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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）

Sheng-Fu Tong

Department of Chemistry
Graduate School of Science
Hokkaido University

2013
# Table of Contents

Chapter 1  
INTRODUCTION .................................................................................. 1  

1.1 General Introduction ...................................................................... 1  

1.2 Mechanism of Oxygen Reduction Reaction on Metal Surfaces .......... 2  

1.2.1 Effect of Surface Structure ....................................................... 4  

1.2.2 Effect of pH ............................................................................ 7  

1.2.3 Effect of Adsorbed Species ..................................................... 10  

1.3 Objectives and Outline of the Thesis ........................................... 17  

Chapter 2  
EXPERIMENTAL .................................................................................. 25  

2.1 Chemicals .................................................................................... 25  

2.2 Preparation of Au(111) Electrode ................................................ 25  

2.3 Electrochemical Measurements .................................................. 27  

2.3.1 Cyclic Voltammetry Measurements ...... 27  

2.3.2 Rotating Disk Electrode Measurements .................................. 28  

2.3.2.1 Principle of Rotating Disk Electrode ................................... 28  

2.3.2.2 Hanging-Meniscus Configuration for Rotating Disk Electrode Measurements ................................................................... 29  

2.3.3 Electrochemical Quartz Crystal Microbalance Measurements .... 31  

2.3.3.1 Principles of Quartz Crystal Microbalance ....................... 31  

2.3.3.2 Quartz Crystal Microbalance in Electrochemistry ............... 32  

2.3.3.3 Configuration for Electrochemical Quartz Crystal Microbalance Measurements ......................................................... 33  

2.4 References ................................................................................... 35  

Chapter 3  
EFFECT OF PH ON OXYGEN REDUCTION REACTION ON  
AU(111) ELECTRODE SURFACE .......................................................... 37  

3.1 Introduction ................................................................................... 37  

3.2 Results .......................................................................................... 38  

3.2.1 pH Effect on the Electrochemical Behavior of Au(111) Electrode ... 38  

3.2.2 Oxygen Reduction Reaction on Au(111) Surface in 0.15 M Na₂SO₄  

Containing 5 mM H₂SO₄ (pH 2.7) ..................................................... 41  

3.2.2.1 Cyclic Voltammetry ............................................................ 41  

3.2.2.2 Rotating Disk Electrode Measurements ............................ 42  

3.2.3 Oxygen Reduction Reaction on Au(111) Surface in 0.12 M Na₂SO₄  

Containing 0.1 M NaOH (pH 12.7) ................................................... 45  

3.2.3.1 Cyclic Voltammetry ............................................................ 45
Chapter 1

INTRODUCTION

1.1 General Introduction

Fuel cell, which can directly convert chemical energy into electricity with hydrogen-rich fuel as the anodic reactant [1-5], is one of the most promising energy conversion devices capable of meeting the increasing demand for renewable energy, reducing the dependence on fossil fuel for human beings, and decreasing of green house gas emission [5-10]. Thus, fuel cells have attracted great attention, undergoing large development over the past decades [11-13].

Figure 1.1 shows a scheme of a fuel cell. The fuel (i.e., hydrogen) is oxidized at the anode, whereas air (i.e., oxygen) is reduced at the cathode in a fuel cell system. The reactions can be written as equations 1.1a and b, respectively. The net reaction in a fuel cell system is expressed in equation 1.1c.

![Fig. 1.1 Scheme of fuel cell systems.](image)

\[ H_2 - 2e^- \rightarrow 2H^+ \quad E = 0 \text{ V} \quad (\text{vs. SHE}) \quad (1.1a) \]

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E = 1.2 \text{ V} \quad (\text{vs. SHE}) \quad (1.1b) \]

\[ O_2 + 2H_2 \rightarrow 2H_2O \]

Equation 1.1 shows that the theoretical output of fuel cell is 1.2 V, but the
practical output of fuel cell usually exhibits an overpotential energy loss by 200 mV ~ 300 mV, including the overpotential caused by the anodic and cathodic reactions, resistance, and mass transfer. However, this loss is mainly due to the slow kinetics of the cathodic reaction [14-18], namely, the oxygen reduction reaction (ORR, equation 1.1b), which is the most serious problem in fuel cell systems [16-22].

Currently, catalysts commonly used for ORR are precious metal-based materials, i.e., platinum (Pt), palladium (Pd), gold (Au), silver (Ag), and Pt-based alloys, etc. [14, 15, 23, 24], which results in the high cost of fuel cells due to the high metal loadings needed to achieve high performance and efficiency [14, 25]. Cost must be reduced to match the commercial application of fuel cell [5]. Thus, the only solution is to better understand the mechanism of ORR [20, 26, 27]. Understanding the mechanism of ORR will facilitate the improvement of the activity and durability of the catalysts, as well as reduce their cost [25, 28]. In the processes of ORR, oxygen adsorption is considered to be the first step, but direct evidence remains very limited. This project aims to provide evidence of oxygen adsorption as the first step in ORR and elucidate its mechanism.

1.2 Mechanism of Oxygen Reduction Reaction on Metal Surfaces

ORR in aqueous solution (equation 1.1b) is a complex electrochemical reaction, involving multi-electron (e) transfer, and it is difficult to identify the route for describing the whole reaction. Of various reaction schemes proposed, the simplified version given by Wroblowa et al., as shown in Fig. 1.2, appears to be the most effective [29].
Fig. 1.2 Simplified process of oxygen reduction reaction in aqueous solution [29].

Figure 1.2 shows that ORR on the electrode surface includes the processes of mass diffusion, reactant adsorption, electron transfer, and product desorption [30-32]. ORR can proceed in two different processes: (i) 4e transfer reaction (H₂O as the final product), which can be sub-divided into a direct 4e transition process (k₁, equation 1.1b) and a series of 2e transfer reactions (k₂ and k₃, equations 1.2 and 1.3); and (ii) 2e transfer reaction, in which H₂O₂ is the final product (k₂ and k₅, equation 1.2) [14, 21].

\[ O_2 + 2H^+ + 2e^- = H_2O_2 \quad E = 0.7 \text{ V (vs. SHE)} \quad (1.2) \]

\[ H_2O_2 + 2H^+ + 2e^- = 2H_2O \quad E = 1.8 \text{ V (vs. SHE)} \quad (1.3) \]

The direct 4e reaction route is preferred in fuel cell systems because of the high energy density generated that can prevent the negative effect of H₂O₂ on catalysts [5, 8]. The processes of ORR can be expressed by elemental reactions, as shown in equations 1.4 to 1.8 [33, 34].

\[ O_2 + e^- \rightarrow O_2^- \quad (1.4) \]
\[ O_2^- + H^+ \rightarrow HO_2^- \quad (1.5) \]
\[ HO_2^- + e^- \rightarrow HO_2^- \quad (1.6) \]
\[ HO_2^- + H^+ \rightarrow H_2O_2 \quad (1.7a) \]
\[ HO_2^- + H^+ + e^- \rightarrow H_2O + O^- \quad (1.7b) \]
\[ O^- + 2H^+ + 2e^- \rightarrow H_2O \quad (1.8) \]
Despite the complicated processes of ORR, studies have not been conducted to understand the mechanism [35-44]. For example, by using rotating ring-disk electrode (RRDE), the product/intermediate (i.e., H$_2$O$_2$) produced in ORR that occurs on the disk electrode can be detected by the ring electrode [40]. The number of electrons ($n$) transferred in the molar reaction can be evaluated by analyzing the RDE results according to the Levich equation if diffusion-limited current is observed. The rate-determining step (rds) can be estimated from the slope of the Tafel plot. By using in-situ spectroscopy, the adsorbed species, which include the reactant, intermediate, or product, such as O$_2$ [45], O$_2^-$ [15], and HO$_2$ [35, 45], can be identified. This information is highly important and helpful in identifying the reaction route.

Based on the efforts exerted over the past decades, ORR has been demonstrated to be largely dependent on the following factors: type of electrode material, electrode potential, properties of electrolyte solutions (such as pH and ions in the solutions), surface structure, and morphology of the electrode materials [20, 24, 27, 31, 46-50]. However, the mechanism of ORR remains unclear [6], especially the role of the catalyst. The mechanism of ORR needs to be elucidated, and the improvement of the activity and durability of catalysts for ORR continues to be main topics of interest [28].

1.2.1 Effect of Surface Structure

As mentioned above, the activity and reaction route of ORR is largely dependent on the type of electrode materials, structure of the electrode, properties of the electrolyte solutions, etc. [20, 24, 27, 31, 46-50]. In this section, the effect of surface structure will be discussed.
In acidic solutions, Pt, known as the most active electrode material for ORR, has attracted great attention over the past decades [21]. Pt is widely used as a model electrode for studying the mechanism of ORR, especially after the high quality of low-index single crystal Pt surface became available [51-54]. Markovic et al. carried out ORR on various Pt(hkl) low-index single crystal electrodes [40, 52]. Typical results of ORR measured by RRDE on the Pt(hkl)-disk (bottom) and Pt-ring (top) electrode in 0.05 M H₂SO₄ solution are shown in Fig. 1.3 [40].

![Potential-dependent ORR current](image)

**Fig. 1.3** Potential-dependent ORR current at the Pt(hkl)-disk (bottom) and Pt-ring (top) electrode in O₂-saturated 0.05 M H₂SO₄ with a rotating speed of 900 rpm at a scan rate of 50 mV·s⁻¹. \(E_R = 0.95\) V vs. SCE. (---) Pt(111), (⋯) Pt(100), and (—) Pt(110), respectively [40].

ORR current was observed on all Pt(hkl) electrode surfaces when the potential was more negative than ca. +0.8 V (vs. RHE). ORR current at +0.8 V followed the sequence (111) < (100) < (110), although it occurs according to a 4e⁻ transfer reaction process on these Pt(hkl) surfaces [40]. This result reveals that ORR is highly sensitive to surface structure. Furthermore, the Tafel slope was −120 mV·dec⁻¹ based on the RDE results obtained on the Pt(111) surface in the entire potential region, whereas −60 and −120 mV·dec⁻¹ were found at low and high current potential region, respectively, both on Pt(100) and Pt(110) surfaces [40]. The difference in Tafel slope was attributed to the effect of adsorbed spectator species on oxygen adsorption [40]. For example, on Pt(100) and Pt(110) surfaces, \(\text{OH}_{\text{ads}}\) formation initiated at ca. +0.4 V to +0.5 V (vs. SCE), but on Pt(111) surface, it did not occur at potentials more negative than ca. +0.8 V (vs. SCE) [40]. Therefore, no
spectator species effect was found on Pt(111) in the potential region ORR, and Tafel slope transition was not observed on the Pt(111) surface.

The effect of surface structure on ORR was also studied on Au(hkl) electrode surface. Adzic et al. firstly carried out ORR on low-index Au(hkl) surfaces in alkaline solution, i.e., 0.1 M NaOH, and the typical RDE measurements are shown in Fig. 1.4 [55].

![Fig. 1.4 ORR on rotating Au single-crystal electrodes, i.e., Au(111), Au(110), and Au(100), in 0.1 M NaOH at a rotating speed of 2500 rpm. Sweep rate: 50 mV·s⁻¹][55]

ORR current was observed on all the Au(hkl) surfaces at potentials more negative than 0 V (vs. Hg/HgO), but the potential for detecting 1 mA·cm⁻² followed the sequence (111) < (110) < (100). The half-wave potential for Au(100) was ca. 200 mV more positive than that for Au(111) and Au(110), indicating that Au(100) exhibited higher activity compared with the other two low-index faces [55].

These results directly confirm the sensitivity of ORR to surface structure [40, 55]. This property on Pt(hkl) was ascribed to the sensitivity of the specific adsorption of anions in the solution [53, 54, 56], which block the approach of oxygen molecules to the surface sites where they undergo reduction. Markovic et al. proposed a model where the kinetics of ORR, which is related to the coverage of spectator species (Θ_ad), such as OH, can be expressed as equation 1.9 [24, 34]:

\[
\text{ORR current} = k \cdot \Theta_{ad}^n
\]
\[ i = nFkC_{O_2}(1-y\Theta_{ad})^x \exp\left(\frac{-\beta FE}{RT}\right) \exp\left(\frac{-r\Delta G^*}{RT}\right) \] (1.9)

where \( i \) is the observed current, \( n \) is the number of electrons transferred, \( k \) is the rate constant, \( C_{O_2} \) is the concentration of \( O_2 \) in the solution, \( \Theta_{ad} \) is the total surface coverage by spectator species, \( x \) is the order of activity of metal sites, \( y \) is the number of metal sites blocked by spectator species, \( E \) is the applied potential, \( \beta \) and \( \gamma \) are the symmetry factors, and the energetic term \( (\Delta G^*) \) reflects the adsorption energy of oxygen and reaction intermediates [24]. Equation 1.9 shows that if the term \( \Theta_{ad} \) is increased, the term \((1-\Theta_{ad})\) will decrease, and the current will decrease because the adsorbed spectator species inhibited the adsorption of oxygen.

The surface structure sensitivity of ORR on Au\((hkl)\) surface was also attributed to adsorption of anions (e.g., \( \text{OH}^- \)), but a critical role (positive effect) of adsorbed \( \text{OH}^- \) was proposed [57]. This suggestion was different from the ORR model on Pt surface [24, 34]. Recently, Prieto et al. suggested that the surface structure sensitivity of ORR on Au\((hkl)\) can be ascribed to the different adsorption properties of \( \text{HO}_2^- \) [58]. The role of \( \text{OH}_{ads} \) in ORR on Au surface remains unknown, but the surface structure sensitivity of ORR is known to be related to the sensitivity of the adsorption of anions, whether reactant or intermediate.

### 1.2.2 Effect of pH

As shown in equation 1.1(b), protons are involved in ORR in aqueous solutions. This reaction must be highly sensitive to the proton concentration in the solution, which is related to the pH of the electrolyte solution. In this section, the effect of pH on ORR will be discussed.

In acidic solution, Pt is considered to be the most active electrode material for ORR [21]. The reaction occurs through a \( 4e^- \) transfer process [40]. The step shown in
equation 1.4 is commonly considered as the \textit{rds} with a Tafel slope of $-120 \text{ mV} \cdot \text{dec}^{-1}$ [40]. However, in alkaline solution (i.e., 0.1 M KOH), the kinetic current at +0.8 V (vs. RHE) on Pt(\textit{hkl}) surface increased in the following sequence $(100) < (110) < (111)$ [34], which is different from the sequence observed in 0.05 M H$_2$SO$_4$ solution previously discussed, i.e., Pt(111) < Pt(100) < Pt(110). The surface structure sensitivity of ORR in alkaline solution was also attributed to the structure-sensitive adsorption of hydroxyl [34]. The Tafel slope was $-75 \text{ mV} \cdot \text{dec}^{-1}$ on Pt(111) surface in the entire potential region, whereas it was ca. $-85 \text{ mV} \cdot \text{dec}^{-1}$ to $-90 \text{ mV} \cdot \text{dec}^{-1}$ in the low overpotential region and ca. $-160 \text{ mV} \cdot \text{dec}^{-1}$ to $-260 \text{ mV} \cdot \text{dec}^{-1}$ in the large overpotential region on Pt(110) and Pt(100) surfaces. This result was attributed to the different coverage of OH$_{\text{ads}}$ in the low overpotential region [34]. The Tafel slope shifted to a value larger than $-120 \text{ mV} \cdot \text{dec}^{-1}$ on the (110) and (100) surfaces in the high overpotential region, implying the change in \textit{rds} [34]. The change was probably from the process shown in equation 1.4 to the adsorption of oxygen [34]. This result showed that pH can change the mechanism of ORR on Pt surface, and the effect of oxygen adsorption was more important in alkaline solution for ORR on Pt surface.

