On the Formal Redox Potential of Oxygen Reduction Reaction at Iron Phthalocyanine/Graphene Composite Electrode in Alkaline Media

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ABSTRACT

The redox reaction of iron phthalocyanine (FePc) combined with electrochemically-reduced graphene oxide (ER-GO) was investigated as a function of FePc fraction. A FePc/ER-GO/GC electrode was fabricated and the redox response of $\text{Fe}^{3+}/2^{+}$ couple was analyzed by cyclic voltammetry. The formal potential was observed to change with the FePc fraction, and the most positive value was obtained at the full monolayer coverage. The onset potential of oxygen reduction reaction at the fabricated electrode shifted linearly with the formal potential of FePc. Such a coverage-dependent potential shift was explained in terms of the electronic interaction between FePc and substrate graphene surface based on the X-ray photoelectron spectroscopy as well as the theoretical DFT calculation of a model adsorption system.

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1. Introduction

In recent years, substantial efforts have been devoted to exploring catalysts for oxygen reduction reaction (ORR) alternative to platinum for polymer electrolyte fuel cell (PEFC) systems.¹ To date, a series of organometallic macrocyclic compounds such as metallo-phthalocyanines has been extensively researched. It is well recognized that iron phthalocyanine (FePc) shows most excellent ORR performance among various metallo-phthalocyanines, and it transforms O_2 molecule via direct 4e^- reduction process into water in alkaline media.² In addition, FePc can easily be synthesized and commercially available inexpensively compared with other specially-designed phthalocyanines and porphyrins. In this respect, FePc has been thoroughly studied as the cathodic catalyst for alkaline fuel cells (AFC) as well as PEFC with alkaline anion-exchange membranes.³ However, the ORR performance of FePc catalyst is generally poor mainly due to the following reasons; first, FePc molecules are prone to aggregation, which greatly reduces the accessibility of O_2 molecule and leads to low ORR efficiency. Secondly, the intermolecular electron conductivity of FePc is too low to support facile electron transfer between FePc and O_2 molecule.⁴ So far, composite catalysts of FePc with carbon materials such as carbon black (CB) and carbon nanotube (CNT) have been investigated to prevent FePc from aggregation.^{5,6}

Recently, graphene has attracted much attention as a unique carbon material that has sp^2 conjugated π electron network systems. It provides prominent physicochemical properties such as high electron-transportation rate, mechanical strength and other specific physical properties.^{7,8} They are the key materials for developing next-generation electronic devices such as transparent electrode in photovoltaic converter⁹ and electric double layer capacitor.¹⁰ Besides, graphene has been studied as a catalyst as well as the catalyst support for fuel cell cathodes; for example, nitrogen atom doped^{11,12} and metal nano-particle deposition on graphene have been reported.^{13,14} Since graphene has the largest relative surface area in the carbon-based nano-materials, it enables us to support metal nanoparticles without agglomeration.¹⁵ Indeed, the catalytic ORR performance of FePc deposited on graphene (FePc/graphene composite) was reported to be superior to those supported on other

carbon materials, which was ascribed to high surface area and intrinsic high conductivity of graphene.⁴ Recently, further enhancement of catalytic performance toward ORR was reported when graphene oxide (GO) was used as the initial substrate.¹⁶ It was considered that the attractive coulombic interaction between the central metal ion in FePc and the negatively charged surface oxygen group on GO promotes the stabilized adsorption of FePc.¹⁷ Establishing the technique for adsorbing FePc on graphene in high density is a challenging subject.

In this paper, we report the influence of mixing ratio of FePc to graphene on the formal redox potential of FePc observed in alkaline solutions. We fabricated the FePc/graphene composite electrode using GO as the initial material for catalyst support. The formal redox potential of FePc embedded in the composite thin films was observed to change apparently with the mixing ratio. In order to understand the phenomenon, we discuss the electronic aspects of adsorbed FePc based on electrochemical as well as spectroscopic measurement results. We believe the study provides useful information not only for the preparation of better catalyst for ORR but also for understanding the adsorption interaction of organic molecules on GO surface.

