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学 位 論 文 内 容 の 要 旨
Abstract of Doctoral Thesis

博士の専攻分野の名称　博士（理 学）　　氏　名　　童　聖富
Degree requested　　Doctor of Science　　Applicant name

学 位 論 文 題 名
Title of Doctoral Thesis

Studies on Electrochemical Oxygen Reduction Reaction – Effects of pH, anion, and electrode materials

（電気化学的酸素還元反応に関する研究 ― pH、アニオン、および電極材料の効果）

Fuel cell is a device that can convert chemical energy into electricity directly. It can match the increasing demand of clean and renewable energy systems. The most serious problem of fuel cell at present stage is the large overpotential energy loss (by 200 ~ 300 mV), which is mainly due to the slow kinetics of oxygen reduction reaction (ORR) at a cathode. To realign the commercial application of fuel cell, it is essential the solution is to clarify the mechanism of ORR on metal electrode surface, so that give a direction in preparing catalysts with high activity can be proposed. It is the motivation of this project.

The ORR on Au and Pt electrode surfaces has been investigated for long time. Although it is known that ORR is very sensitive to the electrode materials, surface structure and the properties of electrolyte solutions such as pH and ions, systematic investigations of these parameters are limited. Furthermore, only a few direct evidence of the adsorption of oxygen, which is considered to be the first step of ORR, is available. In the present thesis, the effects of pH, anion and electrode materials on ORR are investigated. Direct proof of oxygen adsorption was provided by electrochemical quartz crystal microbalance (EQCM).

In **Chapter 1**, the background of ORR on metal electrode surface in aqueous solution is reviewed.

In **Chapter 2**, the experimental details, including the information of chemicals, preparation of samples and setup, and the principles of rotating disk electrode (RDE) and EQCM are given.

In **Chapter 3**, the effect of pH on ORR at Au(111) surface was investigated by rotating disk electrode with a hanging-meniscus configuration. It was found that the overpotential for a given ORR current at Au(111) surface was smaller with increasing pH. ORR mechanism is discussed based on the experimental results.

In **Chapter 4**, the effect of sulfate anion (SO_4^{2-}) and pH on the adsorption of oxygen on Au electrode surface was investigated by EQCM, by measuring the potential

dependent frequency changes in various solutions. **Fig. 1** shows the potential dependent (top) coverage of surface oxide (θ_{AuO}) and (bottom) the mass change difference ($\Delta\Delta m$) between the results obtained in Ar- and O_2-saturated solutions ($\Delta\Delta m = \Delta m_{O2} - \Delta m_{Ar}$) in $HClO_4$ solution with (●) and without (○) sulfate. The increase of $\Delta\Delta m$ should be due to the adsorption of O_2. While θ_{AuO} was not significantly affected by sulfate, the potential for observing the $\Delta\Delta m$ increasing was shifted more negatively, showing the adsorption of oxygen was inhibited by sulfate in solution.

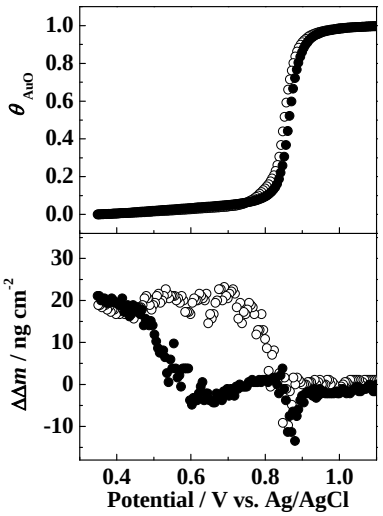

Fig. 1 Potential dependent coverage of surface oxide (top) and $\Delta\Delta m$ between the results obtained in Ar and O_2 saturated solution (bottom) on Au surface in $HClO_4$ solution with (●) and without (○) sulfate.

In all SO_4^{2-}-free solutions at various pH, the adsorption of oxygen started at potential where the surface oxide was partially reduced and the amount of adsorbed oxygen reached saturated value at each pH when the surface oxide was fully reduced. The maximum $\Delta\Delta m$ was increased with increasing pH and reached constant when the pH > 11.4. In this study, it directly proved that the potentials, at which oxygen adsorption was started to be observed, were dependent on anion in solution. It was proposed, therefore, that oxygen adsorbed on the Au surface as anion was desorbed from the surface.

In **Chapter 5**, the effect of sulfate anion on the adsorption of oxygen on Pt electrode surface was investigated by EQCM for comparing the effect of electrode material. The potential at which the adsorption of oxygen started and ORR current flowed was identical in perchlorate and sulfate solutions as can be seen in **Fig. 2**. The inhibition of sulfate anion on the adsorption of oxygen was not significantly observed on Pt(poly) surface in this study. However, the adsorption of oxygen on Pt(poly) surface caused the mass increased in perchlorate solution, while it caused the mass decrease in sulfate solution. It was proposed that the adsorbed sulfate was replaced by oxygen on Pt(poly) surface. The effect of anion on the adsorption of oxygen on Pt(poly) surface is different from that observed on Au surface in Chapter 4.

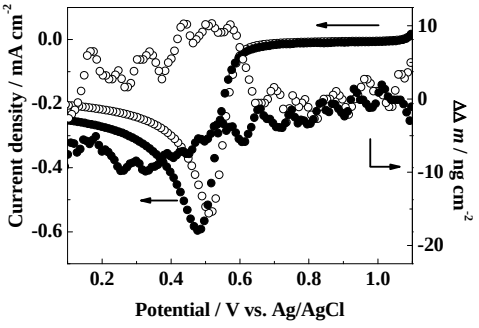

Fig. 2 Potential dependencies of ORR current (left axis) and $\Delta\Delta m$ (right axis) obtained on a Pt surface in 0.1 M $HClO_4$ (○) and 0.05 M H_2SO_4 (●) solution, respectively.

In **Chapter 6**, the general conclusion of this thesis and future prospects are given.