Recently, Strbac studied ORR on Pt(poly) electrode in sulfate solutions by RDE measurements over a wide pH range (from 1 to 13). The RDE results obtained at various pH levels at a rotating speed of 1600 rpm are shown in Fig. 1.5 [59]. The potentials at which the ORR current started overlapped with the region for the reduction of Pt surface oxide at all pH levels and negatively shifted with increasing pH [59]. ORR occurred through a 4\textit{e} reaction at pH < 3 or pH > 10, but the reaction process and the Tafel slope were dependent on the electrode potential at 3 < pH < 6. A double wave was observed in this pH range (Fig. 1.5 at pH 3.5 and 4) [59]. This result indicated that when 3 < pH < 6, the ORR on Pt(poly) electrode surface is affected by local pH, i.e., the concentrations of H$^+$ and OH$^-$ are relatively low in this
pH range, and the H\textsuperscript{+} produced or consumed during the formation or reduction of surface oxide can change the pH at the electrochemical interface.

A more obvious pH effect on ORR was observed on Au electrode surface. In acidic solution, ORR on Au surfaces exhibited large overpotentials and occurred through a 2\textit{e} electron transfer route, which was supported by the detection of HO\textsubscript{2} on Au electrode surface by in-situ IR spectroscopy [45]. However, in alkaline solution, Au electrode shows high activity to ORR and the overpotential is decreased with increasing pH [15, 35, 47, 60-63]. The Au(100) facet shows the highest activity, as described in Fig. 1.4 [55].

Adzic et al. studied the pH effect on ORR on Au(100) by RRDE (as shown in Fig. 1.6) [64]. The route of ORR on Au(100) surface was dependent on the pH of the electrolyte; it changed from 2\textit{e} (pH \leq 3) to 4\textit{e} (pH \geq 6) transition reaction [64]. The Tafel slope of ORR observed on the Au(100) electrode surface in alkaline solutions was the same as that in acidic solution, i.e., ca. −120 mV·dec\textsuperscript{−1} [55, 60], which was different from the finding on Pt(\textit{hkl}) described above [34, 40]. The Tafel slope of −120 mV·dec\textsuperscript{−1} on Au(100) surface, indicating equation 1.4 as the \textit{rds}, was different from the condition proposed on Au(poly) electrode, given that equations 1.10 and 1.11 were suggested to be the \textit{rds} on Au(poly) electrode in acidic and
alkaline solutions, respectively, with a shifted Tafel slope from ca. $-120 \, \text{mV} \cdot \text{dec}^{-1}$ to $-50 \, \text{mV} \cdot \text{dec}^{-1}$ [65].

\[ *O_2 + e^- \rightarrow *O_2^* \]  \hspace{1cm} (1.10)

\[ MHO_2 + e^- \rightarrow MHO_2^- \quad \text{or} \quad MO_2H + e^- \rightarrow MO_2H^- \]  \hspace{1cm} (1.11)

Based on the studies introduced above, pH and anions apparently affect ORR in terms of oxygen adsorption on the electrode surface. Oxygen adsorption may even act as the rds on Pt(110) and Pt(100) surfaces in alkaline solution in the large overpotential region.

1.2.3 Effect of Adsorbed Species

As introduced above, the effect of surface structure and pH on ORR can be related to the adsorption of reactant, product (and/or intermediate), or other species (anions, H$_2$O, etc.) on the electrode surface. For example, oxygen adsorption is
considered to be the first stage in ORR [32, 66], and OH$_{\text{ads}}$ was proposed to inhibit ORR kinetics on Pt surface [34] and to play a critical role in improving the activity on Au surface in alkaline solution [57]. Therefore, studies on the adsorption of oxygen, OH, and/or H$_2$O, and other anions on electrode surfaces would be helpful in understanding the mechanism of ORR.

Different models for oxygen adsorption have been considered according to the literature [66-68], as shown in Fig. 1.7. However, the configuration of adsorbed oxygen on active sites remains unclear because of lack of in-situ techniques [66, 69] despite the fact that configuration is dependent on crystallographic structure, which affects ORR processes [67].

![Fig. 1.7 Scheme of different configurations of O$_2$ adsorption on electrode surfaces, (a) from left to right: on top end-on, bridge end-on, bridge side-on one site and bridge side-on two sites [67]. (b) The different types of the bridge side-on two sites [68].](image)

Adzic et al. used underpotential-deposited Ag layer on Pt(111) surface as the probe and detected the configuration of adsorbed oxygen by surface X-ray scattering measurements [66]. Oxygen was adsorbed at a bridge site on Pt(111) surface with an oxygen molecule oriented flat between two Pt atoms [the fourth one in Fig. 1.7(a)], as proposed by Yeager et al. and further supported by their latter work and that of others [70-73]. This was considered necessary for the 4e reaction of ORR [66].

Meanwhile, oxygen adsorption can be monitored by spectral technique and other techniques such as surface-enhanced IR absorption spectroscopy (SEIRA) and electrochemical quartz crystal microbalance (EQCM) [38, 45], because of their high
sensitivities [45, 63, 74-79]. For instance, Uchida et al. detected the adsorption of oxygen species on Pt surface by EQCM in HF and HClO₄ solutions [38]. The potential-dependent coverage of oxygen species was estimated by combining the EQCM results with the RDE measurements, which is shown in Fig. 1.8 [38].

![Fig. 1.8](image-url) (a) Polarization curves on the Pt-EQCM in 7 mM HClO₄ and 7 mM HF solutions saturated with pure O₂ at 2 mV·s⁻¹ with a solution flow rate of 4.5 mL·min⁻¹ and (b) coverages of oxygen species (θₒ) on the Pt-EQCM in He-purged and O₂-saturated solutions. Open and filled circles indicate the θₒ in He-purged and O₂-saturated HF solutions, respectively. Open and filled triangles indicate the θₒ in He-purged and O₂-saturated HClO₄ solutions, respectively. Filled squares (dotted line) indicate the θₒ in He-purged 0.10 M HF quantified by EC-XPS [38].

The coverage of oxygen species was higher in O₂-saturated solutions than in He-saturated solutions in the potential region between +0.6 and +1.0 V (vs. RHE) in these two electrolyte solutions. The coverage of oxygen species decreased when the potential became negative, which may be due to the fact that ORR occurs at faster kinetics and larger overpotentials [38]. It is interesting that the coverage of oxygen species on Pt surface was not zero even with limiting current [38]. This result suggests that the presence of oxygen species (or intermediates) on the Pt electrode surface and the reaction rate of the ORR was not that fast even at relatively negative potentials [38].

Recently, Ohta et al. observed potential-dependent adsorption of oxygen on Au surface in 0.5 M HClO₄ solution by in-situ SEIRAS [45]. The signal observed at
1540 cm\(^{-1}\) in O\(_2\)-saturated HClO\(_4\) solution at potentials more negative than +1.16 V (vs. RHE), as shown in Fig. 1.9, was assigned to the O-O stretching from O\(_2\)\(_{ads}\) [45]. This is the first direct proof of the adsorption of oxygen on Au electrode surface in acidic solution prior to ORR, which is very important in understanding the mechanism of ORR on Au surface.

![Fig. 1.9 Sets of in-situ SEIRA spectra for an Au film electrode in a 0.5 M HClO\(_4\) solution saturated with (a) Ar and (b) O\(_2\). The spectra were obtained during the first linear sweep voltammetry in negative direction from 1.16 to 0.06 V at 5 mV·s\(^{-1}\). Every plotted spectrum represents the average of a potential interval of 100 mV. The reference potential is 1.11 V. The horizontal dashed lines in each spectrum indicate the reference zero lines. The arrow to the right of panel b indicates the direction of the potential sweep [45].](image)

Besides the adsorption of oxygen, information on the intermediates (or products) is also highly important for describing the reaction process of ORR. Kim et al. studied ORR on Au(poly) surface in 0.1 M NaOH by in-situ surface-enhanced Raman scattering (SERS) [15]. The potential-dependent signal of the O-O stretch mode of superoxide (O\(_2^−\)) at ca. 1150 cm\(^{-1}\) Raman shift was observed at potentials more negative than 0 V (vs. Ag/AgCl) where ORR occurred [15]. The amount of O\(_2^−\)
increased when the potential became more negative [15]. This result supported the presence of the electron transition process shown in equation 1.4. Shao et al. studied ORR on Au surface in alkaline solution using surface-enhanced IR reflection-absorption spectroscopy with an attenuated total reflection configuration (ATR-SEIRA) [35]. In the potential region where ORR occurred, a signal at 1268 cm\(^{-1}\) was observed. This signal is attributed to the anti-symmetric bending mode of OOH of adsorbed HO\(_2^-\) [35]. Therefore, HO\(_2^-\) was suggested to be one of the reaction intermediates in ORR [35].

Besides oxygen and the intermediate, the adsorption of H\(_2\)O and/or OH\(^-\) on electrode surface [80-82] and with the specific adsorbing anions on electrode surface [24, 57, 64, 76, 82-90] have gained interest because the overpotential of ORR was considered influenced by adsorbed molecules that block the approach of oxygen molecules to the surface [81]. Therefore, the adsorption of these species on the electrode surface must be investigated to facilitate the elucidation of the ORR mechanism.

Osawa et al. studied the potential dependent H\(_2\)O structure on Pt surface in H\(_2\)SO\(_4\) and HClO\(_4\) solutions by SEIRAS [91]. They described the change in orientation of H\(_2\)O on Pt surface from a weakly hydrogen-bonded oxygen-up to a nearly flat strongly hydrogen-bonded oxygen when the potential changed from negative \([E < pzc \text{ (potential of zero charge)}]\) to positive \([E > pzc]\), as illustrated in Fig. 1.10. The result based on the sum frequency generation (SFG) reported by Noguchi et al. on Pt surface showed the same conclusion [92], which agrees well with the results studied by IR [93].
Fig. 1.10 Schematic drawing of the possible structures of H$_2$O at the negatively (left) and positively (right) charged Pt surface, deduced from the SEIRA spectra [91].

Nihonyanagi et al. investigated the Au interfacial structure by SFG, and the orientation of H$_2$O on Au electrode surface was proven dependent on the electrode potential (see Fig. 1.11) [83], similar to previous studies [82, 90, 93-96]. Furthermore, H$_2$O molecules are incorporated with the specific adsorbed sulfate anions, with their hydrogen atoms pointing to the surface when the potential was more positive than the pzc [83].

Fig. 1.11 Schematic models of the interfacial structure at potentials (a) more negative than, (b) around, and (c) more positive than the PZC. Arrows show the direction of the water dipole [86].

Although these results were obtained in solutions without O$_2$, information on the potential-dependent structure of H$_2$O and the interaction between H$_2$O and the electrode surface can be used as reference for discussing the adsorption of OH and oxygen given that the OH$_{ads}$ on electrode surface in acidic solution is produced by the oxidation of H$_2$O [81].

Desilvestro et al. studied potential-dependent Au(poly) surface structure both in acidic and alkaline solutions by in-situ SERS [84]. Fig. 1.12 shows the (A) CV and (B) SERS spectra obtained at various potentials in 0.1 M KOH solution [84]. The signal from OH$_{ads}$ [as the signal at 300 cm$^{-1}$ to 500 cm$^{-1}$ Raman shift shown in Fig.
1.12(B)] became very weak at ca. 0 V where the surface oxide was almost reduced (Fig. 1.12(A)). No spectral features were observed at −0.25 V, where the surface oxide was fully reduced (Fig. 1.12(A)) [84]. This result may be useful for elucidating the role of OH in ORR on Au electrode surface in alkaline solutions.

Fig. 1.12 Potential-dependent (A) current density (B) SER spectra at Au(poly) surface in 1 M KOH. The spectra were recorded sequentially from bottom to top, using a spectrometer scan rate of 1 cm$^{-1}$·s$^{-1}$. Laser excitation was 647.1 nm, 55 mW at the sample [84].

Besides oxygen, the intermediate, H$_2$O, and OH, ions in solution are also considered to affect the ORR. The surface structure sensitivity of ORR was assumed to have resulted from the sensitive adsorption of anions in solution [34, 40], which influences the kinetics of ORR [40, 53]. In line with this assumption, the effects of anions and cations on ORR, both on Pt and Au surfaces, were discussed [36, 54, 58, 97-100]. The negative effect of specifically adsorbed anions on the adsorption of oxygen (i.e., inhibits the kinetics of ORR or blocks the adsorption of oxygen) was proposed. The non-covalent interaction between the cation and electrode was
suggested for consideration [36, 54, 58, 97-100]. These are important parameters for designing the system of a fuel cell.

Studies (or evidence) of the adsorption of oxygen and other species, e.g., the product, intermediates, H₂O, and OH, are very important for elucidating the mechanism of ORR, which has indeed developed greatly during the past decades. However, any conclusions on the mechanism of ORR are yet to be finalized.

1.3 Objectives and Outline of the Thesis

ORR on Au and Pt electrodes has been studied for a long time. Although ORR is known to be highly sensitive to electrode material, surface structure, and the properties of electrolyte solutions such as pH and ions, systematic investigations of these parameters are limited. Furthermore, only limited 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 were investigated. Direct proof of oxygen adsorption was provided by EQCM.

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

In chapter 2, experimental details, including information on chemicals, preparation of samples and setup, and principles of RDE and EQCM are given.

In chapter 3, the effect of pH on ORR on Au(111) surface was investigated by RDE with a hanging-meniscus (HM) configuration. The overpotential for a given ORR current on Au(111) surface decreased with increasing pH. ORR mechanism is discussed based on the experimental results.