2. Experimental

2.1 Sample preparation

GO was prepared from graphite powder via the modified Hummers method.¹⁸ The C:O ratio of the prepared sample was estimated from X-ray photoelectron spectroscopy (XPS) (ESCA-3400, SHIMADZU) and found to be ca. 1.5:1, which is consistent with the previous reports.^{19,20} The chemical composition analysis of the sample indicated that the relative concentrations of graphitic carbon (284.8 eV): 41%, phenolic, alcohol and ether groups (286.6 eV): 30%, carbonyl or quinone groups (287.3 eV): 21% and carboxyl or ester groups (288.6 eV): 7%.^{21,22} An aqueous colloidal suspension of GO (0.5 g l^{-1}) was obtained by dispersing GO in a Milli-Q water. FePc solution (0.5 g l^{-1}) was prepared by dissolving FePc powder (Kanto Chemical) in Ar saturated N, N-dimethylformamide (DMF). After sonication, the FePc solution was mixed with GO suspension and the resulting mixture was

again subjected to ultrasonication for 15 min to yield FePc-GO mixture. Hereafter, we denote the FePc-GO mixture that contains $x\%$ weight fraction of FePc as “ $x\%$ FePc/GO”. Eight kinds of mixture solution ($x = 10, 20, 30, 40, 50, 60, 70$ and 80) were prepared and used for measurements. The chemically-reduced GO (CR-GO) was prepared by the reaction of GO with hydrazine monohydrate (Kanto Chemical), which was dissolved in a water and permeated in a filter paper. GO powders were put on the filter paper and heated for 15 min at 90°C in a petri dish. After the reaction, the product was dissolved in DMF. The solution color was black, suggesting the successful conversion of GO to CR-GO. XPS analysis of the product revealed that the C:O ratio of 4.7:1, and the relative concentrations of phenolic, alcohol and ether groups (286.6 eV , 15%), carbonyl and quinone groups (287.3 eV , <1%) and carboxyl or ester groups (288.6 eV , 6%) were determined.

2.2 Electrochemical measurement

A Pt wire auxiliary electrode with large surface area and an Ag|AgCl|KCl (sat.) reference electrode connected via a salt bridge were used. A glassy carbon (GC) disk electrode of 5 mm in diameter was used as the working electrode. The FePc/electrochemically reduced GO (ER-GO)/GC composite electrode was prepared as follows; The electrode was subjected to potential cycling between 0 and 0.7 V for 10 times in $0.1\text{ M H}_2\text{SO}_4$ solution, and a known amount of FePc-GO mixture solution was casted on the electrochemically-pretreated GC electrode with a micro pipette and the solvent was dried under reduced pressure. Then, the electrode was subjected to the electrochemical reduction treatment in $0.1\text{ M Na}_2\text{SO}_4$ solution by applying a constant potential of -1.1 V for 5 min in order to remove the oxygen moieties on GO.¹⁶ Thus obtained FePc/ER-GO/GC electrode was further pretreated by applying potential cycling between -0.8 and 0.2 V for 10 times in deaerated 0.1 M KOH before use. XPS analysis of the ER-GO/GC sample revealed that the relative concentration of phenolic, alcohol and ether groups (286.6 eV) was 16% and that of carbonyl and quinone groups (287.3 eV) was 2%, which suggests that a small amount of oxygen groups still remained after electrochemical reduction. Hereafter, all the potentials cited in this paper are referred to RHE. Hydrodynamic voltammetry using rotating disk electrode ($\phi = 6\text{ mm}$) was performed in 0.1 M KOH solution. The electrode rotation rate was changed with a controller (SC-4, NIKKO KEISOKU). $20\text{ }\mu\text{l}$ of 0.5 g l^{-1} FePc/GO dispersion was pipetted onto the disk electrode, and the solvent was dried. The electrode was then subjected to the same electrochemical treatment described above, giving the FePc/ER-GO/GC. Note that the amounts of FePc included in the FePc/GO, FePc/ER-GO, FePc/CR-GO samples of the same FePc fraction are same. The electrochemical parameters used in this study were; $1.2 \times 10^{-6}\text{ mol cm}^{-3}$ for the concentration of O_2 dissolved in 0.1 M KOH solution (C_{O_2}), $1.9 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ for the diffusion coefficient of O_2 (D_{O_2}), and $0.01\text{ cm}^2\text{ s}^{-1}$ for the kinetic viscosity of the water (ν).¹¹

2.3 Computational calculation

All the theoretical calculations were performed within density functional theory (DFT) framework as implemented in DMol³ code.^{23,24} We used the Perdew–Zunger functional (LDA).²⁵ The atomic positions were fully relaxed until the forces were less than 10^{-5} Ha/a.u. In these calculations, the double numerical atomic orbital augmented by a polarization d-function (DND) was chosen as the basis set,²⁶ and plane-wave energy cutoffs of 10^{-6} Ha were used. The polybenzenoid hydrocarbons (PBH) which has 91 aromatic rings ($\text{C}_{222}\text{H}_{42}$) and D_{6h} symmetry was used for a FePc adsorbed ER-GO model to find an interaction between FePc and ER-GO. Molecular atomic charges were calculated by Mulliken population analysis.

