

Study on Electrocatalytic Hydrogen Evolution Reaction by Ligand-centered Reduction of Porphycene Complexes

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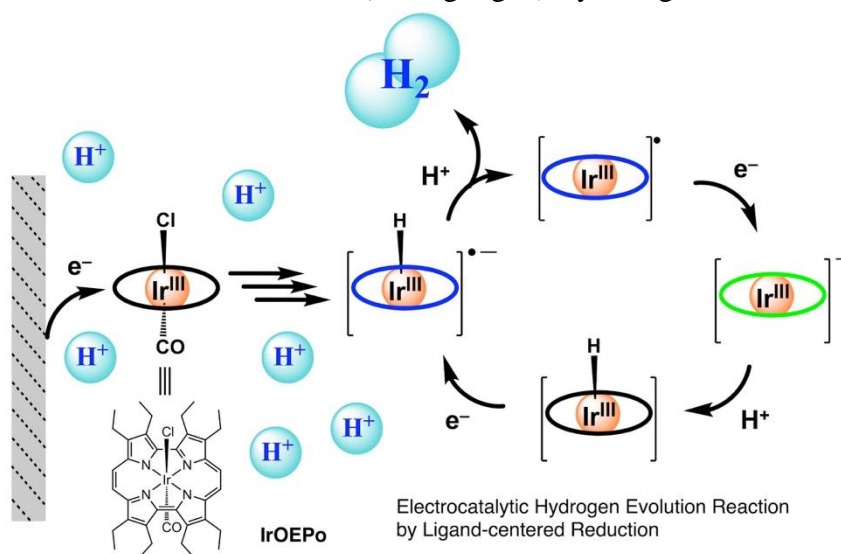
論 文 名 : Study on Electrocatalytic Hydrogen Evolution Reaction by Ligand-centered Reduction of Porphycene Complexes (ポルフィセン錯体の配位子中心還元による触媒的電解水素発生反応に関する研究)

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論 文 内 容 の 要 旨

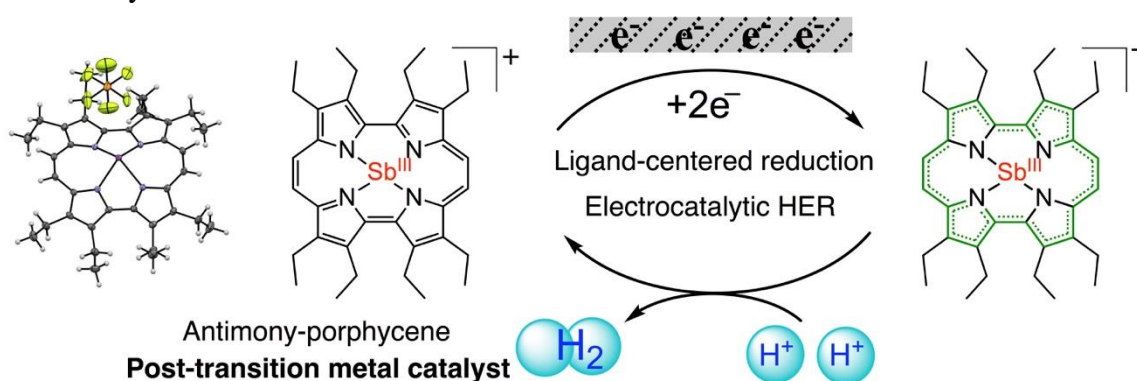
In order to solve the challenges of traditional energy sources, sustainable and renewable energy sources have been attended. At present, lots of new energy researches have been focusing on the activation of small molecules, which include hydrogen evolution reaction, reduction of carbon dioxide and soon. Due to the energy density and the product, hydrogen production has been receiving more attention. Although the generation of hydrogen gas is very simple by chemical reaction. However, due to high energy barrier, it is relatively difficult to carry out this kind of reaction without the catalyst. Therefore, we would like to develop the catalyst with macrocyclic porphycene as a ligand to carry out this kind of reaction.

In Chapter 2, the comparison of the electrocatalytic hydrogen evolution reaction (HER) by iridium complexes have been carried out. We developed novel catalytic system by combining the high catalytic activity of iridium with the electrochemical properties of porphycene. For the iridium octaethylporphycene (**Ir-OEPo**), the reduction of ligand was occurred during the catalytic reaction, while the reduction of iridium porphyrin (**Ir-OEPor**) was occurred at metal center. In a word, **Ir-OEPo** exhibited a two-step one-electron ligand-centered reduction while **IrOEPor** showed an irreversible metal-centered reduction. Hydrogen gas production was occurred at -1.4 V (vs. Ag/AgCl) by using **IrOEPo** and **IrOEPor** as catalysts in DMF with 99.0% and 86.8% faradaic yields, respectively. Compared with **IrOEPor**, the **IrOEPo** shows a higher catalytic activity with a new catalytic characterization. The new characterization can provide a simple method for changing



the catalytic activity by modifying the ligand substituents.

In Chapter 3, antimony porphycene complexes were synthesized at the first time, and characterized by spectroscopic measurements and single crystal diffraction analysis. The redox behavior of these complexes was clarified by the Cyclic voltammetry (CV) and electro-spectro measurements. The catalytic reactivity of antimony(III) octaethylporphycene (**Sb(III)OEPo**) and antimony(V) octaethylporphycene (**Sb(V)OEPo-Br₂**) for HER was demonstrated by the CV and bulk electrolysis under reductive conditions at -1.0 V with TFA. The hydrogen production was driven by the ligand-centered reduction of antimony porphycenes, suggesting that the redox feature of the porphycene enables the utilization of main-group element as a central element of the complex and anodically shifted potentials for HER. This result could be beneficial for the development of post-transition metal catalyst.



In conclusion, we introduced the hydrogen production by the different porphycene complex with the ligand-centered reduction. Particularly, this method can provide a very good to develop different catalytic systems by modifying the ligand substituents. On the other side, the antimony porphycene complexes were demonstrated with an electrocatalytic function for hydrogen evolution reaction, which is important for the perspective of scarce precious metal resources of earth. Therefore, these works put potential application values for the development of molecular catalytic chemistry and noble metal catalysis.