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<th>Deprotonation of a dinuclear copper complex of 3,5-diamino-1,2,4-triazole for high oxygen reduction activity</th>
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A dinuclear copper(II) complex of 3,5-diamino-1,2,4-triazole is one of the highly active copper-based catalysts for the oxygen reduction reaction (ORR) in basic solution. Our in situ X-ray absorption near edge structure measurements revealed that deprotonation from the triazole ligand might cause coordination geometrical changes, resulting in enhancement of the ORR activity.

Polymer electrolyte fuel cells (PEFCs) generate electricity from oxygen and hydrogen, where only water is produced without the formation of any toxic or greenhouse gases. PEFCs are sustainable power sources for mobile phones, laptop computers and vehicles, and have great potential to shift away from the fossil-fuel economy we have today toward a carbon-emission-free economy, where hydrogen will be used as an energy source. To develop practical PEFCs, we need to overcome many technical obstacles, and one scarce and the Pt-based cathodes still require a large overpotential of > 200 mV for ORR. It is highly desirable to find low-cost electrocatalysts that can fulfill demands in PEFCs.

In nature multicopper oxidases (MCOs) such as laccases are able to catalyze the ORR with great efficiency. MCOs reduce oxygen to water at their multi-nuclear copper active site with almost no overpotential (ca. 20 mV). It is most unlikely that the enzymes would be used as biocathodes in practical PEFCs, since the enzymes are easily denatured and their footprints are large (ca. 160 nm³ for laccase)., resulting in low stability and power outputs, respectively. The active site structures of MCOs, however, have inspired us to design artificial copper-based ORR catalysts, and many bio-inspired electrocatalysts have extensively been studied.

A bio-inspired dinuclear copper(II) complex of 3,5-diamino-1,2,4-triazole (Cu-Hdatrz, Scheme 1) supported on a carbon black shows high ORR activities in basic solutions. Although many studies on the Cu-Hdatrz catalyst have been done, for example, its tolerance to poisoning ions and its ORR activity in a lipid layer, its detailed catalytic mechanism has not been understood yet. The investigation of the chemical nature of Cu-Hdatrz under reaction conditions will give us insights into such high ORR activities in basic solutions, and will facilitate further development of bio-inspired ORR catalysts.

Here we report electrochemical and in situ X-ray absorption fine structure (XAFS) studies of the carbon-supported Cu-Hdatrz under neutral and basic conditions. In situ XAFS is a powerful technique to probe the electronic structure or coordination geometry of metal-based electrocatalysts under catalytic conditions. In this work we studied X-ray absorption near-edge structure (XANES) spectra of the Cu-Hdatrz at various bias potentials under neutral and basic conditions (pH 7, 10 and 13) to understand relationships between deprotonation of the active species and the ORR activity.

A carbon black-supported Cu-Hdatrz was synthesized from CuSO₄·5H₂O, Hdatrz and Ketjenblack ECP300 (KB), based on the method in the literature with slight modifications (See ESI†). KB was a carbon black with a relatively high BET surface area (813 m² g⁻¹), compared to Vulcan (247 m² g⁻¹), which was used as a carbon support in the original catalyst. Carbon supports with high surface areas, in principle, allow us to load well-dispersed catalysts, which are suitable for fluorescent XANES measurements with high data quality.

Cyclic voltammograms (CVs) of the copper(II) complex of Hdatrz supported on KB (Cu/KB) were recorded under Ar to understand the redox behavior of Cu/KB in a non-catalytic condition (Fig. 1). At pH 7 an oxidation wave at +0.73 V vs RHE and a reduction wave at +0.39 V vs RHE were observed, and these waves were assigned to an oxidation wave to CuII and a reduction wave to CuI, respectively. The peak separation

[Scheme 1 Molecular structure of the dinuclear copper(II) complex of 3,5-diamino-1,2,4-triazole (Cu-Hdatrz).]
between these peaks was approximately 0.33 V, which was much greater than 0 V for electrochemical active species strongly adsorbing on electrode surfaces, indicating that the electrochemical redox behavior of Cu-Hdatrz was irreversible. We also recorded CVs of Cu/KB at pH 4, pH 10 and pH 13, and obtained the similar results on the peak separation. Thus, the redox reaction of Cu\textsuperscript{II}-Hdatrz may involve structural changes such as geometrical changes around the metal center.

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The ORR activity of Cu/KB was studied using rotating ring disc electrodes (RRDEs) in buffered aqueous solutions at pH 4, 7, 10 and 13. Linear sweep voltammograms of Cu/KB were recorded at 1600 rpm under oxygen (Fig. 2). An onset potential of Cu/KB for ORR was observed at +0.77 V vs RHE at pH 7 and a diffusion-limited current reached ca. -1.0 mA. A quite similar ORR activity was observed for Cu\textsuperscript{II}-Hdatrz on Vulcan under the same condition (Fig. S1, ESI†), suggesting that there was no obvious effect of the carbon supports (KB and Vulcan) on catalytic activity. The ring current of Cu/KB is less than 5 μA at pH 7, indicating that almost no hydrogen peroxide generation during ORR. Thus, Cu/KB is able to selectively reduce molecular oxygen to water.

