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Immobilization of a non-heme diiron complex encapsulated in an ammonium-type ionic liquid layer modified on an Au electrode: reactivity of the electrode for O₂ reduction[†]

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An unstable diiron(II,II) complex possessing O_2 binding ability at low temperature was encapsulated and stabilized in an ammonium-type ionic liquid layer polymerized on an electrode. The encapsulated complex revealed catalytic reactivity for four-electron reduction of O_2 at an ambient temperature in aqueous solution.

Four electron reduction of dioxygen is an important cathode reaction in fuel cells. At the present time, Pt nanoparticles are typically used as a cathode catalyst in fuel cells, because they promote four electron reduction of dioxygen.¹ However, Pt is very expensive and thus restricts widespread commercial development of fuel cells. Therefore, many researchers have been motivated to develop novel electrode catalysts such as Ag or Fe alloy nanoparticles as substitutes for Pt.² In addition, metal-complex-based molecular catalysts have been investigated.³ Miyazato et al. succeeded in promoting the four electron reduction of dioxygen using dinuclear cobalt complexes.³ Lei et al. also developed a Co complex polymer and deposited it onto a glassy carbon electrode in an effort to develop an electrode-based catalyst for dioxygen reduction.3 Ogo et al. recently reported a Ru complex for use as both the anode and cathode catalysts of a fuel cell.³ However, Co and Ru are also expensive materials. There are few reports on the study using iron complexes. We have studied inexpensive iron complexes as molecular catalysts for dioxygen reduction and reported two electron reduction of dioxygen using a non-heme

diiron complex (Fe_2) modified on an Au electrode.⁴ In the same study, we reported that Fe_2 , a non-heme enzyme model complex with a dinucleating ligand bearing bulky pivalamide groups on its pyridine rings, binds O_2 in acetone at low temperatures. The Fe_2 complex is fixed to the Au electrode. The diiron complex is substituted with alkanethiol to provide a self-assembled monolayer (SAM).⁴ However, the redox potential of the diiron complex in the Fe_2 -modified electrode is shifted towards a negative direction relative to that of Fe_2 under homogenous conditions. The SAM method often alters the chemical properties of the molecules immobilized on the surface.⁵ As a result, the Fe_2 -modified Au electrode would be incapable of activating dioxygen efficiently.

To resolve this problem, we investigated a new method to entrap a functional compound on the surface as an alternative to the use of SAMs. We focused on using an ionic liquid (IL) to provide a reaction field on the Au surface.⁶ Generally an IL, an ionic compound in the liquid state at room temperature, exhibits properties such as ionic conductivity, incombustibility, low vapor pressure and a wide-potential window. These properties are quite useful for the development of lithium batteries, fuel cells, dye-sensitized solar cells, and other related applications.⁷ Previously, Chi et al. entrapped a negatively-charged metal complex on an imidazolium-type IL SAM modified-electrode.⁸ Unfortunately, a positively-charged complex could not be entrapped on the IL modified-electrode because of the electrostatic repulsion between them. Thus, an electrostatic interaction was found to be important for entrapping the complex. On the other hand, in our previous report, we modified an Au electrode with a bulky phosphonium-type IL,6 and have succeeded in entrapping three types of metal complexes into the vacant space generated among the IL molecules, regardless of the net charge of the complexes and without generating any chemical bonds. We applied this method to modify an Au surface with Fe2. Interestingly, the redox potential of Fe_2 for O_2 activation appears in a more positive potential region relative to that of the SAM method.^{4,6} Moreover, the O₂ activation process catalyzed by the Fe2 complex entrapped on the IL-modified Au surface includes a four electron reduction process in addition to the two electron reduction process. The O2 reduction activity was

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[†] Electronic supplementary information (ESI) available: Details of the preparation of **1**, IR spectrum and CV for **1**/Au electrodes, IR spectra, CVs, and relationships between peak current densities and scan rates for Fe_2 @**1**/Au and Fe_2 @**poly-1**/Au, CVs and LSVs of Fe_2 @**1**/Au and Fe_2 @**poly-1**/Au under O₂ condition, Koutecky–Levich plots for Fe_2 @**1**/Au and Fe_2 @**poly-1**/Au. See DOI: 10.1039/c5cc10263d



Fig. 1 Schematic view of the ammonium-type IL containing a disulphide group and six terminal olefins, **1**. **1** can be constructed on an Au surface using a self-assembled monolayer method to give **1**/Au. **1**/Au can entrap an external metal complex inside its IL monolayer, **Fe**₂@**1**/Au. This IL monolayer can be polymerized in an olefin metathesis reaction and encapsulate the entrapped metal complex in order to prevent its decomposition and release from the monolayer, **Fe**₂@**poly-1**/Au.

apparently enhanced. However, the reactivity of the Fe_2 complex entrapped on the IL-modified Au surface might decrease through the O_2 activation process because the entrapped Fe_2 complex may be gradually released from the IL-modified Au surface.

