Catalytic Characteristics of β -Iron Phthalocyanine Prepared by Vacuum Heat Treatment for Fuel Cell Oxygen Reduction Reaction

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ABSTRACT

Non-precious metal catalyst materials such as carbon-based catalysts and transition metal chelate compounds have been investigated for reducing the cost of polymer electrolyte fuel cells (PEFCs). Our research on the synthesis of such catalysts has involved vacuum heat treatment for the preparation of iron phthalocyanine (FePc). When a composite of FePc and Ketjenblack carbon was synthesized by vacuum heat treatment at $\geq 350^\circ\text{C}$ for 10 h, FePc was deposited as a thin film on the Ketjenblack. Furthermore, synthesis with the vacuum heat treatment at 400°C for 10 h (FePc/C-400) transformed the FePc structure from the α phase to the β phase. The oxygen reduction reaction (ORR) activity of FePc/C-400 was higher than those of other FePc/C catalysts treated at different temperatures. The coordination of Fe and N in β -FePc was found to be related to the high ORR activity.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are regarded as ideal candidates for mobile and home power generators because of their high power density. High-efficiency PEFCs can be achieved by speeding up the otherwise slow reaction steps at low operating temperature (ca. 80°C) through the use of catalysts.¹ Platinum-based electrocatalysts have been traditionally used to catalyze the oxygen reduction reaction (ORR) and achieve high efficiency; however, such materials raise the cost of PEFC systems. Therefore, non-precious metal catalysts such as carbon-based catalysts and transition metal chelate compounds should be examined to reduce the cost of PEFCs.² Since 1964, when Jasinski observed that cobalt phthalocyanine catalyzed the ORR,³ a number of approaches have been explored to create practical non-precious metal catalysts. The activity and the stability of Co- and the Fe-N₄ macrocycle complexes adsorbed onto a carbon support can be improved by heat treatment in an inert atmosphere and at high temperature.⁴ Charretier et al. concluded that three components are required to form catalytic sites at high temperature: (1) nitrogen (2) Fe or Co ions and (3) carbon.⁵ High ORR performance Fe-N₄/C catalysts have been synthesized from rare carbon materials, such as graphene or carbon nanotubes, and nitrogen precursors.^{6–8} However, synthetic method to obtain these catalysts is complicated and requires strictly controlled conditions.

Iron phthalocyanine (FePc) is a chelate complex with an Fe-N₄ structure in the middle. The FePc catalyst is stable in inert saturated electrolytes; however, in oxygen saturated electrolytes, the ORR activity of the FePc catalyst decreases due to replacement of the iron center ion.⁹ FePc is a planar molecule, that forms linear chains by vertically-directed stacking. These planar molecules have two common polymorphs, referred to as α and β phases, which have different angular and planar positions. The tilt angle of the molecule stack from the *b*-axis is 26.1° for the α phase, while it is 44.8° for the β phase.¹⁰ β -FePc is an especially stable structure compared with α -FePc because the Fe ion in the β phase has coordination with pyrrolic N atoms at both neighboring planar molecules.¹¹ The catalyst electrode containing β -FePc catalysts supported on carbon

material is expected to maintain the active site density because of the replacement inhibition of iron atoms. It is considered that the higher active site density lead to the more increase of ORR onset potential. Therefore, we believe that replacement of the iron center ion in a β -FePc catalyst supported on carbon material would be inhibited and high ORR performance should be observed. Our approach to the synthesis of a non-precious metal catalyst for the ORR has been to use vacuum heat treatment. Here, we demonstrate that vacuum heat treatment can be used to transform FePc from the α to the β phase, and the electrocatalyst performance of the resultant FePc/C catalyst is evaluated.

2. Experimental

FePc (Aldrich, assay of 90%) and Ketjenblack (EC600JD) were mixed in a weight ratio of 1:2 in N,N-dimethylformamide (Kishida Chemical), and ultrasonicated for 30 min, followed by drying at 150°C overnight. The synthesized composite was vacuum heat-treated for 10 h at 300, 350, 400 and 450°C . The FePc/Ketjenblack carbon composite synthesized at these various vacuum heat treatment temperatures are denoted as FePc/C-XXX, where XXX is the temperature, e.g. a sample vacuum heat-treated at 350°C is denoted FePc/C-350.