In chapter 4, the effect of sulfate anion (SO₄²⁻) and pH on the adsorption of oxygen on Au electrode surface was investigated through EQCM by measuring the potential-dependent frequency changes in various solutions. The adsorption of oxygen on Au surface was first observed at potentials more positive than that at
which ORR starts to occur. The mass change difference between Ar-saturated and O₂-saturated solutions was attributed to the adsorption of oxygen. The amount of adsorbed oxygen increased and reached saturation value as potential became more negative in all solutions in this study. The adsorption of oxygen on Au electrode surface started at ca. +0.82 V in perchlorate solution (SO₄²⁻-free), whereas it started at ca. +0.60 V in sulfate solution. This result shows the inhibition of the adsorption of oxygen by adsorbed sulfate anion. In all SO₄²⁻-free solutions at various pH levels in this study, the mass change difference started to increase at the potential where the surface oxide was partially reduced, and the saturation value at each pH was reached when surface oxide was fully reduced. The maximum mass change difference increased with increasing pH and became constant at pH > 11.4. In this study, the potentials at which oxygen adsorption was first observed were dependent on the anions in solution. It was proposed, therefore, that oxygen adsorbed on bare 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 to compare the effect of electrode material. The adsorption of oxygen was first observed at ca. +0.60 V where the surface oxide was partially reduced and the ORR current flowed both in perchlorate and sulfate solutions. The presence of sulfate anion on the adsorption of oxygen was not significantly observed on Pt electrode surface in this study. However, the adsorption of oxygen on Pt electrode surface resulted in mass increase in perchlorate solution, whereas it caused mass decrease in sulfate solution. It was proposed that the adsorbed sulfate was replaced by oxygen on Pt electrode surface. The effect of anion on the adsorption of oxygen on Pt surface is different from that observed on Au surface in chapter 4.

In **Chapter 6**, the general conclusion of this work and future prospects are presented.
1.4 References


Chapter 2

EXPERIMENTAL

2.1 Chemicals

The chemicals, involving acetone (CH\textsubscript{3}COCH\textsubscript{3}, 99%), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}, 99%), ethanol (CH\textsubscript{3}CH\textsubscript{2}OH, 99.5%), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), silver nitrate (AgNO\textsubscript{3}, 99.8%), sodium chloride (NaCl, 99.9%), sodium hydroxide (NaOH, 97%), sodium perchlorate monohydrate (NaClO\textsubscript{4}·H\textsubscript{2}O, 98%), sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}, 99%), and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 98%) are all from Wako Pure Chemical Industries, Ltd., Japan. All the chemicals were used without further purifying, and all the solutions used in the experiments were prepared freshly with Milli-Q water (≥18.2KΩ·cm, WRX10, Yamato Scientific Co., Ltd.). Au wire (Ø1mm, 99.99%, Noble Metal Co. Ltd.). Polishing paper (#400, #1000, and #2000) and diamond slurry (3 µm, 1 µm and 0.5 µm) were purchased from Maruto Instrument.

All the glassware, including electrochemical cells and others, were washed by heated concentrated H\textsubscript{2}SO\textsubscript{4}, then boiled in Milli-Q water for at least three times, and ready for use. This process for washing glassware is to remove the organic or some domination adsorbed at the surface [1].

2.2 Preparation of Au(111) Electrode

The single crystal Au electrode was prepared using Au wire according to Clavilier’s method [2], as previously reported [3]. A spherical gold single crystal, as shown in Fig. 2.1, was prepared by the crystallization of a molten ball at the end of the gold wire in butane oxygen flame; the Au wire was washed with Piraha solution (H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{2}O\textsubscript{2} = 3:1) and Milli-Q water. One Au(111) facet was fixed parallel to the
reference plane by laser beam, and the bead was fixed in a cylinder. The liquid epoxy resin was poured into the cylinder with the bead. One Au(111) surface was obtained by cutting the bead parallel to the Au(111) facet using a diamond saw (Buehler) and was then sequentially polished by #400, #1000, and #2000 polishing paper and 3, 1, and 0.5 µm diamond slurry at a polishing equipment (Maruto Instrument Co., Ltd., ML 150-P). Overnight immersion in CH₂Cl₂ at room temperature was performed to remove the epoxy resin, with subsequent sonication in CH₂Cl₂, acetone, and Milli-Q water. As the (111) face was covered with uncrystalline processing layers, annealing at 850 °C was conducted for 8 h in an electric furnace (Denken, KDF-S70G) in air for re-crystallization prior to use.

![Image](image.jpg)

**Fig. 2.1** Image of the molten ball at the end of the gold wire in butane oxygen flame; the (111) and (100) facets are indexed in the figure.

Before each electrochemical measurement, the single crystal electrode was annealed in H₂ flame, protected with a droplet of Milli-Q water to avoid contamination from the air, and subsequently transferred into the cell for measurement. **Figure 2.2** shows the electrochemical behavior of Au(111) in Ar-saturated 50 mM H₂SO₄ solution. The sharp peaks in the double layer potential region (between −0.20 and +0.95 V) and redox potential region (between −0.20 and +1.45 V) reflect the high quality of the single crystal. The electrochemical active
surface area was estimated by the electric charge for reduction of gold surface oxide with 440 μC·cm\(^{-2}\) as reference [4].

![Diagram showing potential-dependent current density of Au(111) in 50 mM H\(_2\)SO\(_4\) saturated with Ar at a scan rate of 50 mV·s\(^{-1}\).]

**Fig. 2.2** Potential-dependent current density of Au(111) in 50 mM H\(_2\)SO\(_4\) saturated with Ar at a scan rate of 50 mV·s\(^{-1}\).

### 2.3 Electrochemical Measurements

#### 2.3.1 Cyclic Voltammetry Measurements

All electrochemical measurements in this thesis were carried out in a three-electrode system. A Pt wire and homemade Ag/AgCl (sat. NaCl) were used as counter and reference electrode, respectively. In all electrochemical measurements, a Luggin-Haber capillary was used to reduce the IR drop [5]; this configuration will be introduced in section 2.3.2.2. Prior to each experiment, the electrolyte solution was saturated with Ar or O\(_2\) by passing Ar or O\(_2\) through the solution for at least 20 min. The gas was continuously flowed above the solution during the measurements. All experiments were carried out at room temperature.

In chapter 3, the electrochemical measurements were carried out via an automatic polarization system HZ-5000 (Hokuto Denko) that was controlled by a personal computer.
In chapters 4 and 5, electrode potential was controlled by a potentiostat (Model 2001, Toho Technical Research) and external potential was provided by a function generator (Hokuto Denko, HB-111).

### 2.3.2 Rotating Disk Electrode Measurements

#### 2.3.2.1 Principle of Rotating Disk Electrode

RDE is one of the most powerful equipment for studying the kinetics of ORR [1, 5, 6]. The configuration and structure of the electrode are shown in Fig. 2.3.

![Fig. 2.3 Configuration and structure of the electrode for RDE measurements [6].](image)

The solution diffuses onto the electrode surface vertically when the electrode is rotating, and the diffusion rate and the thickness of diffusion layer are dependent on the rotation rate. In RDE measurements, all sites on the electrode surface are considered the same. A diffusion-limited current is usually observed in large overpotential regions. The relationship between the limited current and rotating rate is given by the Levich equation 2.1 [5-7]:

\[
i_L = 0.62nFAD^{2/3} v^{-1/6} \omega^{1/2}
\]  

(2.1)

where \( n \) is the overall electron transfer number in mol reaction, \( F \) is the Faraday constant (96 485 C·mol\(^{-1}\)), \( A \) is the surface area (cm\(^2\)), \( D \) is the diffusion coefficient.
(mol·cm$^{-2}$·s$^{-1}$), $\nu$ is kinematic viscosity of the solution (mol·cm$^{-1}$), $C$ is bulk concentration of the reactant (mol·cm$^{-3}$), and $\omega$ is the rotating rate (rad·s$^{-1}$). The plot of $i$ versus $\omega^{1/2}$ can yield a straight line, i.e., the Levich plot, and $n$ in the reaction can be estimated by fitting the plot with the Levich equation.

To avoid any mass-transfer effects on the current, the kinetic current ($i_k$) must be at a value that would allow flow under the kinetic limitation if the mass transfer were efficient enough to keep the concentration at the electrode surface equal to the bulk value [5]. The relation between the potential and logarithmic kinetic current gives a Tafel plot, reflecting the $rds$ of the reaction and the adsorption model of the intermediate [9], which is very important for discussing the mechanism of the electrochemical reaction. The kinetic current can be estimated according to the Koutecky-Levich (K-L) equation 2.2 [5-8]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_L}$$

Therefore, a plot of $i^1$ versus $\omega^{-1/2}$, i.e., K-L plot, should be linear and can be extrapolated to $\omega^{-1/2} = 0$ to yield $i_k^{-1}$ [8].

### 2.3.2.2 Hanging-Meniscus Configuration for Rotating Disk Electrode Measurements

Figure 2.4 shows the HM configuration for the RDE measurements (HM-RDE) on Au(111) electrode, which can also be found elsewhere [10]. A Luggin-Haber capillary was used to make the reference electrode as close as possible to the working electrode to reduce the IR drop. The Au(111) disk electrode was fixed on a dynamic electrode HR-201 (Hokuto Denko), and the rotation speed was controlled by an HR-202 unit (Hokuto Denko).
Fig. 2.4 Hanging-meniscus (HM) configuration for rotating disk electrode (RDE) measurements on Au(111) electrode surface.

The reliability of the configuration for this system was confirmed using the RDE measurements in 0.1 M Na$_2$SO$_4$ containing 1 mM K$_3$[Fe(CN)$_6$] by analyzing the results according to the Levich equation, as shown in Fig. 2.5.

![Levich plot](image)

**Fig. 2.5** Levich plot of the Au(111) in 0.1 M Na$_2$SO$_4$ containing 1 mM K$_3$[Fe(CN)$_6$] using diffusion-limited current.

Figure 2.5 shows the Levich plot of Au(111) in 0.1 M Na$_2$SO$_4$ containing 1 mM K$_3$[Fe(CN)$_6$] using diffusion-limited current obtained by RDE measurements with an HM configuration. By fitting the plot according to the Levich equation (dash line), the diffusion coefficient of Fe(CN)$_6^{3-}$ was found to be $7.3 \times 10^{-6}$ cm$^2$·s$^{-1}$, which was similar to the theoretical value of $7.6 \times 10^{-6}$ cm$^2$·s$^{-1}$ with an error of ca. 5%. This result indicates the reliability of the configuration.
2.3.3  Electrochemical Quartz Crystal Microbalance Measurements

2.3.3.1  Principles of Quartz Crystal Microbalance

Quartz crystal microbalance (QCM) is a device that is highly sensitive to surface mass change and can be used for studying surface processes, such as metal deposition as well as formation and reduction of surface oxide. The electrode used in QCM comprises a thin quartz crystal (AT-cut, at an angle of approximately 35° with respect the x-axis) sandwiched between two metal electrodes [Fig. 2.6(A)] that establishes an alternating electric field across the crystal. This setup causes vibrational motion in the quartz crystal with amplitude parallel to the surface of the crystal [6, 11]. This vibrational motion results in a transverse acoustic wave that propagates across the thickness of the crystal ($t_q$) and is reflected back into the crystal at the surfaces [Fig. 2.6(B)]. If the acoustic wavelength is equal to $2t_q$, the frequency of the acoustic wave in this resonant condition can be given by equation 2.3.

\[
f_0 = \nu_r / 2t_q = \frac{\mu_q}{2t_q \sqrt{\rho_q}}
\]  

(2.3)

**Fig. 2.6** (A) Configuration of electrode for QCM measurements (upper image is the edge view, and the bottom is the top view). (B) Schematic representation of the transverse shear wave in a quartz crystal and a composite resonator comprising the quartz crystal and a layer of a foreign material [12, 13].
where \( v_{tr} \) is the transverse velocity of sound in AT-cut quartz, \( \mu_q \) is the shear modulus of quartz (2.9 \( \times \) 10\(^{11}\) g\( \cdot \)cm\(^{-2}\)\( \cdot \)s\(^{-1}\)), and \( \rho_q \) is the density of quartz (2.5 g\( \cdot \)cm\(^{-3}\)) [11, 14].

When a uniform layer of a foreign material is firmly attached to the surface of the quartz crystal, the acoustic wave will travel across the interface and propagate through the foreign layer [Fig. 2.5(B)]. Based on the assumption that the acoustic properties of the foreign layer are identical to those of quartz, the thickness of the foreign layer can be treated as a change in the quartz crystal thickness. Subsequently, the change in frequency (\( \Delta f \)) resulting from the change in thickness (\( \Delta t \)) can be addressed by equation 2.4. The well-known Sauerbrey equation is obtained by appropriate substitutions using equation 2.3 and 2.5, as shown in equation 2.6 [15]. Thus, mass change on the surface can be estimated according to equation 2.7:

\[
\frac{\Delta f}{f_0} = -\frac{\Delta t}{t_q} = -2f_0\Delta t / v_{tr}
\]  \hspace{1cm} (2.4)

\[
\Delta t = \frac{\Delta m}{A\rho_q}
\]  \hspace{1cm} (2.5)

\[
\Delta f = -\frac{2f_0^2\Delta m}{A\sqrt{\mu\rho}}
\]  \hspace{1cm} (2.6)

\[
\Delta m = -S \cdot \Delta f
\]  \hspace{1cm} (2.7)

where \( \Delta m \) is the mass change (ng\( \cdot \)cm\(^2\)), \( A \) is the piezoelectrically active area (cm\(^2\)), and \( S \) is the sensitivity constant of the equipment (ng\( \cdot \)Hz\(^{-1}\)\( \cdot \)cm\(^2\)).

2.3.3.2 Quartz Crystal Microbalance in Electrochemistry

After the first application of QCM in solution systems [16], it has been widely utilized for studying surface process in electrochemistry [13, 14, 16–29], known as EQCM. Figure 2.7 shows the configuration commonly used.
In the practical operation of EQCM, the working electrode is mounted in the holder with O-rings. One side of the electrode is in contact with the electrolyte and the other is exposed to air. If both sides are in contact with the electrolyte, the solution conductance acts as a shunt across both faces of the crystal and prevents the electrical circuit from oscillating [25]. The sensitivity of EQCM (the term \( S \) in equation 2.7) is usually calibrated by bulk deposition of Ag or Pb [16, 18, 19].

2.3.3.3 Configuration for Electrochemical Quartz Crystal Microbalance Measurements

The configuration of EQCM shown in Figure 2.7 was utilized in this study. All EQCM measurements were carried out in a glove bag filled with \( \text{N}_2 \) to eliminate the effect of oxygen from air.

In chapter 4, the working electrode for the EQCM measurements was a 10 MHz AT-cut quartz crystal plate covered with a Au film (W32053, Hokuto Denko) mounted in an EQCM sensor (Hokuto Denko, HQ-601DK). The oscillating frequency of the quartz crystal electrode was monitored by an EQCM controller (Hokuto Denko, HQ-101D) controlled by a personal computer through a GPIB interface with a sampling time of 1 s. Prior to each experiment, the electrode was
electrochemically cleansed in an Ar-saturated 50 mM H$_2$SO$_4$ solution by continuous potential cycling in the double layer potential region (−0.2 V to +0.95 V vs. Ag/AgCl), which was reported to improve the (111) orientation [30]. After removal from H$_2$SO$_4$ solution, the electrode was subsequently washed with Milli-Q water thoroughly prior to use.