Figure 1. (a) Cyclic voltammograms of 50% FePc/GO/GC (thick) and 50% FePc/ER-GO/GC (thin) measured in deaerated 0.1 M KOH solution ($\nu = 10\text{ mV s}^{-1}$). The current for FePc/GO/GC was multiplied by 5. The amount of FePc-GO deposited was $2\text{ }\mu\text{g}$. (b) Fe $2p_{3/2}$ XP spectra obtained for FePc/GO (i) and FePc/ER-GO samples (ii). (c) Cyclic voltammograms of 50% FePc/CR-GO/GC (thick) and FePc/ER-GO/GC (thin) in deaerated 0.1 M KOH solution ($\nu = 10\text{ mV s}^{-1}$). The amount of FePc-GO deposited was $10\text{ }\mu\text{g}$. The current for FePc/CR-GO/GC was multiplied by 10.

3. Results and Discussion

Figure 1 shows the CVs obtained at FePc/graphene/GC composite electrode in 0.1 M KOH solution. FePc is known as a methallo-phthalocyanine whose center-metal undergoes redox reactions, and the redox couples appeared ca. 0.9 V and 0.4 V vs. RHE in Fig. 1 correspond to $\text{Fe}^{3+/2+}$ and $\text{Fe}^{2+/+}$ redox reactions, respectively.² The peak currents of both couples showed linear dependence on the potential sweep rate utilized, which suggests that they are ascribed to the response from the FePc incorporated in the deposited film. As seen in the figure, the FePc/ER-GO/GC shows much larger response than FePc/GO/GC, despite the same quantity of FePc molecules. Based on the $\text{Fe}^{3+/2+}$ redox charges, it is apparent that the amount of electrochemically active FePc in FePc/ER-GO/GC was almost fifty times larger than that at FePc/GO/GC electrode. The small response observed for FePc/GO/GC suggests that most of the FePcs included are electroinactive. It has been pointed out that the introduction of oxygen groups in graphene considerably modify the electronic conjugate system by changing the hybridization of the bonded carbon atoms from sp^2 to sp^3 . As a result, the electron conduction through the graphene sheet as well as the electron transfer through the oxygen moiety at which the FePc molecule adsorbed becomes to be strictly hindered (Fig. 2).²⁷ Of course, some FePc molecules would also be adsorbed at the non-oxidized region of GO surface, and they are electroactive and respond on CV.²⁸ In order to understand the difference in adsorption state at both electrodes more clearly, we carried out XPS measurement of FePc/GO and FePc/ER-GO samples. Figure 1(b) compares the Fe $2p$ spectra obtained for 50% FePc samples. Two peaks were observed in the region; the signals around 724 and 710 eV correspond to $2p_{1/2}$ and $2p_{3/2}$, respectively. Since the former peak is not clearly seen, we will focus on the latter peak in the following discussion. The peak location of 710 eV indicates the Fe^{2+} state of

Figure 2. (a) Schematic images of the interaction between FePc and GO or ER-GO. The FePc in pale and deep colors indicates electroactive and inactive states, respectively. (b) the images of FePc/CR-GO.

the central iron in FePc.²⁹ On the other hand, the $2p_{3/2}$ peak for FePc/GO sample seems to be asymmetric in shape and its foot extended to the higher binding energy, suggesting the presence of Fe^{3+} state (713 eV¹⁶) in the sample. It may be explained as follows; FePc is considered to adsorb at the oxygen site of GO preferably via coulombic interaction (Fig. 2), and a partial charge transfer from central iron to the substrate might be induced by the difference in electronegativity. On the other hand, FePc adsorbs on ER-GO not via coulombic but electronic π - π interaction, and no net change in molecular charge can be expected.

