Anomalous Magnetic Property and Capability of Reducing Oxygen to Water of Heat-treated Chloro(tetraphenylporphyrinato)iron(III)

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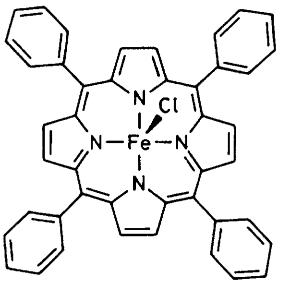
Heat-treatment of chloro(tetraphenylporphyrinato)iron(III) (ClTPPFe^{III}) in an Ar atmosphere gives a product with an anomalously high molar magnetic susceptibility, and on it the cathodic reduction of oxygen occurs through a 4-electron pathway, namely oxygen to water.

Heat-treatment of metallo-macrocycles in an inert atmosphere is of active interest, because it makes the original catalyst a more stable and more active one in the cathodic reduction of oxygen.[1] However, the structures and properties of heat-treated metallo-macrocyles have not yet been fully clarified. The present study shows that the heat-treatment gives rise to a material with a magnetic characteristic not observed in the unheated material and this magnetic property is strongly correlated to the mechanism for the cathodic reduction of oxygen.

A ClTPPFe^{III}-coated disc electrode was prepared by loading 3×10^{-7} mol cm^{-2} of ClTPPFe^{III} onto the top surface



ClTPPFe^{III}

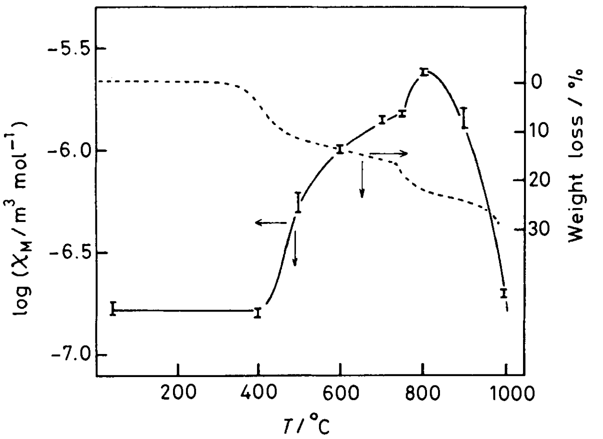


Figure 1. Molar magnetic susceptibility χ_M of ClTPPFe^{III} heat-treated at different temperatures (solid line) and thermogravimetric behaviour of ClTPPFe^{III} (dotted line).

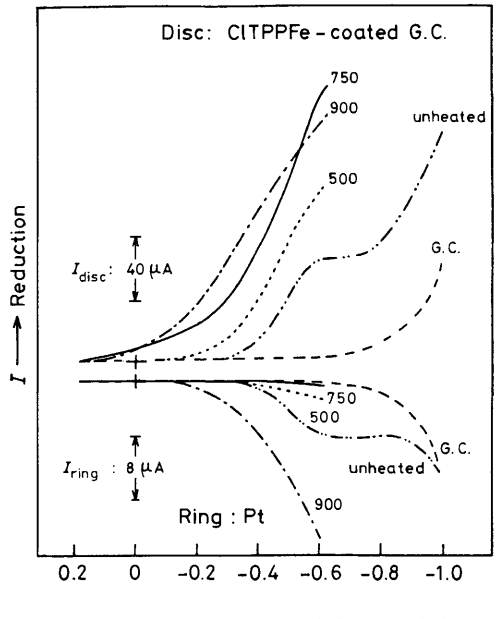


Figure 2. Voltammograms at the rotating ring–disc electrodes for the cathodic reduction of oxygen in O_2-saturated 0.5 M H_2SO_4. The figures by each line represent the heat-treatment temperature of ClTPPFe^{III} on the disc. Glassy carbon (G.C.) was used as the base electrode for the disc. Potential of the reference electrode: Hg/Hg_2SO_4 in 0.5 M H_2SO_4, 0.670 V *vs.* normal hydrogen electrode (NHE). Ring potential, 1.27 V *vs.* NHE; sweep rate at the disc, 0.1 V s^{-1}; rotation rate, 1000 r.p.m.

of a glassy carbon rod (0.28 cm^2, Tokai Carbon GC 20) and then heating it in an Ar atmosphere at different temperatures. ClTPPFe^{III} powder was also heat-treated, and the magnetic properties of the products were investigated.