In chapter 5, the working electrode for the EQCM measurements was a 10 MHz AT-cut quartz crystal plate covered with a Pt film (W23619, Hokuto Denko) mounted in an EQCM sensor (Hokuto Denko, HQ-601DK). The current, potential, and oscillating frequency of the quartz crystal electrode were recorded by a data logger (GRAPH-TEC, GL-200A) interfaced to the potentiostat (Model 2001, Toho Technical Research), function generator (Hokuto Denko, HB-111), and frequency counter (Hokuto Denko, EQCM controller HQ-101D) with a sampling time of 1 s. Prior to each measurement, electrochemical cleansing in an Ar-saturated 0.1 M HClO$_4$ or 0.05 M H$_2$SO$_4$ solution was performed through continuous potential cycling in the potential region −0.22 V to +1.10 V vs. Ag/AgCl) until an obvious and sharp hydrogen adsorption/desorption peak appears. Milli-Q water was used for washing prior to subsequent use.

Mass change (Δm) for all EQCM results was estimated from the resonant frequency shift (Δf) by the Sauerbrey equation 2.7, where $S$ is the mass sensitivity that is calibrated to be 5.4 ng·Hz$^{-1}$·cm$^{-2}$ by Ag bulk deposition in Ar-saturated 0.1 M HClO$_4$ containing 1 mM AgNO$_3$. 
2.4 References


Chapter 3

EFFECT OF PH ON OXYGEN REDUCTION REACTION ON
AU(111) ELECTRODE SURFACE

3.1 Introduction

ORR on Au electrode surface has been studied for a long time. However, the mechanism remains unclear because of its complex processes [1–11], although it has been proven that ORR is highly sensitive to electrode material, surface structure, and the properties of electrolyte solution, such as pH and ions [12–14].

Adzic et al. first carried out ORR on low-index Au(hkl) surfaces in alkaline solution [13], which demonstrated that the Au(100) surface has the highest ORR activity compared with the other two low-index facets [13]. They studied the pH effect on ORR on Au(100) facet through RRDE [14]. The results revealed that the overpotential of ORR on Au(100) surface decreases with increasing pH of the electrolyte solution [14]. ORR on Au(100) surface was dependent on the potential and pH of the electrolyte solution: at pH ≤ 3, H₂O₂ was the main product in the entire potential region where ORR occurred; at 3 < pH < 6, the ORR product was dependent on electrode potential; at pH ≥ 6, the ORR product was OH⁻ [14]. The adsorbed OH on Au electrode surface may play a critical role in ORR [15], which is different from the situation on Pt surface [16]. However, a general conclusion elucidating the mechanism of ORR on Au surface is yet to be formed [11, 17, 18].

To elucidate the mechanism of ORR on Au electrode surface, the pH effect on ORR on other faces of the Au electrode must be investigated. Au(111) electrode has been extensively utilized as a model surface for various electrochemical processes because of its extremely clean, well-defined, and highly stable surface [19].
In this chapter, the effect of pH on ORR was investigated through RDE on Au(111) surface with an HM configuration. The overpotential for generating an identical ORR current on Au(111) surface decreased with increasing pH. The Tafel slope shifted from ca. $-130 \text{ mV} \cdot \text{dec}^{-1}$ to ca. $-80 \text{ mV} \cdot \text{dec}^{-1}$ when the pH of the solution increased from 1.5 to 12.7.

3.2 Results

3.2.1 pH Effect on the Electrochemical Behavior of Au(111) Electrode

The effect of pH on the electrochemical behavior of Au(111) was first surveyed by cyclic voltammetry. The pH was adjusted by mixing different concentrations of H$_2$SO$_4$ or NaOH with Na$_2$SO$_4$ solutions. The ionic strength (calculated according to equation 3.1) is usually considered to affect electrochemical reactions by changing the double layer structure. Hence, it was kept at a level that approximates 0.15 M Na$_2$SO$_4$ for all electrochemical measurements in this section, i.e., 0.45.

$$I = \frac{1}{2} \sum c_i z_i^2$$

(3.1)

where $c_i$ and $z_i$ are the concentration and charge number of species of $i$ in the solution, and the term $I$ on the left side of the equation is the ionic strength. Table 3.1 lists the composition of the electrolyte solutions at various pH levels.
Table 3.1 Composition of the electrolyte solutions at various pH levels.

<table>
<thead>
<tr>
<th>pH</th>
<th>H₂SO₄ / mmol·L⁻¹</th>
<th>Na₂SO₄ / mol·L⁻¹</th>
<th>NaOH / mmol·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>50</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>2.7</td>
<td>5</td>
<td>0.145</td>
<td>0</td>
</tr>
<tr>
<td>3.7</td>
<td>0.5</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>4.7</td>
<td>0.05</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>6.0</td>
<td>0</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>6.8</td>
<td>0</td>
<td>0.15</td>
<td>0.001</td>
</tr>
<tr>
<td>8.2</td>
<td>0</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>9.6</td>
<td>0</td>
<td>0.15</td>
<td>0.1</td>
</tr>
<tr>
<td>12.7</td>
<td>0</td>
<td>0.12</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 3.1 shows the cyclic voltammograms (CVs) of Au(111) electrode in the electrolyte solutions with various pH levels of (1) 1.5 to (2) 6.1, (3) 6.8, and (4) 12.7 saturated with Ar at the scan rate of 50 mV·s⁻¹.

Fig. 3.1 Cyclic voltammograms (CVs) of Au(111) electrode in electrolyte solutions of various pH levels (1) 1.5 to (2) 6.1, (3) 6.8, and (4) 12.7 saturated with Ar. Scan rate: 50 mV·s⁻¹.

Curve (1) in Fig. 3.1 is similar to a typical CV of Au(111) in an Ar-saturated H₂SO₄ solution. The anodic and cathodic peaks attributed to the formation and reduction of surface oxide [20–23] were observed at +1.30 and +0.85 V,
respectively, without other peaks, which indicate the high quality of Au(111) [24]. This pair of redox peaks related to the formation and reduction of surface oxide was also observed in solutions at other pH values, although the potentials were negatively shifted when the pH increased, as shown by the other curves in Fig. 3.1. This result can be explained by the Nernst equation (3.2) at 25 °C. That is, the redox peak potential will be negatively shifted by ca. 60 mV when the pH is increased by 1 unit.

\[
E_{eq} = E^{\circ} + \frac{RT}{nF} \ln \frac{C_{O}^{\circ}}{C_{R}^{\circ}} = E^{\circ} - 0.059 pH \quad (25 \, ^\circ C) \quad (3.2)
\]

A small anodic peak prior to the formation of surface oxide was observed in the potential region between 0 V to +0.40 V, as shown in curve (4) when the pH of the solution was higher than 9. The result was in good agreement with the results reported previously [18, 25, 26]. This finding is considered related to the adsorption of OH\(^-\), which can be written as equation 3.3 [10, 13]:

\[
Au^{n^+} + \lambda OH^- \rightarrow Au^{(n+\lambda)\circ} (OH)_\lambda + \lambda e^- \quad (3.3)
\]

However, when 5 < pH < 10, the separation of the redox peak increased. This result was attributed to the effect of local pH, similar to the case observed on Pt surface [27]. When 5 < pH < 10 in this study, the concentrations of proton or OH\(^-\) were relatively low. Therefore, the proton produced or consumed during formation or reduction can change the pH of the electrochemical interface (local pH). By contrast, in both acidic (e.g., pH < 5 in this study) and alkaline solutions (e.g., pH > 10 in this study), the concentration of proton (acid) or OH\(^-\) (base) is very high. The proton produced during the formation or consumed during the reduction of surface oxide cannot alter the pH at the electrode surface level.
3.2.2 Oxygen Reduction Reaction on Au(111) Surface in 0.15 M Na$_2$SO$_4$

Containing 5 mM H$_2$SO$_4$ (pH 2.7)

3.2.2.1 Cyclic Voltammetry

Figure 3.2 shows the CVs of Au(111) electrode for the first (solid) and second (dash) potential cycles in 0.15 M Na$_2$SO$_4$ containing 5 mM H$_2$SO$_4$ solution (pH 2.7) saturated with O$_2$ at a scan rate of 50 mV·s$^{-1}$. The potential was positively scanned from +0.35 V to +1.35 V, negatively scanned to −0.10 V, and then positively scanned to +0.35 V. The second potential cycle was recorded in a similar manner to the potential scanned in the first cycle.

![Cyclic Voltammetry Graph](image)

Fig. 3.2 CVs of Au(111) electrode for the first (solid) and second (dash) potential cycles in 0.15 M Na$_2$SO$_4$ containing 5 mM H$_2$SO$_4$ solution (pH 2.7) saturated with O$_2$ at a scan rate of 50 mV·s$^{-1}$.

During the first potential scanning, CV was identical to that in Ar-saturated solution when the potential was higher than +0.30 V. This result indicates that the presence of oxygen in the solution does not affect the formation and reduction of surface oxide, similar to the case observed on Pt surface [28]. ORR current was
obtained at potentials more negative than +0.30 V, indicating a large overpotential of ORR on Au(111) electrode surface under this condition.

When the electrode underwent the second potential scanning, the anodic current increased in the potential region between +0.75 and +1.35 V. This current can be ascribed to the oxidation of the product of ORR in the first potential cycle that is H₂O₂, as shown in equation 3.4.

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \]  

(3.4)

3.2.2.2 Rotating Disk Electrode Measurements

To study the kinetics of ORR on Au(111) electrode surface, RDE measurements were carried out. An HM configuration was preferred in this study to ensure that only the Au(111) surface gets in contact with the solution.

Figure 3.3 shows the polarization curves of Au(111) on an RDE with an HM configuration measured in an O₂-saturated 0.15 M Na₂SO₄ containing 5 mM H₂SO₄ (pH 2.7) with various rotation speeds of 400 rpm to 3600 rpm, with a potential scan rate of 10 mV·s⁻¹.

Fig. 3.3. Polarization curves of Au(111) on an RDE with an HM configuration measured in an O₂-saturated 0.15 M Na₂SO₄ containing 5 mM H₂SO₄ (pH 2.7) with various rotation speeds from 400 rpm to 3600 rpm at a potential scan rate 10 mV·s⁻¹, and the rotation speed was indicated in the figure.

Figure 3.3 shows that the ORR current gradually increased with increasing rotating speed, similar to the previous study [29]. The relationship between the
diffusion-limited current density ($i_L$) and rotation rate is given by the Levich equation (equation 3.5), which was also given in chapter 2 [30, 31]:

$$i_L = 0.62 n F C_{O_2} v^{-1/6} D^{2/3} \omega^{1/2}$$  \hspace{1cm} (3.5)

where $F$ is the Faraday constant (96 485 C·mol$^{-1}$), $C_{O_2}$ is the concentration of oxygen in bulk solution ($1.13 \times 10^{-6}$ mol·cm$^{-3}$) [32], $D$ is the diffusion coefficient ($1.8 \times 10^{-5}$ cm$^2$·s$^{-1}$) [32], $v$ is the viscosity of the liquid (0.01 cm$^2$·s$^{-1}$) [32], and $\omega$ is the rotation rate of disk electrode (rad·s$^{-1}$). The plot of $i$ versus $\omega^{1/2}$, that is the Levich plot, is expected to yield a straight line (Levich plot) and the number of electrons transferred in mol reaction can be determined from the slope. However, as shown in Fig. 3.3, no diffusion-limited current was observed even in a very large overpotential region. Thus, the Levich equation cannot be utilized here.

The current density can be expressed as equation 3.6a for the non-limiting current condition [30].

$$i = 0.62 n F D^{2/3} v^{-1/6} \omega^{1/2} \left[ C_{O_2} - C_{O_2}^s \right]$$  \hspace{1cm} (3.6a)

where $C_{O_2}^s$ is the surface concentration of oxygen. By substitution of equation 3.5 for the terms in equation 3.6a, the following is obtained:

$$i = i_L \left[ \frac{C_{O_2} - C_{O_2}^s}{C_{O_2}} \right]$$  \hspace{1cm} (3.6b)

The disk current density is shown as equation 3.7(a) because ORR is an irreversible reaction:

$$i = n F k C_{O_2}^s$$  \hspace{1cm} (3.7a)

where $k$ is the reaction constant as a function of electrode potential. From equation 3.6, equation 3.7a can be expressed as equation 3.7b:
\[ i = nFkC_O(1 - \frac{i}{i_L}) \]  

(3.7b)

with rearrangement and definition

\[ i_k = nFkC_O \]  

(3.8)

Equation 3.9, known as the K-L equation, which is valid for analyzing RDE results can be obtained:

\[ \frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_L} \]  

(3.9)

where \( i_k \) is the current density in the absence of any mass transfer.

**Figure 3.4** (A) shows the K-L plots for the Au(111) electrode calculated from HM-RDE results shown in Fig. 3.3. Therefore, a plot of \( i^{-1} \) versus \( \omega^{-1/2} \) (K-L plot) should be linear and can be extrapolated to \( \omega^{-1/2} = 0 \) to yield \( i_k^{-1} \).

\[ \text{Fig. 3.4 (A) Koutecky-Levich (K-L) plots for the polarization curves of the Au(111) electrode obtained from the HM-RDE results at different electrode potentials from the results shown in Fig. 3.3. (B) Relation between the potential and logarithm of kinetic current density, known as Tafel plot, calculated from the K-L plot in Fig. 3.4(A).} \]

Figure 3.4(B) shows the Tafel plot calculated from the kinetic current density in Fig. 3.4(A). The slope of the Tafel plot was \(-135 \text{ mV} \cdot \text{dec}^{-1}\) in the low overpotential region, which is slightly different from the value of ca. \(-120 \text{ mV} \cdot \text{dec}^{-1}\)
obtained from Au thin film electrode surface in 0.5 M H$_2$SO$_4$ solution [32] and the value previously obtained on Au(111) surface (−175 mV·dec$^{-1}$ in 0.05 M H$_2$SO$_4$) [33]. This discrepancy may be due to the error in the calculation of $i_k$. $i_k$ in a previous study [33] was estimated by $i_k = \frac{i \cdot i_s}{i_s - i}$, but the diffusion-limited current was not observed.

### 3.2.3 Oxygen Reduction Reaction on Au(111) Surface in 0.12 M Na$_2$SO$_4$ Containing 0.1 M NaOH (pH 12.7)

As discussed previously, Au(111) shows a large overpotential for ORR in an acidic solution. Effects of pH on ORR on Au(111) surface were investigated.

#### 3.2.3.1 Cyclic Voltammetry

Figure 3.5 shows the CVs on Au(111) surface in 0.12 M Na$_2$SO$_4$ containing 0.1 M NaOH solution (pH 12.7) saturated with Ar (solid line) and O$_2$ (dot line) at a potential scan rate of 50 mV·s$^{-1}$.