Herein, we propose an improved method as shown in Fig. 1. This method includes the step of introduction of an original ammonium-type IL having a disulphide group at the terminus and six terminal olefins in the IL-head groups, **1**. **Fe**₂ was encapsulated in the IL SAM modified on the Au electrode by performing a cross-linking reaction among the olefins of IL-head groups in order to protect Fe_2 on the Au surface from external materials. Fe_2 was stabilized on the Au surface and was found to promote effective O₂ activation.

The ammonium-type IL, 1, was synthesized by a modified version of the previously published method.⁶ 1 is in a liquid state at room temperature, and was characterized by spectroscopic measurements (Schemes S1 and S2, ESI⁺). It was determined that 1 was able to construct its self-assembled monolayers (SAMs) on an Au electrode by forming Au-S bonds and also by cross-linking among molecules of 1 on the Au electrode in an olefin metathesis reaction. The Au electrode modified with 1, 1/Au, was prepared by directly casting a few drops of 1 onto the Au disk electrode of a rotating ring-disk electrode (RRDE) over the course of a few days. After washing with EtOH and CH₃Cl, 1/Au was successfully obtained. Modification of the Au disk electrode with 1 as a SAM was confirmed by IR-reflectionabsorption spectroscopy (IR-RAS) measurements and various electrochemical measurements (Fig. S1 and S2, ESI[†]). The surface coverage of **1** was estimated to be 2.7×10^{-10} mol cm⁻² from charges for a reductive desorption wave of 1 in linear sweep voltammetry measurements of 1/Au (Fig. S3, ESI⁺). The resulting coverage is greater than that of a previous SAM on an Au electrode which was generated using a phosphonium-type IL $(9.1 \times 10^{-11} \text{ mol cm}^{-2})$.⁶ The coverage of **1** was found to be three times greater than that of the previous SAM. This may be explained in terms of the atomic sizes of the cation of the modified ILs. The ammonium-type IL is smaller than the phosphonium-type ion. Therefore, the electrostatic repulsion between cations of 1 is smaller than that of the phosphonium type SAM.

The soaking of Fe_2 into the IL SAMs of 1/Au, to obtain Fe_2 @1/Au, was carried out in MeOH solution (1 mM). After washing with

CH₂Cl₂ and acetone, Fe₂(**1**/Au was successfully obtained. Introduction of Fe₂ onto 1/Au was confirmed by IR-RAS measurements and various electrochemical measurements (Fig. S4 and S5a, ESI[†]). The cyclic voltammogram of Fe₂(**1**/Au in 0.1 M NaClO₄ (scan rate = 0.1 V s⁻¹) has two redox waves at 0.13 V *vs*. Ag/AgCl. The redox waves are assignable to two-electron redox waves of Fe₂(**n**,**n**/**m**,**m**), as deduced from a comparison with the previous data.^{4,6} In order to evaluate the situation of Fe₂ in 1/Au, the peak current densities of Fe₂ *vs*. the scan rates were plotted. Interestingly, a linear relationship (Fig. S5b, ESI[†]) was obtained, obviously indicating that Fe₂ is entrapped in SAMs of 1/Au.

Finally, we performed a polymerization of 1 by conducting an olefin metathesis reaction with 0.4 mg mL⁻¹ Grubbs 2nd generation catalyst solution to obtain a new device, Fe₂@poly-1/ Au, that was encapsulated with Fe_2 in the SAMs of 1/Au. The obtained Fe2@poly-1/Au would prevent Fe2 from being released from the SAMs. The IR-RAS spectrum of the resultant surface has a peak at 1647 cm^{-1} , which is assignable to the C=C stretching frequency of terminal olefins of 1. This peak disappears after the olefin metathesis reaction, indicating that Fe2@poly-1/Au is generated (Fig. S4, ESI⁺). The peaks near 1450 cm^{-1} and a peak at 718 cm^{-1} , which are assignable to the pyridyl backbone of Fe2 and the C-H bending vibration of benzoate related to Fe2, respectively, were still observed in the spectrum of Fe₂@poly-1/Au. Furthermore, the peaks assignable to C=C bond stretching were not found in the spectrum after polymerization of 1. On the basis of the selection rule for IR-RAS, this implies that the C=C bond is parallel to the Au electrode surface.