The ORR activity of Cu/KB depends on pH, and Cu/KB is more active in the basic solutions than in the neutral solution: the onset potentials for ORR were shifted in the positive direction with increasing pH, and the plot of the onset potential against pH gave a linear relationship with a slope of 26 mV / pH (Fig. 2C), which is equivalent to -33 mV / pH using a pH-independent reference electrode. This value is approximately half the value of -60 mV / pH, implying that the rate-limiting step involves the transfer of two electrons and one proton. The same results were reported on Cu\textsuperscript{II}-Hdatrz supported on a carbon black of Vulcan, where the reduction of two copper centers and the concomitant protonation of a bridging OH\textsuperscript{-} or O\textsuperscript{2-} ligand.\textsuperscript{17} These results suggest that carbon supports may not influence the ORR mechanism of Cu-Hdatrz in the pH range from 4 to 13.

In situ XANES spectra of Cu/KB were recorded at pH 7, 10 and 13 in catalytic (under O\textsubscript{2}) and non-catalytic conditions (under N\textsubscript{2}) to gain insights into active species during ORR. The potential dependent XANES spectra of Cu/KB are shown in Fig. 3. The spectra have isosbestic points, indicating that Cu\textsuperscript{II}-Hdatrz was electrochemically converted to one reduced species, and a characteristic peak appeared at ~8981 eV in the edge region upon the electrochemical reduction. This peak is assigned to the 1s → 4p\textsubscript{π} transition of a Cu\textsuperscript{I} complex.\textsuperscript{22-24} Thus, Cu\textsuperscript{II}-Hdatrz was electrochemically reduced and converted to the Cu\textsuperscript{I} species.
of Cu-Hdatrz under basic conditions is different from that under the neutral condition.

Considering the amounts of Cu calculated (Fig. 3) and two simplified electron transfer steps (Scheme 2), we concluded that the second electron transfer might be faster in the basic solutions than that in the neutral solution. The first step is the electron transfer from the electrode or KB to the CuII-Hdatrz complex and the second step is the electron transfer from the CuI species to molecular oxygen (the ORR step). The XANES spectra at pH 7 under N2 and O2 exhibited the same relative amounts of CuI at each potential, indicating that CuII-Hdatrz can be immediately reduced to the CuI species even in the presence of oxygen. At pH 10 and pH 13 less relative amounts of CuI were observed under O2 than those under N2, suggesting that the ORR was faster than the reduction of CuII-Hdatrz by the electrode or KB at pH 10. The second electron transfer (the ORR step) may be faster in the basic solutions than that in the neutral solution, which is consistent with the high ORR activity observed in the basic solution (Fig. 2).

Scheme 2 Simplified electron transfer steps in the Cu-Hdatrz/KB system: (i) electron transfer from the electrode/KB to CuII-Hdatrz and (ii) electron transfer from CuI-Hdatrz to O2 (the ORR step).

Since XANES spectra are sensitive to coordination geometrical changes around the element measured, the XANES spectra of Cu/KB recorded at pH 7, pH 10 and pH 13 were overlaid to compare the shape of them (Fig. 4). Although the almost same shape of the spectra was observed at pH 7 and pH 10 in the same oxidation state, the XANES spectra at pH 13 were different from those at pH 7 and pH 10, indicating that the coordination geometries of the CuII and CuI centers were the same in the pH range from pH 7 to pH 10, but these might be different at pH 13. Furthermore, spectral differences were observed between the XANES spectra under nitrogen and oxygen at pH 13 (Fig. S2, ESI†). Since a pKa value of Hdatrz was reported to be 12.12,25 it is most likely that deprotonation occurred from the Hdatrz ligands at pH 13. Thus, deprotonation from the Cu-Hdatrz in basic solutions may affect the electronic state of the Hdatrz ligands and induce coordination geometrical changes, resulting in highly active ORR catalyst in basic solutions.
In summary, the electrochemical ORR activity Cu/KB was studied in the neutral and basic aqueous solutions using the in situ electrochemical XANES techniques. Our electrochemical studies revealed that the faster ORR kinetics of Cu/KB resulted in the higher ORR catalytic activity under the basic conditions, compared to that under the neutral condition. The coordination geometry at pH 13 was different from those at pH 7 and pH 10, and this difference might be caused by deprotonation of the Hdatrz ligand. The structural information on the deprotonated Cu(I) species or O₂-bound intermediates in basic solutions may be a key to understand the high ORR activity of Cu/KB or to design highly active Cu-based ORR catalysts.

Further in situ XAFS studies on the Cu-Hdatrz complex are under way to obtain more detailed structural information in basic solutions.

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Notes and references

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In situ XAFS studies on a copper catalyst revealed that deprotonation from the triazole ligand might cause the coordination geometrical changes, resulting in enhancement of the oxygen reduction reaction activity.