![Figure 3.5](image)

Ar-saturated solution (solid line) is similar to curve (4) shown in Fig. 3.1. In the O$_2$-saturated solution (dot line), no significant difference was observed when the potential was more positive than +0.05 V, compared with that obtained in
Ar-saturated solution (solid line). This result indicates that the presence of oxygen in the solution does not affect the formation and reduction of surface oxide, which is similar to the situation observed in the acidic solution (pH 2.7) discussed in Fig. 3.2.

ORR current was observed at potentials more negative than 0 V, which is similar to a previous report [34]. ORR current was enhanced as the potential became more negative and almost reached the diffusion-limited current of ca. −0.50 V, which was not observed in the acidic solution shown in Fig. 3.2. ORR current was increased further when the potential was more negative than −0.60 V because of the improved activity of large overpotentials [10] and partial H₂O₂ that may be further reduced. Reversing the potential to positive direction, the ORR current still can be observed and diminished when the potential became positive. An anodic current peak was observed in the potential region between −0.10 and +0.05 V, which can be attributed to the oxidation of H₂O₂ produced from ORR in the negative potential region similar to the case in the acidic solution discussed earlier (equation 3.4). This result is in good agreement with the previous result that ORR occurred through a 2e transition reaction route in alkaline media on Au(111) surface [9]. Figure 3.6 shows that the assignment of this peak was also confirmed by the negative potential limit dependence under the same condition.
In Fig. 3.6, the potential started from +0.05 V, where ORR was not existent, and positively swept to +0.50 V, then negatively swept to various negative potential limits, and then positively swept and reverted to the initial potential, i.e., +0.05 V. The negative potential limit for each curve was (1) +0.05, (2) 0, (3) −0.10, and (4) −0.20 V, respectively. Neither ORR current nor the anodic current peak in the potential region between −0.10 V and +0.05 V was observed (curves 1 and 2) when the negative potential limit was more positive than 0 V. ORR current was observed (curve 3) when the negative potential limit reached −0.10 V. However, the anodic current in the potential region between −0.10 V and +0.05 V was still not observed when the potential was positively swept. ORR current increased and the anodic current in potential region between −0.10 V and +0.05 V was obviously observed (curve 4) when the potential limit was more negative than −0.10 V. These results suggested that the anodic current in the potential region between −0.10 V and +0.05 V must be due to the oxidation of the species produced in the potential region more negative than −0.10 V, i.e., H$_2$O$_2$.

Figures 3.5 and 3.6 show that the potential where the oxidation current of H$_2$O$_2$ was first observed was ca. −0.1 V, showing an overpotential of ca. 0.15 V ($E^\circ_{O_2/H_2O_2} = −0.25$ V vs. Ag/AgCl at pH 12.7). However, in acidic solution (Fig. 3.2, $E^\circ_{O_2/H_2O_2}$...
= +0.34 V vs. Ag/AgCl at pH 2.7), the oxidation current of H₂O₂ was observed at potentials more positive than +0.75 V, showing an overpotential of ca. 0.4 V. These results indicated that Au(111) also exhibits higher activity for the oxidation of H₂O₂ in alkaline solution.

### 3.2.3.2 Rotating Disk Electrode Measurements

Figure 3.7 shows the polarization curves of Au(111) on an RDE with HM configuration measured in an O₂-saturated 0.12 M Na₂SO₄ containing 0.1 M NaOH solution (pH 12.7) with various rotation speeds from 400 rpm to 2500 rpm at a potential scan rate of 10 mV·s⁻¹.

![Polarization Curves](image)

Figure 3.7 shows that ORR current gradually increased when rotation speed was increased from 400 rpm to 2500 rpm, similar to a previous report [11]. The absence of diffusion-limited current was in agreement with the results shown in Fig. 3.3.

**Figure 3.8**(A) shows the K-L plots for the Au(111) electrode calculated from the HM-RDE results shown in Fig. 3.7. According to the results in Fig. 3.4, the plot of \(i^{-1}\) versus \(\omega^{-1/2}\) (K-L plot) should be linear and can be extrapolated to \(\omega^{-1/2} = 0\) to yield \(i_k^{-1}\).
Fig. 3.8 (A) Koutecky-Levich (K-L) plots for the polarization curves of the Au(111) electrode obtained from the HM-RDE results at different electrode potentials from the results shown in Fig. 3.7. (B) Relation between the potential and logarithm of kinetic current density, known as Tafel plot, calculated from the K-L plot in Fig. 3.8(A).

Figure 3.8(B) shows the Tafel plot calculated from the kinetic current density from Fig. 3.8(A). The slope of the Tafel plot was ca. −86 mV·dec⁻¹ in the low overpotential region, which was different from the value of −60 mV·dec⁻¹ obtained on the Au(111) surface in 0.1 M KOH solution reported previously [35]. The discrepancy may be due to the different electrolyte solution utilized in the study.

3.3 Discussions

The Tafel plot, which shows the relation between the potential and logarithm of kinetic current density, can be extrapolated to the equilibrium potential of ORR under the corresponding condition (i.e., the overpotential is zero) to yield log (-iₚ₀), where iₚ₀ is the exchange current density [30]. However, in such a case, a large aberration can be introduced because of the large overpotential [36]. The comparison of the potentials in generating identical ORR current density at different pH values was preferred. Converting potential to reversible hydrogen electrode (RHE) scale is more convenient, thereby preventing any potential shift that may be caused by the pH of the electrolyte solutions.
Figure 3.9 summarizes the polarization curves of Au(111) on an RDE with HM configuration measured at the rotation speed of 1200 rpm in an O$_2$-saturated electrolyte solution with various pH levels of (solid) 1.5, (dash) 6.1, (dot) 9.6, and (dash dot) 12.7 at a potential scan rate of 10 mV·s$^{-1}$.

Figure 3.9 shows that the potential for generating 0.1 mA·cm$^{-2}$ ORR current density (as indicated by the horizontal short dot line in Fig. 3.9) was positively shifted with increasing pH, which indicates a decrease in overpotential.

Adzic et al. ascribed the superior activity of Au(100) in ORR to the larger amount of OH$_{ads}$ on its surface in alkaline solutions, which may play a critical role in ORR [15]. In line with this assumption, the improved activity of Au(111) in ORR with the increase in pH may be related to the adsorbed OH$_{ads}$. However, ORR current was detected only when the potential was more negative than that when the surface oxide was fully reduced. Desilvestro et al. studied the Au(poly) surface structure in acidic and alkaline media by in-situ SERS, and the signal of AuOH at potentials more negative than that when the surface oxide was reduced was not observed [37]. Recently, Prieto et al. suggested that the different activity of Au(hkl) in ORR resulted from the different adsorption properties of HO$_2^-$ rather than OH$^-$.
However, any conclusion on the role of OH/OH$_{ads}$ in ORR on Au electrode surface is yet to be formed for lack of evidence.

Figure 3.10 shows the summary of the Tafel slopes in the low current density potential region obtained at various pH levels (from 1.5 to 12.7). With the increase in pH, the Tafel slope shifted from ca. $-130$ mV·dec$^{-1}$ to $-80$ mV·dec$^{-1}$. The slope of the Tafel plot is considered a characteristic of the rds if the elementary reactions in the sequence of elementary reactions were the rds [39]. The expected Tafel slope for rds was calculated according equation 3.10 [39]:

$$
-b = \frac{2.303v_j RT}{n_c + \beta_cn_j} \frac{RT}{F}
$$

where $-b$ is the Tafel slope, $v_j$ is the stoichiometric number of the rds, $n_c$ is the total number of electrons transferred before rds, $n_j$ is the number transferred in rds, and $\beta_c$ is the symmetry factor of rds, which is usually assumed as 0.5. For example, the elemental reaction $O_2 + e^- \rightarrow O_2^-$ is considered as the rds, $v_j$ is 1 in this reaction, $n_c$ is 0 because there is no electron transferred prior to this reaction, and $n_j$ is 1.
Therefore, \( b = \frac{2.303 v_j}{n_c + \beta n_j} \frac{RT}{F} = \frac{2.303}{0 + 0.5 \times 1} \frac{RT}{F} = 118 \text{ mV} \cdot \text{dec}^{-1} \). If \( rds \) is the adsorption of oxygen, the Tafel slope should be infinity, given that both \( n_c \) and \( n_j \) are 0. Table 3.2 lists the expected Tafel slopes for each \( rds \).

| Tafel slope for each \( rds \) in acidic and alkaline solutions [39] |
|---------------------------------|-----------------|-----------------|-----------------|
| Acidic | Tafel slope mV \( \cdot \) \( \text{dec}^{-1} \) | Alkaline | Tafel slope mV \( \cdot \) \( \text{dec}^{-1} \) |
| \( O_2 + e^- \rightarrow O_2^- \) | -118 | \( O_2 + e^- \rightarrow O_2^- \) | -118 |
| \( O_2^- + H^+ \rightarrow HO_2 \) | -59 | \( O_2^- + H_2O \rightarrow HO_2^- + OH^- \) | -59 |
| \( HO_2 + e^- \rightarrow HO^-_2 \) | -40 | \( HO_2 + e^- \rightarrow HO^-_2 \) | -40 |
| \( HO_2^- + H^+ \rightarrow H_2O \) | -30 | \( HO_2^- + H_2O \rightarrow H_2O_2^- + OH^- \) | -30 |
| \( HO^-_2 + H^+ + e^- \rightarrow H_2O + O^- \) | -24 | \( HO^-_2 \rightarrow OH^- + O \) | -30 |
| \( O^- + 2H^+ + e^- \rightarrow H_2O \) | -33 | \( O + H_2O + e^- \rightarrow OH^- + OH \) | -24 |
| | | \( OH + e^- \rightarrow OH^- \) | -17 |

The combination of data in Fig. 3.10 and Table 3.2 reveals that in acidic solutions (pH < 8), the Tafel slope was in the region between ca. −130 and −110 mV \( \cdot \) \( \text{dec}^{-1} \), and the probable \( rds \) of ORR on Au(111) was \( O_2 + e^- \rightarrow O_2^- \). At pH < 4, the Tafel slope was larger than −120 mV \( \cdot \) \( \text{dec}^{-1} \). According to equation 3.10, it may be considered that the step prior \( O_2 + e^- \rightarrow O_2^- \) without electron transfer, e.g., adsorption of oxygen, partially contributed to the \( rds \). This step could only be a part of the \( rds \) because the diffusion-limited current was not observed in the RDE measurements. At pH > 8, the Tafel slope changed to ca. −80 mV \( \cdot \) \( \text{dec}^{-1} \), \( rds \) seemed to have changed to the process \( HO_2 + e^- \rightarrow HO^-_2 \), or a mix controlled process as the \( rds \). Kim et al. studied ORR on Au(poly) in 0.1 M NaOH solution by SERS recently, and the signal of O-O stretching of \( O_2^- \) was observed at potentials where ORR occurred. The amount of \( O_2^- \) is likely to increase at more negative potentials [11]. Their results suggested that the presence of electron transfer process, i.e.,
$O_2 + e^- \rightarrow O_2^-$ cannot be rds, because if this process is rds, $O_2^-$ would be consumed as soon as it was produced, which will make it difficult to detect.

Meanwhile, the Tafel slope was considered to reflect the coverage of the intermediates of ORR [40, 41], e.g., $O_{ads}^-$, $O_2H_{ads}$, and $OH_{ads}$. The slope shifted from ca. $-120 \text{ mV} \cdot \text{dec}^{-1}$ to ca. $-60 \text{ mV} \cdot \text{dec}^{-1}$, which indicated the increase of the coverage of these species [40, 41]. Studying the adsorption of these species and the adsorption of oxygen is important for elucidating the mechanism of ORR on Au electrode surface. For this purpose, EQCM may be helpful because of its very high sensitivity to surface mass change. This study will be discussed in chapter 4.

3.4 Conclusion

In this chapter, the effect of pH on ORR was investigated by RDE with a HM configuration on Au(111) electrode surface. The results of this study showed that the overpotential in generating an identical ORR current on Au(111) electrode surface decreased with increasing pH, and the Tafel slope shifted from ca. $-130 \text{ mV} \cdot \text{dec}^{-1}$ to ca. $-80 \text{ mV} \cdot \text{dec}^{-1}$ when the electrolyte solution was changed from acidic to alkaline solution. This result indicates that the rds changed from $O_2 + e^- \rightarrow O_2^-$ to $HO_2 + e^- \rightarrow HO_2^-$. At pH < 4, the Tafel slope was larger than $-120 \text{ mV} \cdot \text{dec}^{-1}$, suggesting that the adsorption of oxygen may partially contribute to the rds. Furthermore, the direct evidence of oxygen adsorption is still weak. Therefore, studying oxygen adsorption is very important in discussing the mechanism of ORR.
3.5 References


Chapter 4

DIRECT PROOF OF POTENTIAL DEPENDENT OXYGEN ADSORPTION ON A GOLD ELECTRODE SURFACE BY ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE

4.1 Introduction

As discussed in chapter 3, the Tafel slope was larger than \(-120 \text{ mV} \cdot \text{dec}^{-1}\) when the pH of the electrolyte solutions was lower than 4, and the adsorption of oxygen may partially contribute to the \(rds\). Furthermore, the adsorption of oxygen is considered the first step of ORR [1, 2], which may be critical for the reduction. However, direct evidence of oxygen adsorption on Au electrode surface is still limited [3, 4]. Thus, the effect of anion and pH on the potential-dependent adsorption of oxygen must be understood, which is helpful in revealing the mechanism of ORR on Au surface.

EQCM is widely utilized in studying surface processes, such as metal deposition, surface oxidation, adsorption species in double layer potential region, formation of surface oxide, hydrogen adsorption, and so on because of its very high sensitivity to surface mass change [5-13]. Thus, EQCM could be useful in detecting adsorbed oxygen.

In this chapter, the effect of anion and pH on the potential-dependent adsorption of oxygen on Au surface as studied by EQCM is described. The adsorption of oxygen was observed at potentials more positive than the potential where ORR occurred. The amount of adsorbed oxygen increased as potential became more negative and reached the saturation value at all pH levels. The critical
potentials where oxygen adsorption was observed were dependent on the anions in solution.

4.2 Results and Discussions

4.2.1 In HClO₄ Solution

Figure 4.1(A) shows the potential dependencies of current density (upper panel) and frequency change (lower panel) on the Au coated 10 MHz AT-cut quartz crystal electrode in a 10 mM HClO₄ (pH 2.3) saturated with Ar (○) and O₂ (●) when the potential was positively swept from ca. +0.45 to +1.45 V, then negatively to -0.30 V, and then positively to the initial potential, i.e., +0.45 V.