Fabrication of the working electrodes was conducted by pasting catalyst ink onto a glassy carbon electrode (5 mm diameter). The catalyst ink was formed by mixing 10 mg of FePc/C, 200 μL of a 5 wt% Nafion solution in 2-propanol, and 800 μL of ethanol under ultrasonic dispersion for 15 min. 5.04 μL of the ink was dropped onto a glassy carbon electrode. A solution of 0.1 M HClO₄ was used as the electrolyte, and a saturated calomel electrode (SCE) and Pt wire were used as the reference and counter electrodes, respectively. As a pretreatment of the electrode surface, cyclic voltammetry was performed from -0.19 to $+0.95$ V (vs. SCE) at 50 mV/s for 10 cycles after bubbling with N₂ gas for 30 min before the catalyst performance measurement. Slow cyclic voltammetry was then measured from -0.19 to $+0.95$ V (vs. SCE) at 10 mV/s using a rotating ring-disk electrode (RRDE) system at 500 rpm after bubbling with N₂ or O₂ gas for 30 min. The current density of the

ORR was calculated as the difference in the current density between bubbling with N_2 and O_2 .

Characterization of the electrocatalysts was performed using X-ray diffraction (XRD; Rigaku, SmartLab) with $CuK\alpha$ radiation and X-ray photoelectron spectroscopy (XPS; PHI, ESCA Quantum 2000) with monochromatic Al $K\alpha$ radiation (1486.6 eV).

3. Results and Discussion

Figure 1A shows XRD patterns of the FePc synthesized by vacuum heat treatment at 350, 400, and 450°C for 10 h. The XRD patterns of FePc-350 and FePc-400 were assigned to α -FePc (JCPDS 00-022-1771) and β -FePc (JCPDS 00-014-0926), respectively. Thus, the FePc raw material is transformed from the α phase to the β phase by vacuum heat treatment at 400°C. The XRD pattern of FePc-450 was assigned to β -FePc and Fe_2O_3 . The formation of Fe_2O_3 is probably due to the reaction of Fe ions in FePc with oxygen from impurities in the FePc raw material (assay of 90%).

Figure 1B shows XRD patterns of the composite of FePc and Ketjenblack synthesized by vacuum heat treatment at 300, 350, 400, and 450°C for 10 h, in addition to that for the non-treated composite. The XRD patterns of all samples show a broad peak at around 25°, which indicates graphite,¹² from the presence of Ketjenblack. Furthermore, FePc/C and FePc/C-300 exhibited peaks at 7°, 9° and 16°, which indicate the presence of α -FePc. In contrast, FePc/C-350, FePc/C-400 and FePc/C-450 exhibited only the characteristic peak for Ketjenblack, and not that for FePc. These facts indicate that FePc was deposited as a thin film on the Ketjenblack when prepared by heat treatment at temperatures greater than 350°C under high vacuum. Note that when Pc powder sublimates near 350°C under high vacuum, polycrystalline thin films can be deposited.¹³ Figure 1A suggests that the crystal phase of the thin film of FePc/C-400 may be β phase. However, it would be necessary to clarify the evidence through more detail analyses in progress, because FePc/C-400

Figure 1. XRD patterns for (A) FePc and (B) FePc/C prepared by vacuum heat treatment at various temperatures.

Figure 2. XPS (A) Fe 2p, (B) N 1s, (C) O 1s and (D) C 1s spectra for FePc/C, FePc/C-300, FePc/C-350, FePc/C-400 and FePc/C-450 (bottom to top).

deposited as a thin film is expected to have a different α - β phase transition temperature.

Figure 2 shows XPS profiles of the FePc/Ketjenblack composites synthesized by vacuum heat treatment at 300, 350, 400, and 450°C for 10 h, in addition to the non-treated composite. The Fe 2p broad peak for FePc/C, FePc/C-300 and FePc/C-450 was observed at a binding energy of 710 eV (Fig. 2A). This peak indicates an Fe-N bond¹⁴ in these vacuum heat-treated samples and the non heat-treated sample (FePc/C). On the other hand, no Fe 2p peaks were observed for the FePc/C-350 and FePc/C-400 catalysts. Similarly, N 1s peaks were observed for FePc/C, FePc/C-300 and FePc/C-450, but not for FePc/C-350 and FePc/C-400. N 1s peaks were not observed in FePc/C-350 and FePc/C-400, which can be explained by considering that FePc got into pores of Ketjenblack aptly since FePc was not completely sublimed by vacuum heat treatment at 350°C or 400°C. XPS, which is a surface sensitive technique, can be used to analyze to depths of ca. 5–6 nm. However, the Ketjenblack support is known as a porous carbon¹⁵ and it is considered that the FePc of FePc/C-350 and FePc/C-400 is possibly not exposed at the surface of the Ketjenblack support due to forming a thin film of the FePc in the internal pore of the Ketjenblack, which is consistent with the XRD results. The N 1s peaks for FePc/C, FePc/C-300 and FePc/C-450 were pyridinic (at 398 eV) and pyrrolic (at 400 eV), which indicates the presence of FePc.¹⁶ It is considered that, in the case of FePc/C-450, some FePc sublimates at 450°C in the vacuum deposited on the Ketjenblack carrier surface, while in the cases of FePc/C-350 and FePc/C-400, FePc got into Ketjenblack pores aptly. The O 1s spectra for all samples had a broad peak in the range of 530–535 eV. The peak at 523.8 eV is associated with COOH or OH group and absorbed water on the Ketjenblack surface.¹⁷ The C 1s spectra revealed sharp peaks at 284.5 eV, which was assigned to the C-C bond of Ketjenblack.

