

Investigation on Oxygen Reduction Reaction Activity of Multi-Copper Complex Deposited on Electrodes by XAFS

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1 Introduction

The oxygen reduction reaction (ORR), which occurs at the cathode in polymer electrolyte fuel cells (PEFCs), requires a large overpotential (more than 200 mV) even at the highly active platinum group metal (PGM) catalysts, since this reaction contains 4-electrons and 4-protons transfer to yield two water molecules from a dioxygen molecule. However, the biocathodes which are constructed by covalently attaching multi-copper enzymes, such as laccase (Lac), at electrode surfaces show nonexistent overpotential (ca. 20 mV) toward ORR [1-2]. Unfortunately, the pH region, where the Lacs works well as an electrocatalyst for ORR, is limited and the spatial density of reactive sites at such the biocathode seems to be insufficient as compared with the state-of-the-art PGM electrocatalysts. Thus, the extraction of reactive sites in Lac and the effective arrangement on catalyst supports have been desired [3].

Recently, Gewirth and co-workers have achieved a preparation of binuclear copper complex, $\text{Cu}_2(\text{Hdatrz})_2$, (Hdatrz: 3,5-diamino-1,2,4-triazole), as an electrocatalyst for ORR[4-6]. The molecular structure of $\text{Cu}_2(\text{Hdatrz})_2$ complex is shown in Fig. 1. Although the catalyst shows relatively large overpotential for ORR in acidic solution, the activity in alkaline solution is quite high. The active site for ORR in the catalyst has been proved to be bi-copper centers [6-7] and the investigation of the molecular structure of bi-copper complexes and their ORR mechanism at the catalyst seems to be valuable.

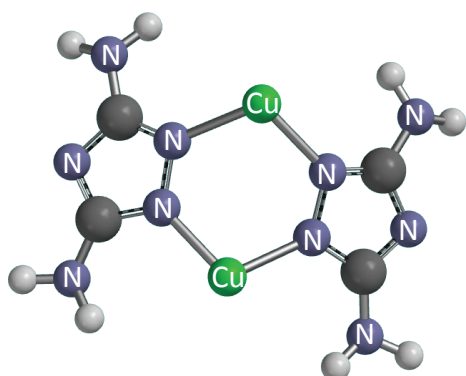


Fig. 1: Molecular structure of $\text{Cu}_2(\text{Hdatrz})_2$.

In the present study, we have adopted X-ray absorption fine structure (XAFS) spectroscopy to monitor the electronic structure of Cu centers during ORR and to

determine the molecular structure of $\text{Cu}_2(\text{Hdatrz})_2$ complexes on electrodes. *In situ* XANES measurements have shown that the ORR at the Cu centers requires the formation of Cu^1 species and the rate-determining step for ORR is dependent on pH.

2 Experiment

Preparation of $\text{Cu}_2(\text{Hdatrz})_2$ complex-deposited carbon black (CB) is fundamentally based on the methods in the literature[4]. In the literature, Vulcan was used as CB support, but Ketjen ECP300 was mainly adopted as catalyst support. The difference in the relative surface area of these CBs ($247 \text{ m}^2 \text{ g}^{-1}$ and $813 \text{ m}^2 \text{ g}^{-1}$ for Vulcan and Ketjen black, respectively) is expected to affect the electrocatalytic activity of the catalysts. The amount of deposited Cu was systematically changed from the same amount in the literature (denoted as $\text{Cu} = 1$) to 10 times larger one ($\text{Cu} = 10$). Catalysts deposited GC electrodes (the diameter is 5 mm) were prepared by casting the catalyst dispersion followed by the cast of Nafion ionomer dispersion and the Cu contents on the electrodes were kept to be ca. $4 \mu\text{g cm}^{-2}$. The electrochemical characterization was carried out using three-electrode configuration with a Pt counter and a double-junctioned Ag/AgCl reference electrodes in Britton-Robinson buffer (pH 7, 10, and 13) solution containing 0.1 M NaClO_4 electrolyte. Electrocatalytic activity of the catalysts was evaluated using rotational disk electrode (RDE) with changing the rotational speed under dioxygen-saturated atmosphere.

For *in situ* XANES measurements, the catalysts were cast on Kapton windows with conductive metal or carbon films to use as working electrodes. The catalysts-cast Kapton window was attached with a proper O-ring on the spectroelectrochemical cell designed for *in situ* XAFS spectroscopy. The *in situ* fluorescent XANES measurements were carried out with the incident angle of 45° and a liquid nitrogen-cooled multichannel solid-state detector (MSSD) was set at around the reflected direction of the incident X-ray. All the XAFS measurements were performed at around the energies of Cu K-edge.