In the Ar-saturated solution, the cyclic voltammogram (CV) (Fig. 4.1(A), top panel, ○) was similar to those reported previously [6]. Frequency change observed in the potential region more positive than 0 V was also similar to that reported before (Fig. 4.1(A), bottom panel, ○) [8, 14]. Briefly, when the potential was positively swept from 0 to +1.45 V, the frequency was decreased due to the adsorption of anions and the formation of surface oxide [7, 8]. When the potential was negatively swept from +1.45 to ca. +0.85 V, the frequency change was kept constant due to the inactivity of surface oxide, and when the potential was swept from +0.85 to 0 V, the frequency was increased due to the reduction of surface oxide and desorption of anions [7, 8]. However, the frequency decrease in the potential region more negative than 0 V observed in the present study was not observed in the previous studies [8, 14]. This discrepancy may be due to the lower concentration of HClO₄ in this study than that in previous studies. It is known that hydronium cation (e.g., H₃O⁺) adsorbs on a negatively charged Au electrode surface [15] and the potential of zero charge (pzc) is more positive in lower concentration solution [16]. Thus, the adsorption of H₃O⁺ might have happened in this potential region.
Fig. 4.1 (A) Potential dependencies of current density (upper panel) and frequency change (Δf, lower panel) at the Au coated 10 MHz AT-cut quartz crystal electrode in a 10 mM HClO₄ solution saturated with Ar (○) and O₂ (●) in potential region between -0.30 and +1.45 V, scan rate: 5 mV·s⁻¹. (B) Expanded presentation in potential region between +0.82 and +0.35 V displayed in Fig. 4.1(A), and the plot (■, bottom panel) is the mass change difference (ΔΔm) as a function of potential.

The CV obtained in the O₂-saturated solution (Fig. 4.1(A), top panel, ●) was similar to that observed in the Ar-saturated solution in the potential region more positive than +0.35 V as more clearly shown in expanded presentation for the potential region between +0.82 and +0.35 V in negative going scan (Fig. 4.1(B) top panel). The current due to ORR was observed at potentials more negative than +0.35 V as previously reported [4]. The frequency change (Fig. 4.1(A), bottom panel, ●) was also similar to that obtained in the Ar-saturated solution as far as potential was more positive than +0.82 V but it was smaller than that in Ar-saturated solution in the potential region more negative than +0.82 V as clearly seen in the expanded presentation shown in the lower panel of Fig. 4.1(B) in which frequency changes in
Ar- and O2-saturated solutions are presented. Based on the assumption that the adsorption of electrolyte anion and water on the electrode surface is only dependent on the electrode potential and the amounts of these adsorbed species are the same in Ar- and O2-saturated solutions. Therefore, it is reasonable to consider that the difference in the frequency change in Ar-saturated solution and that in O2-saturated solution is due to the adsorption of oxygen.

The mass change difference, $\Delta \Delta m$, between the mass change in O2-saturated solution, $\Delta m_{O_2}$, and that in Ar-saturated solution, $\Delta m_{Ar}$, as shown in equation 4.1, which should correspond to the mass of the adsorbed oxygen, was calculated from the corresponding frequency change in Ar- and O2-saturated solutions and is also shown in the bottom panel of Fig. 4.1(B) as a function of potential. This relation shows the potential dependent adsorption of oxygen.

$$\Delta \Delta m = \Delta m_{O_2} - \Delta m_{Ar}$$  \hspace{1cm} (4.1)

It is clear that the amount of adsorbed oxygen increased steeply as the potential became more negative than +0.82 V where gold oxide was partially reduced, reached ca. 20 ng·cm$^{-2}$ at ca. +0.70 V where the Au oxide was fully reduced, and remained constant as potential was scanned negatively to +0.35 V. The present result is in good agreement with that of recent study by Yagi and his colleagues on the adsorption of oxygen on a Au electrode surface in acidic media by in-situ surface enhanced IR absorption (SEIRA) spectroscopy [4], in which potential dependent adsorption of O2-species, namely O$_2$ and HO$_2$, was suggested as the O-O stretching signal was detected at potentials more negative than +1.16 V (vs. RHE) where Au oxide was absent. There are a few models were proposed for considering the adsorption of oxygen, involving Griffit, Pauling and Bridge model as summarized in
reference [2]. Based on previous studies the Pauling adsorption configuration [4, 17] was utilized for discussion here, which was considered oxygen adsorbed on the surface with an end-on configuration, although the maximum amount of adsorbed oxygen, ca. 20 ng·cm$^{-2}$, is lower than the amount expected for this configuration (ca. 70 ng·cm$^{-2}$, based on the assumption that the adsorption of oxygen was in a end-on one-by-one configuration and the amount of Au was ca. $1.3 \times 10^{15}$ atoms per cm$^2$ [18]). This is possibly due to small adsorption energy of oxygen on the Au surface and the adsorption sites need to be further considered.

### 4.2.2 Effect of Sulfate Anion

Effect of anion on the adsorption of oxygen was investigated by adding SO$_4^{2-}$ anion, which is known to adsorb on Au surface more strongly than ClO$_4^-$ anion [16, 20, 21]. Figure 4.2 (A) shows the potential dependencies of current density (upper panel) and frequency change (lower panel) on the Au coated 10 MHz AT-cut quartz crystal electrode in a 20 mM HClO$_4$ solution containing 5 mM SO$_4^{2-}$ (pH 2.1) saturated with Ar (○) and O$_2$ (●) when potential was positively swept from ca. +0.55 to +1.45 V, then negatively to -0.20 V, and then positively to the initial potential, i.e., +0.55 V.

In the Ar-saturated solution, the CV (top panel, ○) and frequency change (bottom panel, ○) in the measured potential region were similar to those observed in sulfuric acid solution [14]. Compared with the results obtained in the SO$_4^{2-}$-free HClO$_4$ solution (Fig. 4.1(A), ○), the potential for the formation of surface oxide was positively shifted by ca. 0.13 V, as SO$_4^{2-}$ anion adsorbed strongly on the Au surface [16, 20, 21].
Fig. 4.2 (A) Potential dependencies of current density (upper panel) and frequency change ($\Delta f$, lower panel) at the Au coated 10 MHz AT-cut quartz crystal electrode in a 20 mM HClO$_4$ solution containing 5 mM SO$_4^{2-}$ saturated with Ar (○) and O$_2$ (●) in potential region between -0.20 and +1.45 V, scan rate: 5 mV·s$^{-1}$. (B) Expanded presentation in potential region between +0.82 and +0.35 V displayed in Fig. 4.2(A), and the plot (■, the bottom panel) is the mass change difference ($\Delta \Delta m$) as a function of potential.

The CV obtained in the O$_2$-saturated solution (Fig. 4.2(A), top panel, ●) was similar to that observed in the Ar-saturated solution in the potential region more positive than +0.35 V as shown in expanded presentation for the potential region between +0.82 and +0.35 V in negative going scan (Fig. 4.2(B), top panel). ORR current was observed as potential became more negative than +0.35 V.

The frequency change (Fig. 4.2(A), bottom panel, ●) was similar to that obtained in the Ar-saturated solution as far as potential was more positive than +0.60 V but it was smaller than that in Ar-saturated solution in the potential region more negative than +0.60 V as clearly seen in the expanded presentation shown in the bottom panel of Fig. 4.2(B). This difference in the frequency change in Ar-saturated
and that in O$_2$-saturated solution also should be due to the adsorption of oxygen. The mass change difference, $\Delta \Delta m$, between the mass change in O$_2$-saturated solution, $\Delta m_{O_2}$, and that in Ar-saturated solution, $\Delta m_{Ar}$, is also presented in Fig. 4.2(B) bottom panel (■) as a function potential.

Although the potential for the formation of surface oxide was positively shifted due to the strongly adsorbed sulfate anion as described above, the potential for the reduction of surface oxide was identical to that in the SO$_4^{2-}$-free HClO$_4$ solution and the surface oxide was fully reduced at ca. +0.70 V. However, the adsorption of oxygen (Fig. 4.2(B) bottom panel, ■) did not take place until the potential became as negative as +0.60 V, which was 0.22 V more negative than the potential for oxygen adsorption in the SO$_4^{2-}$-free solution (i.e., +0.82 V). The amount of the adsorbed oxygen increased steeply as the potential became more negative, reached ca. 20 ng·cm$^{-2}$, which is identical to the maximum amount of the adsorbed oxygen in the SO$_4^{2-}$-free HClO$_4$ solution, at ca. +0.45 V, and remained constant as potential was scanned negatively to +0.35 V.

![Fig. 4.3](image.png) The potential dependent coverage of Au surface oxide ($\theta_{AuO}$, top panel) calculated from CVs (top panels of Fig. 4.1(A) and 4.2(A)) and the amount of the adsorbed oxygen ($\Delta \Delta m$, bottom panel) which was already shown in bottom panels of Fig. 4.1(B) and 4.2(B), as a function of potential in the potential region between +1.10 and +0.35 V in the negative going scan in the HClO$_4$ solution without (○) and with 5 mM SO$_4^{2-}$ (●).
Figure 4.3 summarizes the potential dependent coverage of Au surface oxide ($\Theta_{\text{AuO}}$, top panel) calculated from CVs shown in the top panels of Fig. 4.1(A) and 4.2 (A) and the amount of the adsorbed oxygen ($\Delta \Delta m$, bottom panel), which were already shown in bottom panels of Figs. 4.1(B) and 4.2(B), in the potential region between +1.10 and +0.35 V obtained in the solution without (○) and with 5 mM SO$_4^{2-}$ (●).

The top panel of Fig. 4.3 shows that while sulfate does not affect the reduction of Au oxide, it strongly inhibits the adsorption of oxygen as mentioned above. While the adsorption of oxygen in SO$_4^{2-}$-free solution started at +0.82 V, at which Au oxide is not fully reduced, that in the SO$_4^{2-}$-containing solution started at +0.60 V, at which Au oxide is already fully reduced. It is reported that both ClO$_4^-$ and SO$_4^{2-}$ adsorb on the Au surface as soon as the surface oxide is reduced and desorb as potential became negative [22]. But sulfate desorbs from the surface at much more negative potential (ca. +0.6 V vs. Ag/AgCl [23]) than perchlorate. Oxygen seems to adsorb on the Au surface when anion is desorbed from the surface.

4.2.3 In NaOH Solution

Figure 4.4 shows the potential dependencies of current density (top panel) and frequency change (bottom panel) at the Au-coated 10 MHz AT-cut quartz crystal electrode in a 10 mM NaOH (pH 12.2) solution saturated with Ar (○) and O$_2$ (●). The potential was positively swept from ca. +0.10 V to +0.70 V, then negatively swept to −0.68 V, and then positively swept to the initial potential, i.e., +0.10 V, at a scan rate of 5 mV·s$^{-1}$.

In the Ar-saturated solution, CV [Fig. 4.4(A), top panel, (○)] was similar to that observed for the Au electrode in NaOH solution reported previously [24–26], which is also similar to the CV of Au(111) in the alkaline solution observed in chapter 3.
Fig. 4.4 (A) Potential dependencies of current density (upper panel) and frequency change ($\Delta f$, lower panel) at the Au coated 10 MHz AT-cut quartz crystal electrode in a 10 mM NaOH solution saturated with Ar (○) and O₂ (●) in potential region between -0.68 and +0.70 V, scan rate: 5 mV·s⁻¹. (B) Expanded presentation in the potential region between +0.30 and 0 V displayed in Fig. 4.4(A), and the plot (×, bottom panel) is the mass change difference ($\Delta\Delta m$) as a function of potential

The shape of frequency change in the measured potential region was similar to that reported recently [27], which was completely different from the results obtained in acidic solutions [bottom panel of Fig. 4.1(A) and 4.2(A)]. Frequency change was kept almost constant when the potential was positively swept from +0.10 V to +0.15 V. A decrease in frequency change occurred when the potential was scanned from +0.15 V to +0.70 V owing to the adsorption of OH and the formation of surface oxide [27]. No obvious frequency change was observed when the potential was negatively scanned from +0.70 V to +0.25 V due to the stable surface oxide, similar to the case of acidic solutions. A steep increase was found when the potential was scanned from +0.25 V to ca. 0 V because of the reduction of surface oxide [27].
Frequency change was kept almost constant when potential was scanned from 0 V to 
−0.15 V and decreased significantly when potential was negatively scanned from 
−0.15 V to −0.68 V. Frequency change increased to its original value when the 
potential was stopped at the initial potential, i.e., +0.10 V.

Similar to the results reported previously [27–30], frequency change 
monotonically decreased in the potential region between −0.15 and −0.68 V when 
the potential became negative. This finding was not observed in acidic solutions. 
One possible reason that caused this decrease in frequency change could be the 
adsorption of H₂O. However, mass was increased by ca. 420 ng·cm⁻², corresponding 
to the frequency change when the potential was swept from −0.15 V to −0.68 V, 
which was much larger than the expected amount of monolayer adsorption of H₃O⁺, 
i.e., 42 ng·cm⁻², based on the assumption that the adsorption of H₃O⁺ was in a 
one-by-one configuration and that the amount of Au was ca. 1.3×10¹⁵ atoms per cm² 
[18]. Several other parameters must have affected the frequency change. Tsionsky et 
al. suggested that EQCM response could be influenced by the local electrolyte 
viscosity adjacent to the resonator electrode due to the changes of the surface excess 
concentration of the non-specifically adsorbed ions in the diffuse electric double 
layer by the effect of potential [28, 29]. The local concentrations of cations and 
anions increase when the electrode is positively or negatively charged, and the 
density-viscosity increases, which may cause a change in frequency [27]. The 
frequency change caused by viscosity could be expressed by the Kanazawa-Gordon 
equation (4.2) [31]:

\[
\Delta f_v = -f_0^{3/2} \left( \frac{\rho \eta}{\pi \rho_q \mu_q} \right)^{1/2} 
\]

(4.2)

where \( \Delta f_v \) is the frequency change caused by the change of viscosity of the 
electrolyte, \( f_0 \) is the fundamental resonating frequency of the quartz, \( \rho \) is the density
of the electrolyte solution layer adjacent to the resonator electrode while $\rho_q$ is the density of quartz, $\eta_i$ is the viscosity of the solution layer adjacent to the resonator electrode, and $\mu_q$ is the quartz shear modulus. Based on equation 4.2, frequency change will be significantly influenced by the term $\rho_i\eta_i$.

Surface oxide was formed when the potential was scanned from +0.15 V to +0.70 V, as seen from CV in the top panel of Fig. 4.4(A). The corresponding mass increased by ca. 380 ng·cm$^{-2}$, which was almost nine times larger than expected in the formation of monolayer Au surface oxide (ca. 35 ng·cm$^{-2}$). This result may be also due to the effect of local viscosity of the electrolyte, as observed in the negative potential region (i.e., between −0.1 and −0.68 V).

