

# Development of the Bio-inspired Iron Porphyrin Catalysts for Fuel Cell Cathode Reaction: Synthesis, Spectroscopic Analyses, and Electrochemical Studies

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論 文 名：Development of the Bio-inspired Iron Porphyrin Catalysts for Fuel Cell Cathode Reaction: Synthesis, Spectroscopic Analyses, and Electrochemical Studies

(燃料電池陽極反応のための Bio-inspired ポルフィリン触媒の開発：合成、分光学的分析、および電気化学研究)

区 分：甲

## 論文内容の要旨

This dissertation describes on the design of bio-inspired heme molecules for the study on the oxygen activation and their application as catalysts for oxygen reduction reaction (ORR).

Chapter 1 outlines on heme enzymes concerning oxygen activation and their reaction mechanisms. Particularly, oxygen reduction to water is a typical four electron reaction, thus, it tends to give harmful active oxygen species, such as  $O_2^{\cdot-}$ ,  $H_2O_2$ , and  $HO\cdot$ , and resultantly causes considerable energy loss. Thus, it is important to show how metalloenzymes, such as heme- or Cu-containing ones, attain complete  $4e^-$  reduction of oxygen to water through  $4e^-$ -reduction process by suppressing the formation of any active oxidants. On this line, a new design of enzyme mimic chemical model is proposed.

Chapter 2, first, discusses on enzyme ORR reaction mechanisms and on the importance of a key intermediate, (hydro)peroxy ferric-heme [ $Fe^{III}\text{-OO(H)}$ ], in  $O_2$  activation through the single-electron reduction of the oxy precursor, *i.e.*,  $O_2$  adduct [ $Fe\text{-O}_2$ ]. It is described the synthesis of bio-inspired chemical models bearing a hydroxycarbonyl group as a hanging group above the Fe iron and an imidazole axial ligand. With use of this model, the author unexpectedly found the reduction of an oxy form with the corresponding ferric heme, [ $Fe^{II}(\text{Por})$ ]. The resultant [ $Fe^{III}\text{-OO(H)}$ ] was assigned by spectroscopic methods including electronic, resonance Raman, and EPR spectroscopies. Generally, a ferrous heme has not enough negative potential to reduce the oxy heme. By the incorporation of a suitable proton mediator the an appropriate position of the model, its activation energy is considerably reduced and the product peroxy complex is thermodynamically stabilized by a hydrogen bonding. Proton coupled electron transfer (PCET) mechanism is suggested to play a major role to reduces its activation energy. This is the first example of the reduction of an oxyheme by a ferrous one.

Chapter 3 describes the use of the models for catalytic ORR. Development of base metal catalysts as alternatives of Pt one is an important issue in a fuel cell industry. The author evaluates the electrocatalytic performance of the model compounds for ORR in various pH buffer solutions by using various electrochemical methods, including cyclic voltammetry (CV), rotating disk electrode (RDE), and rotating ring disk electrode techniques (RRDE). Importantly, both the acid and ester models accomplish higher catalytic activity and superior stability than well-known 20 wt % Pt/Vulcan. Here, the author depicts the importance of the rationally designed catalysts in consideration of elemental science and technology and the scope for non-precious metal catalysts.