

Increased Catalytic Activity of Iron Phthalocyanine on the Electrochemical Nitrite Reduction upon Heat-Treatment Probed by X-ray Absorption Fine Structure

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As nitrite is involved in many environmental aspects¹ and it plays important physiological roles in the form of NO,²⁻⁴ the detection of nitrite has been the subject of intensive research. Since the overpotential of nitrite reduction at ordinary solid electrodes is very high, much effort has been directed to look for better electrocatalysts. Meyer *et al.*⁵⁻⁷ found that some metal complexes such as Ru(II)-, Fe(II)-EDTA and Fe(III)-porphyrin displayed high activities when dissolved in solution.

Our ongoing interest is to develop good electrochemical systems for the nitrite detection. We have reported that FePc shows an electrocatalytic activity on an electrode surface⁸ or in a silica matrix prepared by sol-gel techniques.⁹ One of the main problems of FePc on the surface is its instability. Under harsh environment FePc easily loses its activity.¹⁰ One way of overcoming this problem is to treat FePc at high temperatures. Heat-treatment has been used as a way of imparting thermal and mechanical stabilities to the supported electrocatalysts since the discovery of the beneficial effect by Jahnke *et al.*¹¹ This method has been applied to transition metal complexes with porphyrin or phthalocyanine ligand as substitutes for platinum for the oxygen reduction in a fuel cell. It is generally believed that metal-N₄ moiety forms at low heat-temperatures while small metal clusters forms at high heat-temperatures. Recently other explanations, in which FeN₂C₄⁺ may be the active site, have been suggested.¹²

In this paper, we present our results on the heat-treatment effect of supported FePc on the electrochemical reduction of nitrite. We also monitored the structural alteration of FePc brought by heat-treatment by X-ray absorption fine structure (XAFS) and related it to the catalytic activity.

Electrochemical behaviors of FePc before and after heat treatment, and corresponding nitrite reduction in 0.5 M H₂SO₄ containing 5.0 mM NO₂⁻ were examined by cyclic voltammetry (Figure 1). Two redox peaks I and II are largest for a nonheat-treated sample and gradually become smaller as heat-treatment temperature increases, implying structural alteration takes place. The peak I is responsible for the nitrite reduction but rapidly disappearing upon heat-treatment. It is noticeable that the nitrite reduction activity gradually increases with heat-treatment temperature and reaches the maximum at 800 °C (Figure 2). Temperature was raised at

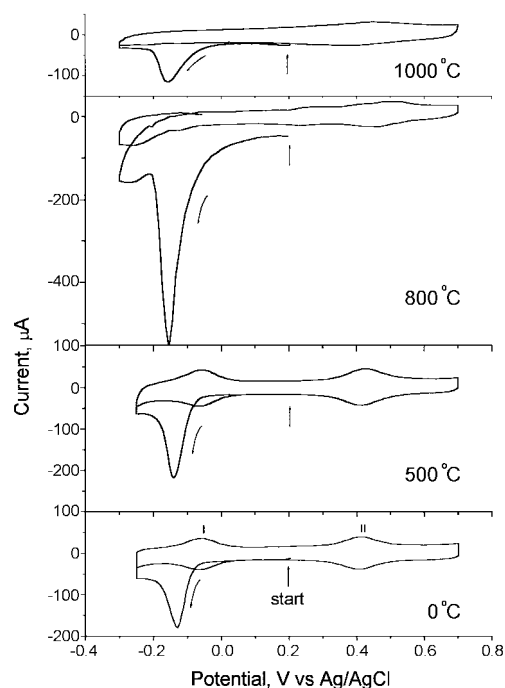


Figure 1. Cyclic voltammetry of supported FePc on high area carbon and nitrite reduction in 0.5 M H₂SO₄ by unheat-treated and heat-treated samples at 500, 800, and 1000 °C. [NO₂⁻] = 5 mM; scan rate = 10 mVs⁻¹.

10 °C min⁻¹ to the desired value and maintained for 2 hrs. The activity at 800 °C is about three times higher than that of unheat-treated sample. XANES analyses (data not shown) shows that fine structures due to 1s → 4p transitions, characteristics of FePc, rapidly disappear above 600 °C and metallic iron features begin to appear, indicating that the square planar geometry of Fe-N₄ is not maintained. This indicates that heat-treatment at high temperature causes the decomposition of Fe-N₄ to metallic Fe. The similar phenomenon was observed in cobalt porphyrin and phthalocyanine.^{13,14} Detailed structural information can be obtained from Fourier transformed spectra of EXAFS (Figure 3). Well-defined Fe-N_p and Fe-C shells at 1.57 and 2.57 Å (phase-shift uncorrected) were observed for the unheat-treated sample, indicating adsorption itself does not induce structural alteration. Upon heat-treatment a new peak began to grow at *ca.* 2.1 Å at the expense of the magnitude of Fe-N_p shell. With reference to Fe foil, this new peak is assigned