Here we need to consider additional factor that promotes the adsorption of FePc on GO. It has been pointed out that the molecular adsorption can be promoted by the defects (vacancies) introduced by the oxidation treatment of graphite.²⁷ To evaluate the effect, we prepared chemically reduced GO (CR-GO) sample by using hydrazine as the reducing agent. FePc was adsorbed to the CR-GO surface to form FePc/CR-GO [Fig. 2(b)], while FePc was introduced to GO surface before submitting electrochemical reduction in the case of FePc/ER-GO. Although the reduction conditions were different, the recovery of sp^2 carbon up to 80% was confirmed by XPS measurement for both samples. The fabricated FePc/CR-GO/GC electrode showed a CV response shown in Fig. 1(c), and one can recognize that the current peak is almost two orders smaller in magnitude than that of FePc/ER-GO. From this result, the effect of defects toward FePc adsorption on GO could be safely excluded.

We observed the formal potential of $\text{Fe}^{3+/2+}$ couple changed with the amount of FePc included in the FePc/GO mixture. Figure 3(a) plots the measured formal potential (E^0) against the weight fraction of FePc. Here we define E^0 as the midpoint potential of anodic/cathodic peaks. As seen in the figure, E^0 ($\text{Fe}^{3+/2+}$) initially shifted to the positive direction up to 50% and then it turned to negative potentials. We tried the same experiment using differently aged FePc/GO mixture samples to check the reproducibility, and found similar tendency as shown in the figure. The reason for this potential shift depending on the FePc fraction will be discussed later.

Next, we consider the ORR behavior observed at the FePc/ER-GO/GC electrode. Figure 3(b) shows an ORR voltammogram measured in O_2 saturated 0.1 M KOH solution. The reduction current started to flow around the $\text{Fe}^{3+/2+}$ redox potential of FePc, which strongly suggests that the couple plays a role in the catalytic reduction of O_2 . We carried out RDE measurement in order to discuss the detail of ORR. Figure 4(a) and (b) show LSVs obtained at 60% FePc/ER-GO and the Koutecky-Levich plot, respectively. The results indicated that oxygen was reduced via 4-electron process

Figure 3. (a) The relationship between E^0 ($\text{Fe}^{3+/2+}$) of FePc and its fraction in FePc/GO composite. Open squares, open triangles, open inverse triangles indicate the data obtained for electrodes fabricated with aged FePc-GO mixture solution for 1, 3 and 7 days. (b) Cyclic voltammograms of 10% FePc/ER-GO/GC in deaerated (solid) and O_2 saturated (dotted) 0.1 M KOH solution. The deposited amount of FePc-GO was 10 μg .

Figure 4. (a) RDE-LSVs tests obtained for 60% FePc/ER-GO at various speed. (b) Koutecky-Levich plots for 60% FePc/ER-GO obtained from RDE measurements (a). (c) The relationship between E^0 ($\text{Fe}^{3+/2+}$) and the onset potential of ORR. The onset potential was determined as the potential where the ORR current reached at $-50 \mu\text{A}$. The onset potential was estimated by RDE measurement at 1600 rpm.

at the FePc catalyst, which was confirmed by no response in the ring current (not shown). Thus, the number of electrons involved in ORR for a series of FePc/ER-GOs estimated from the slope of the Koutecky-Levich plots was four irrespective of the FePc content.

The onset potential of ORR was shifted depending on the FePc fraction; as indicated in Fig. 4(c), almost linear relationship between the onset potential and E^0 ($\text{Fe}^{3+/2+}$) was observed. The rate constants (k^0 s) for ORR at 0.95 V for 60% FePc/ER-GO and 20% FePc/ER-GO estimated from the intercept of the Koutecky-Levich plot were $2.4 \times 10^{-3} \text{ cm s}^{-1}$ and $1.4 \times 10^{-3} \text{ cm s}^{-1}$, respectively. Such a small change in k^0 cannot solely explain the overall shift in onset potentials. Instead, it may be reasonable to consider the observed shift in connection with the change in E^0 ($\text{Fe}^{3+/2+}$).

Now we consider why E^0 ($\text{Fe}^{3+/2+}$) shifted as the FePc fraction changed. Figure 5 shows XP spectra obtained for 10, 50 and 80% FePc/ER-GO samples. Fe $2p_{3/2}$ spectra [Fig. 5(a)] revealed that both of the Fe^{3+} and Fe^{2+} states^{16,29} are present in 80 and 50%

Figure 5. XPS spectra of Fe 2p_{3/2} (a) and N 1s (b) obtained for 10% (i), 50% (ii), 80% (iii) FePc/ER-GO. The intensities of both N 1s and Fe 2p_{3/2} spectra of 10% sample were multiplied by 2.

