

Reductive Activation of O₂ by Electrons from H₂- Application to H₂-O₂ Fuel Cells and Direct Synthesis of H₂O₂

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論文名 : Reductive Activation of O₂ by Electrons from H₂ – Application to H₂–O₂ Fuel Cells and Direct Synthesis of H₂O₂
(H₂の電子による O₂の還元的活性化 – H₂–O₂燃料電池及び H₂O₂の直接合成への応用)

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論 文 内 容 の 要 旨

In a sustainable hydrogen economy, green H₂ finds important applications in the H₂–O₂ fuel cells and the direct synthesis of H₂O₂. These two applications are based on the reduction of O₂ by H₂. The H₂–O₂ fuel cells involve the four-electron reduction reaction and the direct synthesis of H₂O₂ entails the two-electron reduction one, both of which require proper catalysts in order to perform efficiently. In response to their requirement of appropriate catalysts, we particularly focus on molecular catalysts, which have flexible molecular designs and traceable catalytic mechanisms, so as to acquire a deeper understanding of the two reactions. The molecular catalysts reported so far, however, are beset with problems. Those for the H₂–O₂ fuel cells have fragile hydrogenase (H₂ase)-inspired structures and those for the direct synthesis of H₂O₂ seem to have unsuitable molecular designs. Thus, in this dissertation, I convert a H₂ase model into a robust dry-distilled catalyst for the H₂–O₂ fuel cells (chapter 2) and develop a molecular catalyst with suitable designs for the direct synthesis of H₂O₂ (chapter 3).

Chapter 2. Dry-Distilled Catalyst Inspired by O₂-Tolerant Hydrogenases for the Four-Electron Reduction of O₂ by H₂ – Application to the H₂–O₂ Fuel Cells

A new NiRhS molecular catalyst and its dry-distilled derivative are developed for the four-electron reduction of O₂ by H₂. The molecular catalyst, [Ni^{II}Cl(L)Rh^{III}Cl(η⁵-Cp*)] (**1**, L = *N,N*-dimethyl-3,7-diazanonane-1,9-dithiolato, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl), is a functional model of O₂-tolerant [NiFe]H₂ases. It initially activates H₂ in water and stores the electrons obtained from H₂ in a hydride intermediate **2** (Fig. 1), as observed by X-ray analysis. With a strong electron-donating Cp* ligand at Rh^{III}, the intermediate **2** promotes the four-electron reduction of O₂ to H₂O, as proved by ¹⁸O isotope labeling experiments. Dry distillation of **1** forms the NiRhS dry-distilled catalyst, which contains nanoparticles of NiRh sulfides and Rh⁰, as revealed by elemental analysis, TEM, XPS and XRD. The dry-distilled catalyst shows significant improvements in catalytic activities and H₂–O₂ fuel cell performances. It is the first bimetallic sulfur dry-distilled catalyst derived from a H₂ase model and applied to both electrodes of a functioning H₂–O₂ fuel cell.

Chapter 3. A New Rhodium-Based Molecular Catalyst for the Two-Electron Reduction of O₂ by H₂ – Application to the Direct Synthesis of H₂O₂

A new Rh-iMP molecular catalyst is developed for the two-electron reduction of O₂ by H₂. The catalyst, [Rh^{III}(iMP)(OH)(H₂O)₂](NO₃)₂ {[5](NO₃)₂, iMP = 2,6-bis(2-imidazolyl)-1-methylpyridine}, activates both H₂ and O₂ *via* a single catalytic cycle. It first oxidizes H₂ in water and accumulates the electrons from H₂ in a dinuclear Rh^{II} complex **7** (Fig. 1), as observed by X-ray analysis. With a weaker electron-donating iMP ligand at Rh^{III}, complex **7** facilitates the two-electron reduction of O₂ to H₂O₂ (Fig. 1), as confirmed by ¹⁸O isotope labeling experiments. The catalyst catalyzes the direct synthesis of H₂O₂ in water with a turnover number of 3.8 over 3 h, as determined using the oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV) reagent. It is the first molecular catalyst that can activate both H₂ and O₂ *via* a well-defined catalytic cycle to generate H₂O₂ in water.

Based on the specific research in chapter 2 and 3, the dissertation implies three key remarks. The reduction of O₂ by H₂ in this dissertation begins with the oxidation of H₂ in water. The electrons extracted from H₂ are then stored in the catalysts before being used to reduce O₂. The reduction of O₂ by H₂ is mediated by the electron-donating abilities of catalyst ligands, wherein strong electron-donating ligands promote the four-electron reduction reaction and weaker electron-donating ones favor the two-electron reduction reaction. These remarks, together with detailed data and discussions in each chapter, provide a deeper insight into the reduction of O₂ by H₂, which may be beneficial to the development of desirable catalysts for the selective reduction of O₂ by H₂ in the sustainable hydrogen economy.

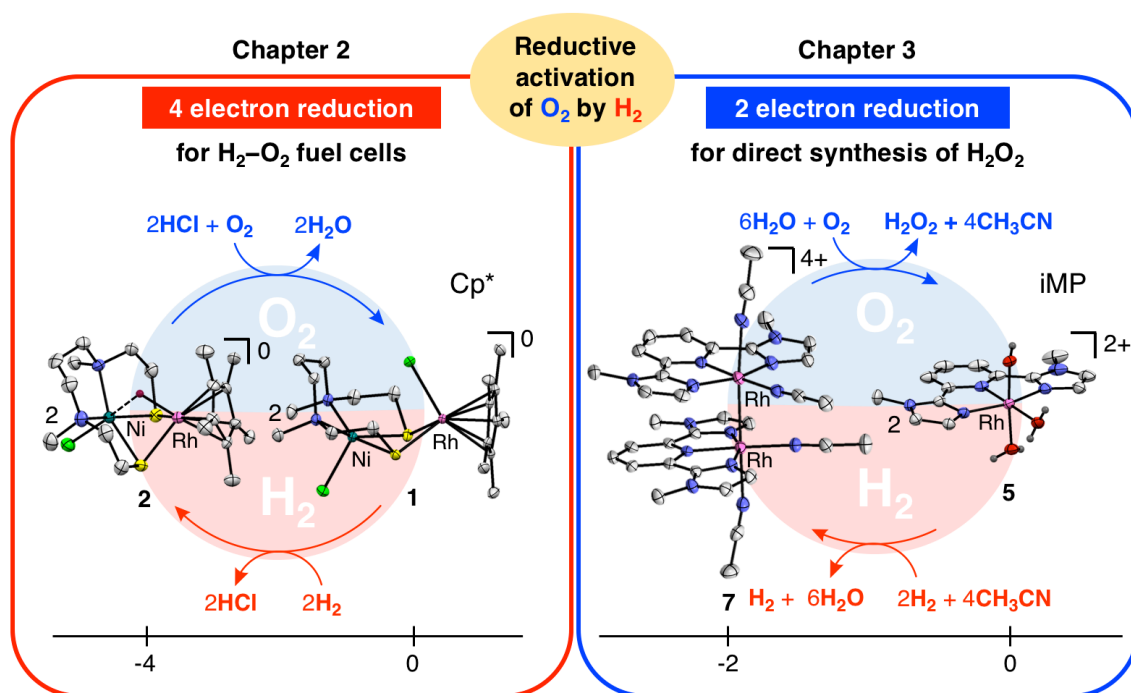


Figure 1. The contents of this dissertation.