Figure 3 shows RRDE voltammograms for the ORR with FePc/C, FePc/C-300, FePc/C-350, FePc/C-400 and FePc/C-450 electrodes. Figures 3A and 3B show the current changes of ring electrodes and the current density changes of disk electrodes against input electric potentials, respectively. The ORR onset potential of the FePc electrodes synthesized by vacuum heat treatment at each temperature are shifted to the positive side with an increase in the vacuum heat treatment temperature, and the ORR current was similarly increased with respect to FePc/C. Furthermore, the ORR potential of FePc/C-400 was higher than that of the other samples, which indicates that the ORR activity of β -FePc is higher than that of α -FePc. A study to reveal the difference of the ORR mechanisms between α -FePc and β -FePc is now in progress. The ORR activity of

Figure 3. RRDE voltammograms (ring electrode (A) and disk electrode (B)) for (a) non-heat-treated FePc/C, (b) FePc/C-350, (c) FePc/C-400, and (d) FePc/C-450. Scan rate and rotation speed were 10 mV/s and 500 rpm, respectively.

FePc/C-450 was lower than that of FePc/C-400 because part of the FePc/C-450 electrode is Fe_2O_3 formed by oxidation of the Fe ion center of FePc, as indicated in the XRD pattern (Fig. 1A). Fe_2O_3 is known to have low ORR activity; therefore, the FePc/C-450 electrode has lost portion of the ORR active sites. If all ORR proceed via four-electron reduction in this experimental conditions, the diffusion current would be ca. 3.38 mA/cm^2 .¹⁸ However, in this case using catalysts prepared by vacuum heat treatment, it was limited to ca. 2.1 mA/cm^2 . Two reasons are considered: (1) the two-electron reduction producing HO_2^- as a by-product proceeds simultaneously, and (2) ORR is the rate-limiting step.

For the RRDE measurement, the percentage of HO_2^- derived at the disk electrode is calculated according to:¹⁹

$$\text{H}_2\text{O}_2 \% = \frac{2i_R/N}{i_D + i_R/N}, \quad (1)$$

where i_R is the ring electrode current, i_D is the disk electrode current, and N is the collection efficiency. In this study, the collection efficiency was determined to be 0.477 in 0.1 M KNO_3 containing 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$. The HO_2^- percentages produced by FePc/C-350, FePc/C-400 and FePc/C-450 were 14.3%, 7.8% and 10.4%, respectively. The HO_2^- yield in FePc/C-400 was lower than those in FePc/C-350 and FePc/C-450. This fact indicates that the β phase formed in FePc/C-400 may have an important role to inhibit the formation of HO_2^- and to improve the ORR onset potential.

Actually, the ORR onset potential of FePc/C-400 shifted to the positive side when the β phase was formed in FePc/C-400. In addition, it is considered that the β -FePc is deposited like the thin film on the Ketjenblack. In the presence of oxygen, the mechanism

for the iron-catalyzed ORR begins with Fe(II) ($1.56 \text{ \AA}$), and the valence of iron is then increased to Fe(III) and Fe(IV).⁹ The diameters of Fe(III) and Fe(IV) are approximately 1.29 and 1.17 $\text{\AA}$, respectively.²⁰ The result of Fe ion replacement is thus a decrease in the ionic radius.²⁰ Furthermore, the replacement of Fe(IV) ions can catalyze the degradation of neighboring FePc molecules and the carbon support because Fe(IV) has high oxidation activity.²¹ However, the FePc/C-400 electrode may inhibit Fe ion replacement because it is predominantly composed of the β phase which has coordination with pyrrolic N atoms at both neighboring planar molecules. Therefore the ORR potential of FePc/C-400 was higher than that of the other samples.

4. Conclusion

In this study, new catalysts were prepared using vacuum heat treatment of a mixture FePc and Ketjenblack. The ORR onset potentials for FePc prepared by vacuum heat treatment at 350, 400 and 450°C were shifted to the positive side with respect to that for the non-heat-treated FePc. The ORR potential of the FePc/C-400 electrode was higher than that of the other samples, which indicates that the ORR activity of β -FePc is higher than that of α -FePc.

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