

## Kinetic study of oxygen reduction reaction on Cobalt-porphyrin-modified electrodes

Shino Sato<sup>a</sup>, Kei Murakoshi<sup>a</sup>, Katsuyoshi Ikeda<sup>a,b</sup>

<sup>a</sup>Department of Chemistry, Faculty of science, Hokkaido University

Sapporo 060-0810, JAPAN

<sup>b</sup>Japan Science and Technology Agency, PRESTO  
[s.shino@mail.sci.hokudai.ac.jp](mailto:s.shino@mail.sci.hokudai.ac.jp)

### [Introduction]

A well-organized molecular monolayer can be self-assembly constructed on a metal surface. Such chemical modification is recognized as one of key issues to realize various functionalities on an electrode surface. For example, metalloporphyrin-modified electrodes are known to act as an electrocatalyst for oxygen reduction reaction (ORR). In such a system, ORR activity is strongly affected by the interface between porphyrin and the electrode. In this work, Cobalt-porphyrins were immobilized on a gold electrode through various types of bridge molecules. The ORR kinetics on the Co-porphyrin-modified electrodes was systematically studied by alternating the bridge molecule.

### [Experimental]

An atomically defined gold electrode was self-assembly covered with various types of bridge molecules as shown in Fig. 1. The bridge monolayer-covered electrode was then immersed in a solution containing 1mM 5, 10, 15, 20-tetraphenyl-21H, 23H-Cobalt(II) porphyrin (Co-TPP) so that Co-TPP monolayer was formed on top of the bridge monolayer. ORR was measured by the hanging meniscus rotating disk electrode (HM-RDE) method in oxygen-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. The reversible hydrogen electrode (RHE) was utilized as a reference.

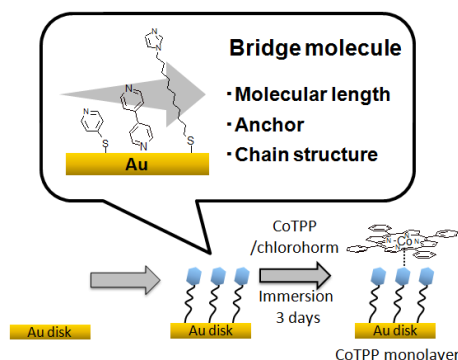


Figure 1. Procedure for preparation of the Co-TPP-modified gold electrode with various types of bridge monolayers.

### [Results and Discussions]

Figure 2 shows a typical example of the ORR polarization curves measured on the Co-TPP monolayer formed on the bridge monolayer of 4,4'-bipyridine. The diffusion limited behavior is clearly seen around 0 V vs. RHE, as expected in the RDE measurement. The limiting current density was dependent on the rotation rate of the electrode. According to the Koutecky-Levich (K-L) analysis, the mechanism for ORR on the Co-TPP was confirmed to be two-electron pathway:  $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ . This agrees with the previous report [1]. For other bridge molecules, the same reaction pathway was experimentally confirmed in a similar manner.

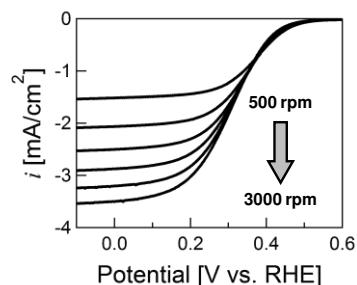


Figure 2. ORR polarization curves on Co-TPP monolayer formed on the bridge monolayer of 4,4'-bipyridine, measured by RDE method at various rotation rates.

The K-L analysis of the ORR polarization curves also provides us the kinetic rate constant ( $k_0$ ) of the reaction. Figure 3 shows  $\log k_0$  as a function of the bridge length. When the molecular length is longer than 10 Å,  $k_0$  exponentially decreased with increasing the molecular length. This indicates that the rate-determining step for ORR is the electron tunneling from Au electrode to Co-TPP. On the other hand, when the bridge molecule is shorter than 10 Å, the reaction rate deviated from the tunneling behavior;  $k_0$  was independent of the bridge length. This result suggests that the rate-determining step in this region is the electron transfer from Co-TPP to oxygen molecules.

In conclusion, we individually measured the elementary steps in the electron transfer from Au electrode to oxygen molecules in the ORR process on Co-TPP-modified electrodes. The interface between the catalyst layer and the electrode is of great importance to improve the overall reaction rate.

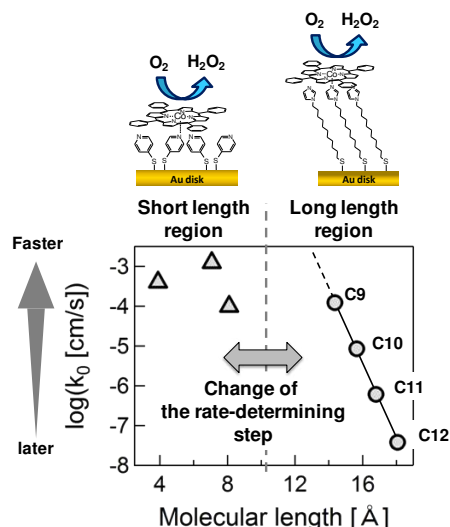


Figure 3.  $\log k_0$  for ORR on Co-TPP as a function of the bridge length.

### Reference

[1] J.H. Zagal. *Coord. Chem. Rev.*, **1992**, 119, 89