In the O$_2$-saturated solution, CV [Fig. 4.4(A), top panel, ●] was similar to that observed in the Ar-saturated solution in the potential region higher than +0.10 V, as clearly shown in the expanded presentation of the potential region between +0.30 V and 0 V in the negative going scan [Fig. 4.4(B), top panel]. ORR current was observed at potentials more negative than 0 V, as previously reported [32, 33]. A small anodic peak was observed in the potential region between 0 and +0.1 V in the positive going scan, which was caused by the oxidation of H$_2$O$_2$ produced in ORR, as discussed in chapter 3.

Frequency change [Fig. 4.4(A), bottom panel, ●] was smaller when the potential was swept from +0.10 V to +0.60 V compared with that obtained in the Ar-saturated solution. The result became identical to that observed in the Ar-saturated solution when the potential was more positive than +0.60 V because the Au surface was fully covered by Au oxide, and it was expected to be identical in both solutions saturated with Ar and O$_2$. In the negative potential scanning, not much difference in frequency change was observed as far as the potential was more positive than +0.22 V but it was smaller than that in the Ar-saturated solution in the
potential region more negative than +0.22 V as more. This is clearly shown in the expanded presentation of the potential region between +0.30 and 0 V in the negative going scan [Fig. 4.4(B), bottom panel]. The difference in frequency change between the Ar-saturated solution and the O₂-saturated solution was due to the adsorption of oxygen. This finding is based on the assumption that the adsorption of electrolyte anion and water on the electrode surface is only dependent on the electrode potential and the amounts of these adsorbed species are the same in Ar- and O₂-saturated solutions. Another assumption is that the presence of oxygen in the solution does not affect the local viscosity on the electrode surface.

The mass change difference, \( \Delta \Delta m \), between the mass change obtained in O₂-saturated solution, \( \Delta m_{O_2} \), and that in Ar-saturated solution, \( \Delta m_{Ar} \), was calculated according to equation 4.1. The corresponding mass of the adsorbed oxygen [Fig. 4.4(B), bottom panel, \( \times \)] was calculated from the corresponding frequency change in the Ar- and O₂-saturated solutions. This relation shows the potential-dependent adsorption of oxygen, as discussed in Figs. 4.1 and 4.2.

The mass change difference on Au surface increased gradually as the potential became more negative than +0.22 V where Au oxide was partially reduced, and reached the maximum (ca.110 ng·cm⁻²) at ca. 0 V, where Au oxide was fully reduced prior to ORR. This value is much larger than that observed in acidic solution (ca. 20 ng·cm⁻²).

4.2.4  pH Effect Summary

Figure 4.5 summarizes the potential-dependent coverage of Au surface oxide (\( \theta_{AuO} \), top panel) calculated from CVs in various pH solutions and the amount of adsorbed oxygen (\( \Delta \Delta m \), bottom panel) in the potential region between +1.4 and +0.6 V obtained in solutions with pH 2.3 (○, 10 mM HClO₄), 5.9 (▲, 10 mM
NaClO₄), 11.4 (□, 5 mM NaOH + 5 mM NaClO₄), and 12.2 (●, 10 mM NaOH). The potential was converted to RHE scale to avoid the pH effect on potential shift.

The adsorption of oxygen was first observed at potentials where the surface oxide was partially reduced in all solutions with various pH levels. The amount of adsorbed oxygen increased as potential became negative and reached the saturation value at the potential where the surface oxide was almost fully reduced at all the pH levels in the absence of strongly adsorbed anions (i.e., SO₄²⁻-free). However, the potentials at which the adsorption of oxygen was first observed were dependent on the pH value. Figure 4.5 shows that the potential where the adsorption of oxygen was first observed was at ca. +1.15 V in the pH 2.3 and 12.2 solutions and at ca. +1.10 V in the pH 5.9 and 11.4 solutions. As discussed in chapter 3, the potentials of the formation and reduction of surface oxide is affected by local pH. The reduction peak potential of the surface oxide in the solutions with medium pH values (e.g., 5 < pH < 10 studied in chapter 3) shifted to more negative potentials compared with that of stronger acidic or alkaline solutions. Here, the adsorption of oxygen is
ascribed to the potential dependence of the effect of local pH, as oxygen seems to adsorb on bare Au surface.

![Graph](image)

**Fig. 4.6** The maximum amount of adsorbed oxygen on Au electrode surface as a function of pH. The amount of adsorbed oxygen was obtained from Fig. 4.5.

**Figure 4.6** shows the maximum mass change between the results obtained in Ar- and O₂-saturated solutions on Au electrode surface as a function of pH. In this study, the maximum mass change difference increased with increasing pH, and the saturation value was reached when pH was higher than 11.4. However, the saturation value of the mass change difference when pH > 11.4, i.e., ca. 110 ng cm⁻², was larger than that expected for a full coverage of oxygen on Au electrode surface with a Pauling adsorption configuration (ca. 70 ng cm⁻² as mentioned earlier). If the adsorbed species on the Au electrode surface had a one-by-one configuration, the apparent molar mass of the adsorbed species on each Au atom would be ca. 50 g mol⁻¹. One possibility is the co-adsorption of H₂O with O₂ on the electrode surface. The other possibility is the presence of oxygen may affect the local electrolyte viscosity adjacent to the resonator electrode, which will result in a larger frequency change. Further studies are needed to fully understand what causes the
larger frequency change difference between the results obtained in Ar- and O₂-saturated solutions.

4.3 Conclusion

This chapter discussed the effect of sulfate anion (SO₄²⁻) and pH on the adsorption of oxygen on Au electrode surface using EQCM. The adsorption of oxygen was first observed at potential more positive than the potential at which ORR initially occurred. The amount of adsorbed oxygen increased and reached the saturation value as the potential became more negative in all the solutions used in this study. The adsorption of oxygen on Au electrode surface started at ca. +0.82 V in perchlorate solution (SO₄²⁻-free) and at ca. +0.60 V in sulfate solution, showing the inhibition of the adsorption of oxygen by the strongly adsorbed sulfate anion, as shown in the model below.

In all SO₄²⁻-free solutions at various pH used in this study, the adsorption of oxygen started at potential where the surface oxide was partially reduced. The mass change difference between the results obtained in Ar- and O₂-saturated solution increased as the potential became more negative, and the saturation value was reached at each pH when the surface oxide was fully reduced. The maximum mass change difference increased with increasing pH and almost reached a constant level at pH > 11.4. This result may be due to the increased co-adsorption of H₂O with oxygen at higher pH or the effect of oxygen on the viscosity of the electrolyte.

This study demonstrated that the adsorption of oxygen started at potentials more positive than the potential where ORR initially occurred in all the solutions
used. The critical potentials at which oxygen adsorption were first observed were dependent on the anions in solution. Thus, oxygen adsorbed on the Au surface as sulfate anion was desorbed from the surface.
4.4 References

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Chapter 5

EFFECT OF SULFATE ANION ON THE ADSORPTION OF OXYGEN ON A PLATINUM SURFACE IN ACIDIC SOLUTION STUDIED BY ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE

5.1 Introduction

In chapter 4, the adsorption of oxygen on Au electrode surface was confirmed by EQCM. Oxygen adsorption on the Au electrode surface started at potentials more positive than that at which ORR occurs. The potential where oxygen starts to adsorb on Au electrode surface is dependent on the anion species in the solution. ORR is known to be sensitive to the type of electrode materials. Therefore, comparing the adsorption of oxygen on the Au electrode surface with that on other electrode materials is important because the result may provide necessary information to elucidate the mechanism of ORR.

Platinum has been widely used as electrode for studying ORR because of its high activity [1–3]. Recently, Omura et al. studied ORR on a Pt electrode surface in 7 mM HClO$_4$ and 7 mM HF solutions by EQCM [4]. The adsorption of oxygen species was discussed with respect to the frequency change when the solution was changed from He-saturated to O$_2$-saturated. However, the effect of sulfate anion on the adsorption of oxygen species is unclear because the adsorption of F$^-$ anion is insignificant and that of ClO$_4^-$ anion is considered to be weak at low concentration [4]. Further study on the effect of anion on the adsorption of oxygen is necessary to clarify the effect of anion on ORR.
In this chapter, the effect of sulfate anion on the adsorption of oxygen on Pt surface was studied by EQCM. The adsorption of oxygen was first observed at ca. +0.60 V when the potential was negatively scanned, at which the surface oxide was partially reduced, and the ORR current was flowed both in perchlorate and sulfate solutions. In this study, the inhibition of sulfate anion on the adsorption of oxygen was not significantly observed on the Pt surface. However, the adsorption of oxygen on Pt surface caused the increase in mass in the perchlorate solution as well as the decrease in mass in the sulfate solution. In contrast to the effect of sulfate anion on the adsorption of oxygen on Au surface in chapter 4, the adsorbed sulfate was replaced by oxygen on Pt surface.

5.2 Results

5.2.1 In HClO₄ Solution

Figure 5.1 shows the potential dependencies of current density (top panel) and frequency change (bottom panel) on a Pt-coated 10 MHz AT-cut quartz crystal electrode surface in 0.1 M HClO₄ solution saturated with Ar (○) and O₂ (●). The potential was scanned from +0.15 V to +1.10 V, then negatively to −0.22 V, then positively swept, and finally terminated at the initial potential, i.e., +0.15 V, at a potential scan rate of 20 mV s⁻¹.
In the Ar-saturated 0.1-M HClO₄ solution, the CV (top panel, ○) was similar to that reported previously [5–7]. Briefly, the hydrogen adsorption and desorption peaks were observed in the potential region between −0.22 and +0.15 V. The current caused by the formation of surface oxide was observed when the potential was positively swept from +0.50 to +1.10 V and that due to the reduction of surface oxide was obtained when the potential was negatively swept from +1.10 V to +0.25 V, respectively.

Frequency change (bottom panel, ○) was also similar to the results of previous studies [4–7]. When potential was positively swept from +0.15 V to +0.50 V, frequency change decreased due to the adsorption of ClO₄⁻ and some co-adsorption of H₂O [4, 8, 9]. When potential was scanned from +0.50 V to +1.10 V, frequency change decreased further due to the formation of surface oxide. When potential was negatively swept from +1.10 V to +0.70 V, frequency change was kept almost at a constant level, and when the potential was swept from +0.70 V to +0.10 V, frequency change increased due to the reduction of surface oxide and the desorption.
of ClO$_4^-$ and/or H$_2$O from the surface [10, 11]. When the potential was swept from +0.15 V to −0.22 V, frequency change monotonically increased with the appearance of hydrogen adsorption. When the potential was reversed by −0.22 V and positively swept back to its initial potential, i.e., +0.15 V, the frequency returned to its initial value.

The CV obtained in the O$_2$-saturated solution (Fig. 5.1, top panel, ●) was similar to that in the Ar-saturated solution when the potential was more positive than +0.70 V. The result conforms to the result of a previous study where the presence of O$_2$ did not affect the formation of Pt oxide on smooth polycrystalline Pt surface [12]. As previously reported, ORR current observed at potentials more negative than +0.70 V overlapped the potential region for the reduction of Pt surface oxide [13].

Frequency change obtained in the O$_2$-saturated solution is shown in the bottom panel of Fig. 5.1 (●), which was lower than the result obtained in the Ar-saturated solution (○) when the potential was positively swept from +0.15 V and became identical at +1.10 V. Frequency change obtained in the O$_2$-saturated solution was identical to that observed in the Ar-saturated solution when the potential was negatively swept from +1.10 V to +0.60 V due to the formation of Pt surface oxide, as mentioned earlier. Frequency change decreased at potentials more negative than +0.60 V compared with that obtained in the Ar-saturated solution.

Frequency change decreased in the O$_2$-saturated solution, indicating an increase in mass on the electrode surface, analogous to the result on the Au electrode surface described in chapter 4. In line with the assumption mentioned in Chapter 4 that the adsorption of anion and H$_2$O on the electrode surface is only dependent on the electrode potential, the frequency change difference obtained between the frequency change obtained in the O$_2$- and Ar- saturated solutions, can be ascribed to the adsorption of oxygen.
An additional experiment was carried out to confirm the difference in frequency change obtained between the O₂- and Ar-saturated solutions (lower panel of Fig. 5.1) caused by oxygen adsorption. Briefly, O₂ was introduced in the Ar-saturated solution while the electrode was held at a constant potential rather than scanning the potential, as shown in Fig. 5.1. The potential where ORR occurred, +0.15 V, was chosen for this experiment.

**Figure 5.2** shows the current density and frequency change on a Pt coated 10 MHz AT-cut quartz crystal electrode as a function of time when the gas passing through the solution was changed from Ar to O₂, which was continuously flowed until diffusion-limited current was observed. The gas was then reverted to Ar when the ORR current decayed. The electrode potential was held at +0.15 V.

When O₂ was introduced into the electrolyte solution, frequency change decreased with the occurrence of ORR current and almost reached a constant level when diffusion-limited current was observed. When the gas was reverted to Ar, frequency increased steeply and returned to its original value when the ORR current
decayed. The decrease in frequency change upon the introduction of O₂ into the solution was in good agreement with the observed results shown in the bottom panel of Fig. 5.1, i.e., the frequency change obtained in the O₂-saturated solution was smaller than that obtained in the Ar-saturated solution. This result further confirmed that oxygen was indeed adsorbed on the electrode surface.

After O₂ was introduced into the solution, frequency change decreased to ca. 30 Hz when diffusion-limited current was observed (Fig. 5.2). The frequency change was much larger than that obtained in the O₂- and Ar-saturated solutions shown in Fig. 5.1 at +0.15 V (almost 0 Hz). The current density observed in Fig. 5.2 (i.e., −0.5 mA cm⁻²) was also much larger than that shown in Fig. 5.1 at +0.15 V (i.e., −0.2 mA cm⁻²). The larger current density observed in Fig. 5.2 may be due to gas bubbling, which is similar to the case involving RDE measurements, i.e., the current increased with increasing rotation speed. In RDE measurements, current is affected by rotation speed because the thickness of the diffusion layer (δ₅) is dependent on rotation speed, as shown in equation 5.1 [14]:

\[
\delta_d = 1.61D^{1/3}ν^{1/6}ω^{-1/2} \quad \text{(5.1a)}
\]

\[
i = 0.62nFD^{2/3}ν^{1/6}Cω^{1/2} \quad \text{(5.1b)}
\]

where \(D\) is the diffusion coefficient (cm⁻²·s⁻¹), \(ν\) is kinematic viscosity (cm⁻¹·s⁻¹), \(ω\) is the rotation speed (rad·s⁻¹), \(F\) is Faraday constant, and \(C\) is the bulk concentration of reactant.

### 5.2.2 In H₂SO₄ Solution

Sulfate is known as a specific adsorption species on metal electrode surfaces, which is experimentally and theoretically studied [15–22]. Sulfate is also considered
to inhibit oxygen adsorption on Pt surface, resulting in a surface structure sensitive to ORR [1]. In this study, the effect of sulfate on the adsorption of oxygen on Pt surface was studied in a 0.05-M H₂SO₄ solution.