The cyclic voltammogram of Fe_2 @poly-1/Au in 0.1 M NaClO₄ aqueous solution (scan rate = 0.1 V s⁻¹) has two redox waves at 0.12 V vs. Ag/AgCl (Fig. 2a), which are assigned to two-electron redox processes of Fe₂(Π,Π,Π,Π) based on a comparison with those of Fe₂@1/Au. In order to evaluate Fe₂@poly-1/Au, the peak current densities of Fe₂ were plotted against the scan rates. The resulting linear relationship, which is similar to that of Fe₂@1/Au, indicates that Fe₂ remains entrapped in SAMs of 1/Au (Fig. 2b). Additionally, the surface coverage of Fe₂ in Fe₂@poly-1/Au was estimated to be 4.4×10^{-12} mol cm⁻² as judged from its redox waves. These electrochemical data are discussed in comparison with those of Fe₂@1/Au.

The redox potential of Fe_2 @poly-1/Au was found to be similar to that of Fe_2 @1/Au (Table S1, ESI†), indicating that



Fig. 2 (a) Cyclic voltammogram of $Fe_2@poly-1/Au$ in 0.1 M NaClO₄ aqueous solution (scan rate = 0.1 V s⁻¹). (b) The plots of the peak current densities of $Fe_2@poly-1/Au$ towards the scan rates of the CV measurement for $Fe_2@poly-1/Au$.

the electrochemical conditions of Fe2 on their respective electrodes are similar and that the polymerization of 1 on the electrode does not affect the electrochemical conditions of Fe2 on the electrode. In addition, stabilities of Fe2 on their respective electrodes are similar to each other, because the redox waves assignable to Fe_2 were observed during several cycles of the CV measurements of the respective electrodes. On the other hand, the surface coverage of Fe2 on Fe2@poly-1/Au is approximately 3 times less than that of Fe2@1/Au. The decrease in Fe2@poly-1/Au might be an indication of a decrease in the space generated among 1 molecules, where Fe_2 should be entrapped on the surface. The polymerization of 1 may have shortened the distances between neighbouring molecules of 1. Approximately 60% of Fe2 that was entrapped in Fe2@1/Au was released outside of the SAMs after the polymerization. This means that the electrochemical characteristics of Fe2 entrapped on an Au electrode, Fe2@poly-1/Au, are similar to its characteristics in CH₂Cl₂ solution. Two major differences were observed between the electrochemical behaviour of Fe2 in Fe2@poly-1/Au and that of Fe₂ in CH₂Cl₂. The first difference is in the number of redox waves and the second difference is in redox potential values. CVs of Fe₂@poly-1/Au (Fig. 2a) and Fe₂@1/Au (Fig. S5a, ESI[†]) both exhibit two redox waves related to Fe₂. However, the CV of Fe₂ in CH₂Cl₂ has three reduction waves and one oxidation wave (Fig. S7, ESI⁺). The decrease in the number of the reduction waves may be due to the restriction in the structural change of Fe_2 during reduction on the electrode surface. In our previous work,⁴ we also reported that Fe₂ undergoes such a structural change during the electrochemical reduction process in solution; Fe2 possesses two reduction processes after one electron reduction of $Fe_2(\pi, m/m, m)$. The $Fe_2(\pi, n/m, m)$ reduction process is accompanied by a structural change and the Fe₂(II,II/II,III) reduction process occurs without any structural change (Scheme S3, ESI⁺). This is because Fe₂ is restricted from undergoing structural changes due to space constraints when it is located in the IL SAMs of Fe₂@1/Au and Fe₂@poly-1/Au, although it can transform freely in a homogeneous solution. In addition, the electron transfer rate between Fe_2 and the electrode on the Au surface is faster than that in bulk solution. Therefore, it is possible that a two electron reduction process of Fe₂ entrapped on the surface proceeds immediately and then only two redox waves are observed in the CVs.