Figure 1 shows the molar magnetic susceptibility χ_M and the theromogravimetric (TG) behaviour of ClTPPFe^{III} as functions of the temperature of the heat-treatment. The χ_M was evaluated by determining the molecular weight of the porphyrin unit per Fe ion, using $\chi_M = \chi_g \times$ (molecular weight), where χ_g is the mass magnetic susceptibility and is corrected for ferromagnetic impurities by extrapolating the plot of (mass magnetization)/(magnetic field strength) $[(M)/(H)]$ against $1/H$ to $(1/H) = 0$. The TG curve was nearly same as that of TPPCo^{II},[2] and two weight loss points were observed (at 430 and 750 °C). In analogy with TPPCo^{II}, thermochemical reactions taking place at 430 and 750 °C seem to be a polymerization owing to a release of phenyl groups and a degradation of the porphyrin skeleton, respectively. ClTPPFe^{III} heat-treated up to 400 °C shows χ_M of 1.57×10^{-8} m^3 mol^{-1}, which is equal to a magnetic moment $\mu_{eff.}$ of 5.5 μ_B (Bohr magneton). This value is in good agreement with the value in the literature,[3] and indicates that Fe^{III} is high spin in ClTPPFe^{III} up to 400 °C. The χ_M of ClTPPFe^{III} heated at 700 °C was, however, 1.41×10^{-7} m^3 mol^{-1} ($\mu_{eff.} = 16.4$ μ_B). This value was too high to be explained by a valence change of iron or formation of an oxygen adduct. It may be that the heat-treated ClTPPFe^{III} has a structure enabling a magnetic interaction among unpaired spins of Fe^{III} in each porphyrin unit. Such a structure might be (i) a co-planar structure with an extended π-electron system (estimated from a sharp *X*-ray diffraction peak corresponding to the spacing $d = 0.34$ nm), or (ii) a polymer structure bridged by chloride ions among Fe sites in addition to (i). The latter structure (ii) seems to explain the anomalous magnetic behaviour of heat-treated ClTPPFe^{III}, because such behaviour was not observed in TPPCo^{II} without an axial ligand.[2] We are now studying the effect of varying the axial ligand of TPPFe^{III} on the above magnetic behaviour. It was found that F^- has a marked effect on the enhancement of χ_M compared to I^- and Br^-.

Figure 2 shows voltammograms at the rotating ring (Pt)–disc(ClTPPFe-coated glassy carbon) electrodes for the cathodic reduction of oxygen in O_2-saturated 0.5 M H_2SO_4. The ring potential was fixed at 0.6 V (*vs.* Hg/Hg_2SO_4 in 0.5 M H_2SO_4) where the diffusion limiting current was observed for the oxidation of H_2O_2. The voltammograms for unheated ClTPPFe^{III} revealed that the reductants at the disc were a mixture of H_2O_2 (majority) and H_2O. This suggests that the oxygen reduction occurs through both a 2-electron pathway (O_2 to H_2O_2) and a 4-electron pathway (O_2 to H_2O). The oxygen reduction on ClTPPFe^{III} heat-treated at 500 and 750 °C, however, occurs through a 4-electron pathway preferentially. But, ClTPPFe^{III} heat-treated at 900 °C showed a pronounced H_2O_2 formation again.

The above change in the mechanism of oxygen reduction with heat-treatment temperature nearly corresponds to the change of χ_M in Figure 1. Thus, the increase in χ_M with increasing heat-treatment temperature seems to be correlated to an increased catalytic activity of Fe sites for the cathodic reduction of peroxide species as an intermediate. In fact, the reduction current of H_2O_2 on ClTPPFe^{III} heat treated at

750 °C was the highest among the heat-treated ClTPPFe^{III} coated discs.

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