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 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 \(\text{O}_2\) 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 \(\text{O}_2\) 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 \(\text{O}_2\) 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 \(\pi\) 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 converter\(^9\) 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, SHIMAZU) 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...
and 0.7 V for 10 times in 0.1 M H2SO4 solution, and a known reduced GO (ER-GO) was used as the working electrode. The FePc (aromatic rings (C222H42) 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 M H2SO4 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 M Na2SO4 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, 15%), carbonyl and quinone groups (287.3 eV, <1%) and carboxyl or ester groups (288.6 eV, 6%) were determined.

Figure 1. (a) Cyclic voltamograms of 50% FePc/GO/GC (thick) and 50% FePc/ER-GO/GC (thin) measured in deaerated 0.1 M KOH solution (v = 10 mV s−1). The current for FePc/GO/GC was multiplied by 5. The amount of FePc-GO deposited was 2 µg. (b) Fe 2p3/2 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 (v = 10 mV s−1). The amount of FePc-GO deposited was 10 µg. 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 Fe3+/2+ and Fe2+/1+ redox reactions, respectively.15 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 Fe3+/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 sp2 to sp3.24 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 2p1/2 and 2p3/2, 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 2p3/2. The peak location of 710 eV indicates the Fe 2p3/2, which suggests that a small 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 2p1/2 and 2p3/2, 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 2p3/2, which suggests that a small

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 10−3 Ha/au. In these calculations, the double numerical atomic orbital augmented by a polarization d-function (DND) was chosen 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.
the central iron in FePc.29 On the other hand, the 2p3/2 peak for FePc/GO sample seems to be asymmetric in shape and its foot extended to the higher binding energy, suggesting the presence of Fe3+ 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 sp2 carbon up to 80% was confirmed by XPS measurement for both samples. The fabricated FePc/CR-GO/GO 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 Fe3+/2+ couple changed with the amount of FePc included in the FePc/GO mixture. Figure 3(a) plots the measured formal potential (E0) against the weight fraction of FePc. Here we define E0 as the midpoint potential of anodic/cathodic peaks. As seen in the figure, E0(Fe3+/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/GO electrode. Figure 3(b) shows an ORR voltammogram measured in O2 saturated 0.1 M KOH solution. The reduction current started to flow around the Fe3+/2+ redox potential of FePc, which strongly suggests that the couple plays a role in the catalytic reduction of O2. 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 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-GO catalysts was determined as the potential where the ORR current reached at −50 μA. The onset potential was estimated by RDE measurement at 1600 rpm.

Now we consider why E0(Fe3+/2+) shifted as the FePc fraction changed. Figure 5 shows XP spectra obtained for 10, 50 and 80% FePc/ER-GO samples. Fe 2p3/2 spectra [Fig. 5(a)] revealed that both of the Fe3+ and Fe2+ states are present in 50%
samples. On the other hand, the Fe$^0$ peak at 708 eV\cite{30,31} was only observed for 50% sample. The reason why the Fe$^0$ peak appeared could be explained based on the occupancy of FePc at ER-GO surface. We estimated the molecular occupancy (\(\theta_{\text{FePc}}\)) 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 (\(A_{\text{FePc}}\)) was calculated assuming the close-packed planer 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 \(\theta_{\text{FePc}}\) 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 (\(C_{22}H_{12}\)) 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 Fe$^0$ peak on XP 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 reported for FePc adsorbed on Au(111)\cite{30} or CoPc adsorbed on Ag(111) and Au(111)\cite{31,32}. 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$^{1/2}$ 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 \(\pi-\pi\) 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 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 \(\pi-\pi\) 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 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.

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 \(\pi-\pi\) 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.

References