To evaluate the catalytic activity of Fe_2 for O_2 reduction in Fe_2 (LSV) measurements

were performed in O_2 saturated aqueous solution using RRDE. Fig. S10 (ESI[†]) shows that the O₂ molecules bound to Fe₂@poly-1/ Au on the disk electrode are converted to the 2-electron reduced species, such as H_2O_2 or O_2^{2-} , at around 0 V vs. Ag/AgCl. The same behaviour was also observed in Fe2@1/Au (Fig. S8, ESI⁺). These findings indicate that both Fe2@1/Au and Fe2@poly-1/Au can reduce O_2 to O_2^{2-} . We estimated the number of electrons related to O₂ reduction in these systems by generating a Koutecky-Levich plot.⁹ In the Koutecky–Levich equation, i_D^{-1} (i_D : the disk current) is proportional to $\omega^{-1/2}$ ($\omega^{1/2}$: square root of the rotation rate) when the electron transfer rate is sufficiently slow (i.e. an irreversible system). For Fe2@poly-1/Au, a linear relationship was observed between $i_{\rm D}^{-1}$ and $\omega^{-1/2}$ only with slower rotation rates (100–1600 rpm) (Fig. S12, ESI⁺). Fe₂(a)1/Au also showed almost the same behaviour as Fe2@poly-1/Au. The apparent number of electrons (n_{app}) related to the O₂ reduction process promoted by Fe₂@poly-1/ Au was estimated to be 3.4 from the plots. The resulting n_{app} in Fe₂@poly-1/Au indicates that two reduction processes for the O₂ molecule, two- and four-electron reductions, coexist in the system. In contrast, n_{app} for Fe₂@1/Au was estimated to be 2.6, indicating that the two-electron reduction process is dominant over the fourelectron reduction, as compared with Fe2@poly-1/Au. Furthermore, the capture rate (N) of H_2O_2 generated on the disk electrode is also estimated from the equation $N = i_R/i_D$ (i_R : ring current). The resulting Ns in Fe2@poly-1/Au and Fe2@1/Au were found to be 0.36 and 0.43, respectively. These findings clearly indicate that the four-electron reduction process of O2 in Fe2@poly-1/Au is more prominent.

Fe2@poly-1/Au and Fe2@1/Au can at least activate O2 to reduce to O_2^{2-} . The four-electron reduction process of O_2 in Fe₂@poly-1/Au is dominant. This indicates that Fe₂@poly-1/Au has the potential to be developed as a cathodic electrode for a fuel cell. Previously, Islam et al. reported that an ionic liquid is capable of lowering the overpotential for O₂ reduction relative to an organic solvent.¹⁰ Therefore, we can conclude that the IL contributes to the activation of the reduced species of O2. The four-electron reduction process of O2 in our system has been achieved by a synergistic effect provided by Fe2 and the ionic liquid 1 immobilized on the surface. Herein, why is the n_{app} value improved after the polymerization of the IL layer on the surface? We believe that the improved n_{app} value in Fe₂@poly-1/ Au is due to the more stabilized intermediate of the complex binding a dioxygen than that in Fe₂(a1/Au. We have suggested that the hydrophobic space constructed with the alkyl chains of the ILs in Fe2@poly-1/Au prevents access of water molecules to the intermediate more than that in Fe_2 (1/Au. As a result, the polymerized IL layer in Fe2@poly-1/Au inhibits a disproportional reaction of the O_2 activated by Fe_2 to H_2O_2 or O_2^{2-} . Therefore, four-electron reduction of O2 has been promoted in the polymerized IL layer. This is reason why the $n_{\rm app}$ value has been improved after the polymerization of the IL layer. Finally, we have concluded that the encapsulation of Fe₂ on the surface by polymerization of 1/Au enhances the synergetic effect.

In summary, we succeeded in promoting four-electron reduction of O_2 using Fe_2 @1/Au (an entrapped and immobilized complex) and Fe_2 @poly-1/Au (an entrapped and immobilized

complex by polymerized IL), under an O_2 atmosphere at ambient temperature. Furthermore, the entrapped Fe_2 complex $Fe_2@poly-1/$ Au exhibits enhanced promotion of the four-electron reduction of dioxygen. This is proposed as the "encapsulation effect".

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