

Doctoral Thesis

Studies on Oxygen Reduction Catalysis of
Dinuclear Cobalt Polypyridyl Complexes

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Abstract

Four-electron oxygen reduction reaction ($4e^-$ -ORR) is a key step of natural and artificial energy conversion systems such as aerobic organism and fuel cell. Current cathode catalyst of fuel cells is platinum impregnated in carbon, but for reasons of scarcity and cost, there has been an intense search for alternatives to precious-metal electrocatalysts of $4e^-$ -ORR. On the other hands, in nature, various enzymes such as cytochrome *c* oxidase which has an active center consisting of a Fe-porphyrin and a Cu-imidazole efficiently catalyze $4e^-$ -ORR in the respiration process. Thus, transition-metal complexes which can be precisely designed has a potential to an excellent $4e^-$ -ORR catalyst. One of the advantages of molecular complex catalyst as a $4e^-$ -ORR catalyst is possibility to elucidate the reaction mechanism. Elucidation of factors to decide reaction selectivity for $4e^-$ -ORR in catalytic cycle can lead to development of the $4e^-$ -ORR catalyst with higher selectivity, reaction rate, and low overpotential. In fact, many kinds of metal complexes have been developed. Among them, cobalt complexes are known as higher active ORR catalyst. However, detailed-reaction mechanism including factors dominating reaction selectivity and rate remains unexplained in high performance catalysts.

The purpose of this study is elucidation of factors that determine reaction selectivity and rate of ORR catalyzed by dinuclear cobalt polypyridyl complexes. Reaction selectivity of ORR catalyst for $4e^-$ -process is crucial to develop ORR catalysts because two-electron reduction process of O_2 ($2e^-$ -ORR; $E^\circ = 0.70$ V vs. NHE, pH = 0) proceeds at a lower standard electrode potential than $4e^-$ -ORR ($E^\circ = 1.23$ V), and thus greatly limits the electromotive force of fuel cell and respiration. In this research, dinuclear cobalt complexes having different bridging structures (xanthene: btpyxa, anthraquinone: btpyaq, and anthracene: btpyan) and bidentate ligands (bipyridine: bpy, 6,6'-dihydroxy-2,2'-bipyridine: 6DHBP, and 4,4'-dihydroxy-2,2'-bipyridine: 4DHBP) were synthesized and these catalytic activity for chemical and electrochemical ORR were investigated. Reaction mechanisms and factors determining reaction selectivity and rate of catalysts are discussed based on kinetic, electrochemical, and spectroscopic analyses of the ORRs.

Chapter I describes introductions of oxygen reduction reactions using transition-metal complex catalysts in natural and artificial energy conversion systems. Previously reported methods for improving catalyst selectivity for $4e^-$ -process in ORR are particularly focused and unelucidated points in these mechanisms are mentioned.

In Chapter II, the ORR catalysis of $Co_2(\mu-O_2)$ complexes bridged by xanthene, $[Co_2(\mu-O_2)(bpy)_2(btpyxa)](PF_6)_4$ (**1**), and anthracene, $[Co_2(\mu-O_2)(bpy)_2(btpyan)](PF_6)_4$ (**2**), and $Co_2(OH)_2$ complex bridged by anthraquinone, $[Co_2(OH)_2(bpy)_2(btpyaq)](PF_6)_4$ (**3**), is discussed. In chemical ORR using $Fe(CpMe)_2$ as a reductant in acidic PhCN, xanthene-bridged complex **1** showed the highest initial reaction rate ($k_{cat} = 6.8 \times 10^2$ s⁻¹) and selectivity for $4e^-$ -ORR (96%) in three complexes. The detailed kinetic analyses have revealed that the rate-determining step (RDS) in the catalytic cycles of these catalysts is O_2 addition to $[Co^{II}_2(OH)_2]^{4+}$ as an intermediate in common. In the only case that **1** was used as catalyst, k_{cat} depended on proton concentration because reaction rate of O_2 addition to $[Co^{II}_2(OH)_2]^{4+}$ was so fast as that of concerted PCET process of **1**. X-ray, Raman and electrochemical analyses, and stoichiometric reactions showed that the face-to-face structure of **1** characterized by slightly flexible

xanthene was advantageous in capturing O₂ and stabilizing Co₂(μ -O₂) structure, thus increasing both reaction rate and selectivity for 4e⁻-ORR.

In Chapter III, a dinuclear cobalt complex with 6DHBP, [Co₂(OH)₂(6DHBP-H⁺)₂(btpyxa)](PF₆)₂ (**4**, 6DHBP-H⁺: mono-deprotonated form of 6DHBP), has been isolated and characterized to study the effect of proton relay via proton-responsive ligands on 4e⁻-ORR. Complex **4** shows high selectivity (99%) and reaction rate ($k_{\text{obs}} = 2.7 \text{ s}^{-1}$) for 4e⁻-ORR using ferrocene (Fe(Cp)₂) as a reductant in PhCN containing low-concentration perchloric acid compared with the dinuclear complexes with bpy (**1**, $k_{\text{obs}} = 2.4 \times 10^{-2} \text{ s}^{-1}$) and 4DHBP ([Co₂(μ -O₂)(4DHBP-H⁺)₂(btpyxa)](PF₆)₂, **5**, $k_{\text{obs}} = 2.4 \times 10^{-2} \text{ s}^{-1}$). A large catalytic current in CV of **4** clearly indicates high reaction rate for electrochemical ORR under low acid concentration conditions. Moreover, X-ray crystallography of the corresponding monomeric analog, [Co(OH₂)(6DHBP-2H⁺)(terpy)](PF₆) (**6**, 6DHBP-2H⁺: doubly-deprotonated form of 6DHBP) suggests that OH groups of **4** can form hydrogen bonds with a μ -O₂ ligand. Hydroxy groups at 6,6'-position of bpy would deliver protons to the μ -peroxo ligand of intermediate, and thereby promote O-O bond cleavage on PCET process.

Lastly, Chapter IV concludes this thesis with the descriptions about catalytic activities on 4e⁻-ORRs of each cobalt complex and these reaction mechanisms containing factors dominating the reaction selectivity and rate. Slight flexibility of xanthene skeleton increase O₂ capturing rate of face-to-face Co₂ complex and effectively stabilizes a Co^{II}₂(μ -O₂) structure as a key intermediate in the catalytic cycle. As a consequence of them, high reaction rate and high reaction selectivity for 4e⁻-ORR were simultaneously achieved by complex **1**. In addition, the proton responsive site close to a μ -O₂ ligand is effective in ORR catalyzed by face-to-face Co₂ complexes under low acid concentration. The accomplishment of this thesis successfully demonstrated molecular design criteria for high performance ORR catalyst.