Figure 6. (Color online) The theoretically predicted model of FePc adsorption on a nanographene composed of 91 aromatic rings. (a) Side view and (b) top view. The average distance between FePc and nanographene was 0.328 nm.

samples. On the other hand, the Fe⁰ peak at 708 eV^{30,31} was only observed for 50% sample. The reason why the Fe⁰ peak appeared could be explained based on the occupancy of FePc at ER-GO surface. We estimated the molecular occupancy (θ_{FePc}) as follows; first, the total surface area of ER-GO ($A_{\text{ER-GO}}$) was calculated from the unit lattice area multiplied by the number of carbon atoms included in ER-GO, which was estimated from the weight of GO taking into account the oxygen content. Then the ideal total area occupied by FePcs (A_{FePc}) was calculated assuming the close-packed planar adsorption (i.e., the number of FePc molecules in FePc/GO composite multiplied by the molecular area of FePc). Finally the occupancy of FePc was obtained as $\theta_{\text{FePc}} = A_{\text{FePc}} / (2 \times A_{\text{ER-GO}})$, in which the surface area of ER-GO was doubled taking into consideration of both sides of the sheet. Following this procedure, the θ_{FePc} values for 10, 50 and 80% FePc/ER-GO samples were estimated as 0.12, 1.10 and 4.38, respectively. The result indicates that the relative content of FePc is too low for 10% fraction sample, while too high for 80% sample. In contrast, the occupancy obtained for 50% sample suggests the amount of FePc molecules that is consistent with almost full monolayer coverage. The theoretically simulated equilibrium structure of FePc adsorbed on nanographene (C₂₂₂H₄₂) is shown in Fig. 6. The calculation predicted that 0.668 electrons are transferred from graphene to FePc. Therefore the surface FePcs are considered not to be a neutral species, but in a negatively-charged state. It might be the reason for the appearance of Fe⁰ peak on XPS spectrum of 50% sample. In contrast, when FePcs forms a multilayer as in the 80% sample, the effective charge transferred from graphene to each FePc would become smaller compared with the case of 50% one. Similar XPS results were

Figure 7. Schematic rough images of the structure for 10% FePc/ER-GO and 50% FePc/ER-GO. The deep and pale colored FePcs charge positively and negatively, respectively.

reported for FePc adsorbed on Au(111)³⁰ or CoPc adsorbed on Ag(111) and Au(111).^{32,33} In consequence, it is plausible that FePc in 50% sample charged more negative than that in 80% sample. The relative peak area of Fe 2p was not in proportion to FePc fraction of the samples, since the surface distribution of the deposits at each sample was not uniform and thus it was difficult to compare them quantitatively.

Since the Fe 2p_{3/2} peak could not be observed clearly in 10% FePc/ER-GO due to low content of FePc, we instead discuss the N 1s peak which was clearly seen as in Fig. 5(b). When we compare the spectra obtained for 10, 50 and 80% samples, we notice that the N 1s peak in 10% sample has additional component in the higher binding energies. Since the coulombic interaction exerting between surface oxygen moiety and central metal of FePc is considerably intense compared to π - π interactions as mentioned previously, FePc molecules in 10% sample are considered to adsorb favorably on the oxygen site (Fig. 7). Such FePcs are apt to lose electrons partially due to the electronegative nature of oxygen atom. It may be the origin for the development of high-energy N 1s component seen in the spectrum of 10% sample. Consequently, adsorbed FePc charges positively while the substrate ER-GO negatively, which is opposite in the case of 50% FePc/ER-GO.¹⁷ From this consideration, we can conclude that the FePc in 50% FePc/ER-GO would be charged most negatively among the three samples. It means that the FePc in 50% sample undergoes the easiest electrochemical reduction, i.e., has the most positive E^0 .

4. Conclusion

It has been revealed that the coulombic interaction between the surface oxygen site and the central metal of FePc was more effective than the π - π interaction at basal plane or the defect effect for stabilized adsorption of FePc on GO. In addition, we found the formal potential of FePc in the composite strongly depended on the FePc fraction, and the most positive value was obtained at 50% sample in which a full monolayer of FePc was considered to be established. The potential shift was thought to be originated from the electronic interaction of FePc with the substrate graphene surface deduced from the XPS results as well as the theoretical calculations.

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