the phenyl groups were diminished by the heat treatment at 500°C, and they were almost disappeared by the heat treatment at 600°C. Since a layered structure was elucidated from the X-ray diffraction patterns with Co-TPP heat-treated above 500°C, the polymerization seems to proceed two-dimensionally.

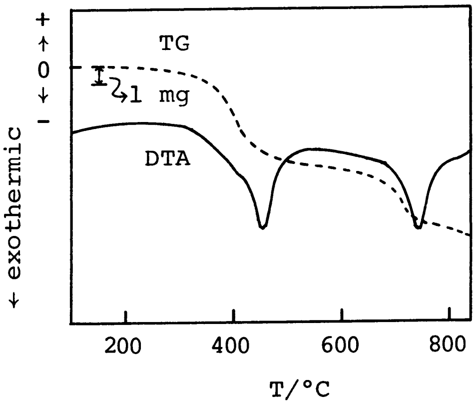

Fig. 1 DTA and TG curves of Co-TPP in an atmosphere of Ar.

Table 1. Molecular weight per cobalt ion with Co-TPP heat-treated at different temperatures

T/°C	M.W.
300	680
400	665
500	411
600	376
700	357
800	262
900	241

Figure 2 shows the variation of the catalytic activity of Co-TPP for O_2 reduction with the heat treatment temperature. A steep rise of the catalytic activity is observed between 400 and 500°C. In the region of 500 and 700°C, the activity increased gradually, but it disappeared beyond 800°C. The above results can be correlated to the two step thermal decomposition reactions which have already been observed in the DTA curve. That is to say, in the heat treatment beyond 500°C, the catalytic activity for O_2 reduction increases with proceeding in the polymerization through a release of phenyl groups. In the heat treatment above 800°C which results in a decomposition of the porphyrin skeleton, however, the resulting Co-TPP had little catalytic activity for O_2 reduction.

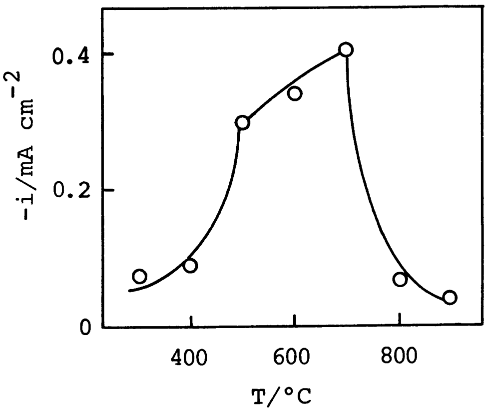

Fig. 2 Variation of O_2 reduction current at -0.4 V (vs. SCE) with heat treatment temperature of Co-TPP.

In order to clarify the heat treatment effect of Co-TPP on the catalytic activity for O_2 reduction, some bulk properties of the heat-treated Co-TPP were measured as a function of temperature. Figure 3 shows the variation of the resistivity ρ of Co-TPP with heat treatment temperature. The Co-TPP heat-treated up to 400°C was virtually an insulator. In the heat treatment above 500°C where the polymerization proceeds, the resistivity of Co-TPP was gradually lowered with a rise in temperature. This is inferred to result from an extension of the π-electron system to neighboring porphyrin ring through a release of phenyl groups by the heat treatment. The increase in conductivity is considered to contribute to the improvement of the catalytic activity for O_2 reduction.

Next, in order to know the d-electrons' configuration in the cobalt ion, magnetic susceptibility χ_g was measured with the heat-treated Co-TPP. In Fig. 4, the molar magnetic susceptibility χ_M is plotted against the heat treatment temperature. The value of χ_M was estimated using the molecular weight given in Table 1, namely $\chi_M=\chi_g/M.W.$. It can be seen from Fig. 4 that the change in χ_M occurs in the two regions of $400\sim500$°C and $700\sim800$°C. The remarkable change of χ_M value in the latter temperature region is considered to result from the deposition of ferromagnetic cobalt metal, which is consistent with the view given for the DTA data. The metal deposition was in fact confirmed by the X-ray analysis. For the purpose of examining the change in χ_M in the region of $400\sim500$°C, magnetic moment μ was calculated, and was given in Table 2. In general, the number of unpaired d-electron of the cobalt(II) (d=7) in Co-TPP is one, and Co-TPP is known as a low spin complex.[6] Theoretical values of μ for the low and high spin complex of Co-TPP are 1.7 and 3.9 μ_B (Bohr Magneton), respectively. Therefore, it is obvious from Table 2 that Co-TPP heat-treated above 500°C changes into

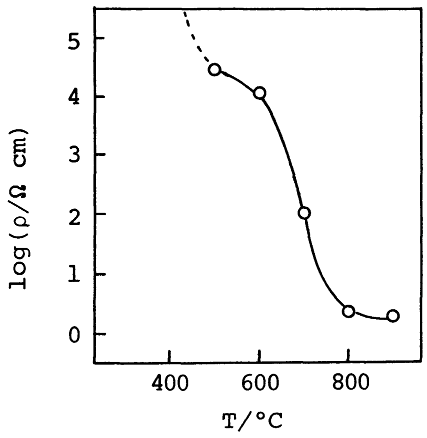

Fig. 3 Variation of resistivity of Co-TPP with heat treatment temperature.

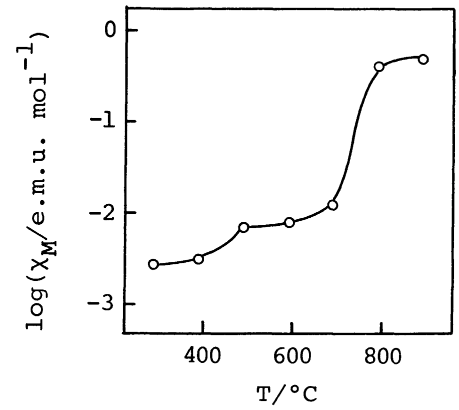

Fig. 4 Change in molar magnetic susceptibility of Co-TPP due to heat treatment temperature.

Table 2. Magnetic moment of Co-TPP heat-treated at different temperatures

T/°C	μ_M/μ_B
300	2.4
400	2.7
500	3.9
600	4.2
700	5.3
800	---

a high spin complex with three unpaired d-electrons. In the region of 500 to 700°C, the high spin character becomes stronger with a rise in the heat treatment temperature or with a progress of polymerization. As the cause of the change in low to high spin complex, it seems most likely that electrons which took part in the bonds among Co(II) and N atoms delocalize owing to the polymerization by the heat treatment. In other words, Co-TPP changes into a high spin complex together with a variation of the ligand field around Co(II)-N bonds from a strong to weak ligand field due to weakening of Co-N bond strength. This weakening of the Co-N bond was confirmed by the infrared data in which the metal-ligand vibrational peak at 1005 cm^{-1} observed for non-heated Co-TPP⁷⁾ was shifted toward a lower wave number by 20 cm^{-1} due to the heat treatment at 500°C. The change into a high spin complex is also considered to contribute to the improvement of the catalytic activity for O_2 reduction. Thus the improved catalytic activity of Co-TPP by the heat treatment is considered to be caused by an increased population of electrons on d_{z^2} orbital, that promotes a partial electron transfer to O_2 molecule coordinated to the cobalt ion.

In summary, the improved catalytic activity of Co-TPP for O_2 reduction by the heat treatment can be attributed to the increased conductivity and the change into a high spin complex due to the polymerization.

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