

In situ XAFS spectroscopy at multi-copper complexes catalyzing oxygen reduction reaction (ORR)

Ichizo Yagi,^{1,2,*} Ken'ichi Kimijima,¹ Mari Shibata,¹ Kazuya Ogino,¹ Hideo Notsu,¹ Kiyoshi Inokuma,¹ Narumi Ohta,¹ Hiromitsu Uehara,² Yohei Uemura,² Satoru Takakusagi² and Kiyotaka Asakura^{2,*}
 FC-Cubic TRA¹ and Hokkaido University²
¹2-3-26 Aomi, Koto-ku, Tokyo, 135-0064, Japan
²N21W8, Kita-ku, Sapporo 001-0021, Japan
 E-mail: i-yagi@fc-cubic.or.jp

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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, Cu₂(Hdatrz)₂, as an electrocatalyst for ORR[4-6]. 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 ORR mechanism at the catalyst seems to be valuable.

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 Cu₂(Hdatrz)₂ complexes on electrodes. In situ XANES measurement has shown that the ORR at the Cu centers requires the formation of CuI species and the rate-determining step for ORR is dependent on pH.

Acknowledgement

This work was supported by New Energy, Industrial Technology Development Organization (NEDO).

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