3 Results and Discussion

Figure 2 shows XANES spectra of various copper species. For both $\text{Cu}_2(\text{Hdatrz})_2$ crystal and the complex-deposited catalysts, the pre-edge peak at around 8980 eV, which can be assigned to $1s-4p$ transition of Cu^1 species,

was not observed, indicating that deposited Cu complex contained Cu^{II} oxidation state. The result seems to be reasonable since the Cu species in Cu₂(Hdatrz)₂ complex was introduced from CuSO₄.

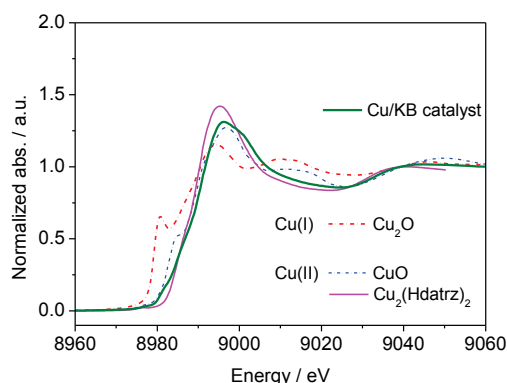


Fig. 2: XANES spectra of various Cu species including Cu₂(Hdatrz)₂ crystal and catalyst.

When the electrode potential of bi-Cu complex deposited electrode in nitrogen-saturated electrolyte solution (pH7) was shifted to the negative direction, the pre-edge peak at ca. 8980 eV gradually grew and the edge jump became smaller, as shown in Fig. 3. The growth of the pre-edge peak in the inert atmosphere means electrochemical reduction of Cu centers from Cu^{II} to Cu^I species. In real, redox peaks have been observed at the catalysts-cast GC electrodes in the inert atmosphere.

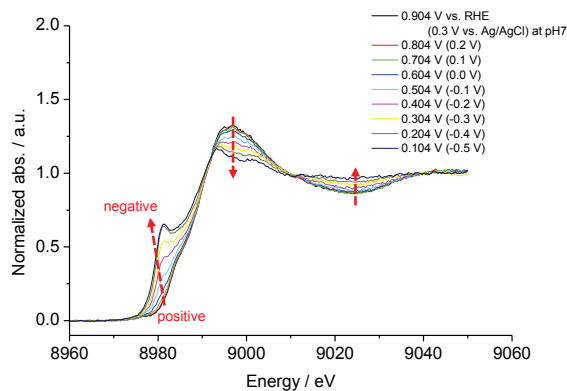


Fig. 3: Potential dependent XANES spectra of Cu₂(Hdatrz)₂/KB catalysts. The dashed arrow shows the change in the spectra by potential shift.

Figure 4 shows the potential dependent XANES spectra in (a) pH7 and (b) pH10 electrolyte solutions, respectively, under inert (solid lines) and dioxygen-saturated (dashed lines) conditions. At pH7, the XANES spectra under inert and dioxygen-saturated conditions at the same potentials overlap each other. At pH10, on the other hand, the XANES spectra under the dioxygen-saturated condition (dashed lines) show smaller pre-edge peak at around 8980 eV than those under the inert condition (solid lines), indicating the decrease in the concentration of reduced (Cu^I) species. Such the pH-dependence can be explained by considering the change

in the rate-determining step for the ORR at bi-Cu complex.

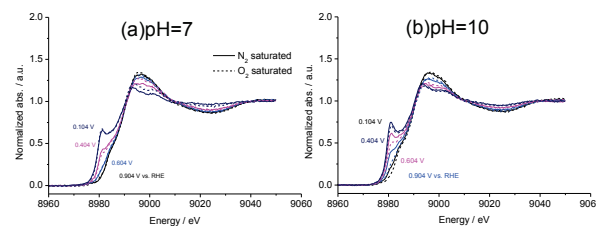


Fig. 4: Potential dependences of XANES spectra at (a) pH7 and (b) pH10 under N₂-saturated (solid lines) and O₂-saturated (dashed lines) conditions

Simply, let us assume two kinetic processes for ORR at bi-Cu complex. The first process is the electron transfer from electrode to Cu^{II} centers and the second process is the electron transfer from Cu^I center to adsorbed dioxygen species. When the first step is much faster than the second step, the Cu^I species can always exist at the electrode surface as a function of the electrode potential regardless of the adsorbed dioxygen at Cu centers. On the other hand, if the second process is much faster than the first process, the surface concentration of Cu^I species decreases by the consumption of electrons to form the ORR intermediates. Thus, the first and second processes are the rate-determining steps at pH10 and pH7, respectively. However, ORR is the 4-electrons and 4-protons transfer reaction and the further resolution of the elemental steps for the ORR at bi-Cu complex to develop the bio-inspired electrocatalysts to be comparable to the metal enzymes.

Acknowledgement

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