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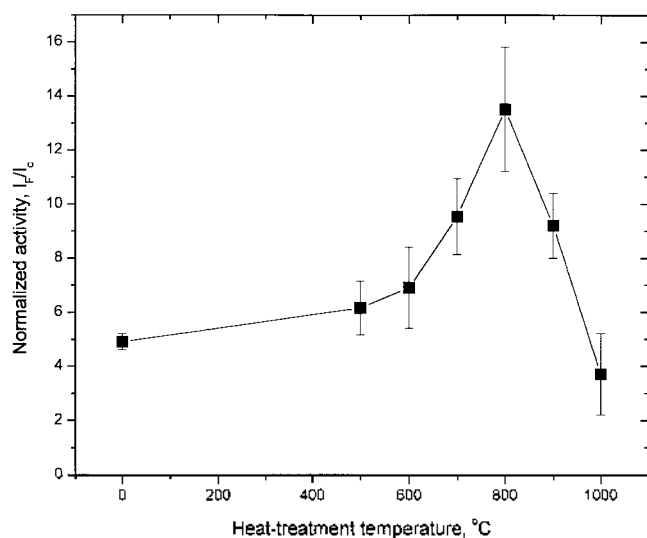


Figure 2. Normalized activities for the nitrite reduction expressed by I_F/I_C as a function of heat-treatment temperature. I_F and I_C are faradaic and charging currents, respectively. I_C was measured at +0.1 V vs Ag/AgCl_{KCl sat'd} with FePc on the surface.

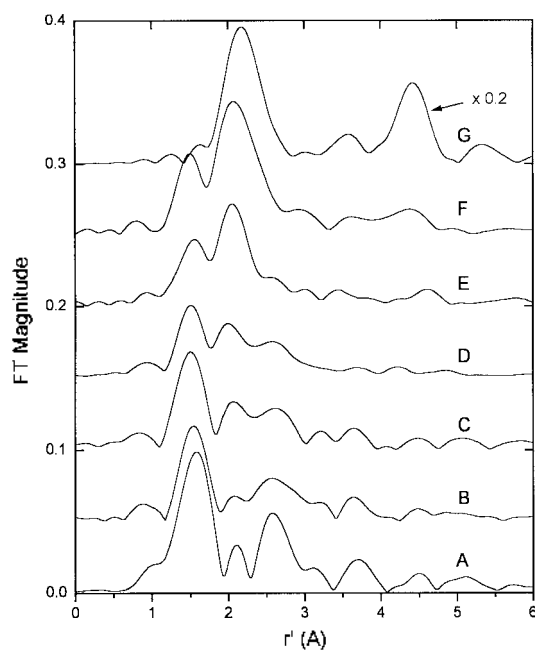


Figure 3. Fourier-transformed spectra of unheat-treated (A) and heat-treated FePc at 600 (B), 700 (C), 800 (D), 900 (E), and 1000 °C (F). Curve G is FT spectrum of iron foil for comparison.

to the Fe-Fe shell. It is peculiar that the highest activity is found at 800 °C. At this temperature, iron exists either as Fe-N complex or as a form of small iron clusters, both of which exhibit catalytic activities. This means Fe-N₄ structure is not an absolute requisite for activity. While only Fe-N₄ structure is responsible for the unheat-treated sample, both Fe-N_x and metallic iron clusters play roles in exhibiting catalytic activities. The decreased activity above 800 °C, despite the

formation of metallic iron, can be attributed to the formation of larger iron clusters. It is well known that the sintering effect of heat-treatment at higher temperatures leads to the larger metallic particles. According to Tourillon *et al.*,¹⁵ larger metallic clusters lose catalytic activities for the oxygen reduction. The same argument may apply to the nitrite case. Although it is not possible to estimate the size of the clusters from EXAFS analysis, the relative amount of metal cluster was shown to increase from fitting the first two peaks in FT spectra. The ratio of coordination numbers for Fe-Fe to that for Fe-N increased from 0.25 at 800 °C to 1.5 at 1000 °C. The exact size of iron particles is not certain at the moment, however. This result is quite contrary to the case of (FePc)₂O, where the catalytic activity reaches almost zero at 1000 °C. But FePc still shows appreciable current even at 1000 °C. There coexist both iron clusters and the Fe-N_x structure when the samples were heat-treated above *ca.* 700 °C. The reason why the best activity is achieved at 800 °C in our case is that the adequate size of metallic iron clusters are formed at this temperature. It may be concluded, therefore, that the Fe-N₄ structure is not essential to maintain the catalytic activity but the best electrocatalyst could be prepared by any means to give the adequate size of iron clusters.

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