Figure 5.3 shows the potential dependencies of current density (top panel) and frequency change (bottom panel) on a Pt coated 10 MHz AT-cut quartz crystal electrode surface in a 0.05-M H₂SO₄ solution saturated with Ar (○) and O₂ (●), respectively. The potential was positively swept from +0.15 V to +1.10 V, then negatively swept to −0.22 V, then positively swept, and then reverted to its initial potential, i.e., +0.15 V, at a potential scan rate of 20 mV s⁻¹.

![Figure 5.3](image)

In the Ar-saturated solution (top panel, ○), the current due to hydrogen adsorption was observed at potential values more negative than +0.1 V, which was negatively shifted by ca. 50 mV compared with that obtained in 0.1 M HClO₄ solution (top panel of Fig. 5.1, ○), in conformity with previous studies on Pt surface [23, 24]. The current due to the formation of surface oxide was first observed at ca. +0.55 V, which was ca. 50 mV positively shifted compared with the situation in
HClO$_4$ solution, also in conformity with a previous study on Pt surface [24]. The suppression of the formation of surface oxide by sulfate was also observed on the Au surface as discussed in chapter 4, but the positive potential shift was larger on the Au surface (ca. 0.13 V) than on the Pt surface (ca. 0.05 V). This shift suggested that the sulfate on the Pt surface was easier to be replaced by OH to form the surface oxide compared with that on Au surface. Although the formation of Pt surface oxide was suppressed by sulfate, the reduction of the surface oxide was not significantly affected by sulfate; this result was similar to that in a previous study [24]. The same phenomenon was observed on Au surface, as described in chapter 4.

Frequency change (bottom panel, ○) obtained in the Ar-saturated 0.05 M H$_2$SO$_4$ solution was analogous to the result shown in Fig. 5.1. Briefly, when the potential was positively swept from +0.15 V to +1.10 V, frequency decreased due to the specific adsorption of (bi)sulfate and the formation of surface oxide. When the potential was swept from +0.55 V to +1.10 V, frequency change decreased due to the formation of the surface oxide; the value was identical to that observed in the HClO$_4$ solution. When potential was negatively swept from +1.10 V to +0.15 V, frequency started to increase at ca. +0.60 V due to the reduction of surface oxide and the desorption of anion, which was re-adsorbed on the surface when the surface oxide was reduced [6, 10]. In the potential region between −0.22 and +0.15 V, frequency monotonically decreased as the potential became more positive due to the adsorption of H$_2$O simultaneous with the desorption of hydrogen [4, 6, 25], which was identical to the finding observed in HClO$_4$ solution.

In the O$_2$-saturated solution, CV (top panel, ●) was identical to that in the Ar-saturated solution at potentials more positive than +0.70 V, and ORR current was observed at the potentials more negative than +0.70 V, analogous to the results in the HClO$_4$ solution (top panel of Fig. 5.1).
The frequency change curve observed in the O₂-saturated solution (bottom panel, ●) was higher than the result obtained in the Ar-saturated solution (bottom panel, ○) when the potential was swept from +0.15 V to +0.90 V. The curves became identical at potentials more positive than +0.90 V due to the formation of the surface oxide. The frequency change obtained in the O₂-saturated solution was identical to that in the Ar-saturated solution when the potential was swept from +1.10 V to +0.60 V and became larger at potentials more negative than +0.60 V. The frequency change difference between the O₂- and Ar-saturated solution could be related to the adsorption of oxygen in contrast to that shown in Fig. 5.1.

To confirm the data obtained in Fig. 5.4, the same experiment described in Fig. 5.2 was conducted in 0.05 M H₂SO₄ solution. Figure 5.4 shows the frequency change and current density on a Pt coated 10 MHz AT-cut quartz crystal electrode as a function of time when the gas used was reverted from Ar to O₂, which was continuously flowed until diffusion-limited ORR current was observed and then reverted to Ar until ORR current decayed. The potential was held at +0.15 V.

**Fig. 5.4** Current density and frequency change on a Pt coated 10MHz AT-cut quartz crystal electrode as a function of time when the gas passed through the solution was changed from Ar to O₂, and kept on flowing until diffusion limited ORR current was observed, then changed back to Ar until ORR current disappeared. The potential was hold at +0.15 V.
Figure 5.4 shows that when O₂ was introduced into the electrolyte solution, frequency increased with the appearance of ORR current. Frequency change decreased after Ar was introduced into the solution and reverted to the initial value when ORR current decayed. The phenomenon observed in Fig. 5.4, i.e., the increase in frequency change when O₂ was introduced into the solution, was in good agreement with the results shown in the bottom panel of Fig. 5.3. In other words, the frequency change obtained in the O₂-saturated solution was larger than that obtained in the Ar-saturated solution. Again, the frequency change difference observed here was larger than that in Fig. 5.3 at the same potential, i.e., +0.15 V. Briefly, the maximum frequency change increased by ca. 15 Hz in Fig. 5.4, whereas it increased by ca. 2 Hz in Fig. 5.3 at +0.15 V. This difference may also be due to the effect of gas bubbling during the experiments in Fig. 5.4, same as shown in Fig. 5.2.

A comparison of the results in Fig. 5.4 with Fig. 5.2 reveals that both solutions show equal ORR current density. However, frequency change decreased in the 0.1-M HClO₄ solution (Fig. 5.2) and increased in the 0.05-M H₂SO₄ solution (Fig. 5.4) when O₂ was introduced into the solutions. This discrepancy may be a result of the effect of sulfate anion in the solution.

5.3 Discussions

Considering that the frequency change difference between the results obtained in the solution saturated with O₂ and Ar is a result of the adsorption of oxygen in both the HClO₄ and H₂SO₄ solutions, the mass change difference (ΔΔm) can reflect the amount of adsorbed oxygen based on the assumption presented in chapter 4. The adsorption of electrolyte anion and/or H₂O is dependent only on the electrode potential, and the amount of adsorbed species is the same with and without oxygen. As discussed in chapter 4, the ΔΔm can be calculated as
\[ \Delta \Delta m = \Delta m_{O_2} - \Delta m_{Ar} \]  \hspace{1cm} (5.2)

where \( \Delta m_{O_2} \) and \( \Delta m_{Ar} \) are the mass change values observed in the solution saturated with O_2 and Ar, respectively.

Figure 5.5 shows the potential-dependent current density obtained in the solution saturated with Ar (dash) and O_2 (solid) and the mass change difference (\( \Delta \Delta m, ■ \)) between the mass change values obtained between the O_2- (\( \Delta m_{O2} \)) and Ar-saturated solutions (\( \Delta m_{Ar} \)), which were calculated from the corresponding frequency change when the potential was negatively swept from +1.10 V to 0 V.

![Graph showing current density and mass change difference](image)

**Fig.5.5** Potential dependent current density in Ar (dash) and O_2 (solid) saturated solutions and mass change difference (■, \( \Delta \Delta m \)) between the mass change in O_2-saturated solution, \( \Delta m_{O2} \), and that in Ar-saturated solution, \( \Delta m_{Ar} \), obtained from the corresponding frequency change observed in O_2 and Ar saturated solutions when the potential was negatively swept from +1.10 to 0 V.

Figure 5.5 show that \( \Delta \Delta m \) started to increase at ca. +0.60 V where the Pt surface oxide was partially reduced (dash line), indicating that the adsorption of oxygen occurs on the bare Pt surface, as in the case on the Au surface in chapter 4. \( \Delta \Delta m \) increased when the potential was negatively swept, and the maximum (ca. 10 ng cm\(^{-2}\)) was reached at ca. +0.50 V where the surface oxide reduction current
reached a maximum. More bare Pt sites were exposed with the reduction of Pt oxide when the potential was swept from +0.60 V to +0.50 V, and more sites became available for oxygen adsorption. This occurrence was similar to that observed on Au electrode surface in chapter 4. However, the maximum amount of adsorbed oxygen observed on Pt surface (ca. 10 ng cm$^{-2}$) was half of that observed on the Au electrode (ca. 20 ng cm$^{-2}$) in acidic solution (chapter 4) because ORR occurred on the Pt surface as soon as oxygen was adsorbed on the surface, as shown in Fig. 5.5 (solid line). The figure shows that ORR current flowed at ca. +0.60 V, equal to the potential where the adsorption of oxygen started to be observed. In contrast to what was observed in chapter 4 regarding the Au surface in HClO$_4$ solution, the adsorption of oxygen was first observed at ca. +0.82 V where the Au surface oxide was partially reduced, but the ORR current was not observed until the potential became more negative than +0.35 V. This discrepancy can be due to the different mechanism of ORR on Pt and Au surface. Figure 5.5 also shows that when the potential became more negative than +0.50 V, $\Delta m$ started to decrease, and a value of almost 0 ng cm$^{-2}$ was reached at 0 V. The decreased amount of adsorbed oxygen was due to the fast consumption of oxygen during the ORR in this potential region as the diffusion-limited current was observed.

Figure 5.6 shows the current density obtained in the 0.05 M H$_2$SO$_4$ solution saturated with Ar (dash) and O$_2$ (solid), respectively, and the mass change difference ($\Delta m$, ■) between the mass change values obtained in the O$_2$- ($\Delta m_{O_2}$) and Ar-saturated solutions ($\Delta m_{Ar}$), calculated from the corresponding frequency change when the potential was negatively swept from +1.10 V to 0 V.
Figure 5.6 shows that the ORR current (solid line) started to flow at ca. +0.60 V, which matches that observed in the HClO₄ solution shown in Fig. 5.5, indicating that the ORR on the Pt surface was not significantly affected by sulfate.

However, the potential-dependent $\Delta m$ observed in the H₂SO₄ (Fig. 5.6, ■) solution was completely different from that observed in the HClO₄ solution (Fig. 5.5, ■) because of the effect of SO₄$^{2−}$. $\Delta m$ in Fig. 5.6 started to decrease at ca. +0.60 V where the ORR current started to flow and decreased further when the potential became more negative, reaching the minimum (ca. −10 ng cm$^{-2}$) at ca. +0.3 V. Then, $\Delta m$ increased when the potential became more negative than +0.3 V and reached ca. −5 ng cm$^{-2}$ at +0 V.

Sulfate is known to be re-adsorbed on the surface as the surface oxide is reduced in the solution without oxygen and gradually desorbed from the surface when the potential becomes negative [10, 18, 22, 26, 27]. Therefore, in the O₂-saturated H₂SO₄ solution, both oxygen and SO₄$^{2−}$ can possibly adsorb on the electrode surface at potentials more negative than +0.60 V with the constant
coverage of sulfate on the Pt surface in the double-layer potential region in the solution containing no oxygen [9, 28].

As discussed in chapter 4, the adsorption of oxygen on Au surface was inhibited by sulfate and occurred with its desorption from the surface, as shown in Fig. 5.7.

![Fig. 5.7 Scheme of the inhibition of sulfate for the adsorption of oxygen on Au electrode surface.](image)

Similar to the Pt electrode surface, if the adsorption of oxygen also occurred with the desorption of \(\text{SO}_4^{2-}\), the mass change difference was expected to increase. This condition is similar to the case of the HClO₄ solution, where mass change started to increase at a relatively negative potential region in the double layer.

As mentioned earlier, the positive shift in potential for the formation of surface oxide with the \(\text{SO}_4^{2-}\) on the Au surface was ca. 130 mV, whereas the value was ca. 50 mV on the Pt surface. This result suggested that the \(\text{SO}_4^{2-}\) on Pt surface may be easier displaced by OH compared with that on Au surface. Conversely, \(\text{O}_2\) adsorbs on free Au with a binding energy of 0.49 eV [29], whereas that on Pt is ca. 0.7 eV [30]. These values indicate a stronger interaction between oxygen and Pt than that between oxygen and Au. The adsorbed CO on Pt surface inhibited the adsorption of \(\text{SO}_4^{2-}\) in the double-layer potential region [31, 32]. Here, adsorbed \(\text{SO}_4^{2-}\) was replaced by oxygen as discussed previously [33]. This process is illustrated in Fig. 5.8. The effect of \(\text{SO}_4^{2-}\) on the adsorption of oxygen on the Pt surface was different from that on the Au electrode surface (Fig. 5.7) shown earlier.
Considering that $\Delta \Delta m$ was minimum at +0.30 V from the results obtained using the 0.05 M H$_2$SO$_4$ solution shown in Fig. 5.6 and the diffusion-limited current almost reached the potential, all adsorbed SO$_4^{2-}$ and H$_2$O can be replaced by oxygen at this potential. The amount of adsorbed SO$_4^{2-}$ and H$_2$O at +0.30 V without the effect of oxygen can be estimated from the frequency change in the Ar-saturated solution in Fig. 5.4 (bottom panel, ○). Based on the assumption that the frequency decrease observed when the potential was scanned from +0.1 V to +0.3 V was completely due to the adsorption of SO$_4^{2-}$ and H$_2$O, the mass with the adsorbed species was ca. 16 ng cm$^{-2}$ at +0.30 V. Therefore, the amount of oxygen, $\Delta m_{O_2}$, can be estimated by equation 5.2, where $\Delta \Delta m$ is the mass change difference observed from Fig. 5.5 (ca. −10 ng cm$^{-2}$ at +0.3 V), $-\Delta m_{ar}$ is the mass change with the desorption of SO$_4^{2-}$ and H$_2$O in the Ar-saturated solution (i.e., −16 ng cm$^{-2}$). In line with that equation 5.2, the amount of oxygen on the surface at +0.30 V was ca. 6 ng cm$^{-2}$, which was equal to 4 ng cm$^{-2}$ observed from Fig. 5.5 at +0.30 V (in the HClO$_4$ solution). The difference of 2 ng cm$^{-2}$ may be due to the experimental error considering that this amount of difference in mass equals the frequency change by ca. 0.4 Hz based on the sensitivity of this system, i.e., 5.4 ng Hz$^{-1}$ cm$^{-2}$.

As mentioned earlier, adsorbed SO$_4^{2-}$ would desorb from the surface when the potential became negative (e.g., +0.10 V, where the amount of adsorbed sulfate was very small [28]), the effect of SO$_4^{2-}$ on oxygen adsorption would become weaker.
Therefore, $\Delta m$ that resulted from the adsorption of oxygen was expected to be zero similar to the observation in the HClO$_4$ solution because the diffusion-limited current flowed at potentials more negative than +0.3 V. Figure 5.6 shows that $\Delta m$ increased but did not reach zero. The reason is not clear and needs further study.

**Figure 5.9** summarized the potential dependencies of ORR current density and mass change difference ($\Delta m$) obtained on a Pt coated 10 MHz AT-cut quartz crystal electrode surface in 0.1 M HClO$_4$ (○) and 0.05 M H$_2$SO$_4$ (●) solutions, respectively.

![Graph](image)

**Fig.5.9** Potential dependencies of ORR current and mass change difference ($\Delta m$) obtained on a Pt coated 10 MHz AT-cut quartz crystal electrode in 0.1 M HClO$_4$ (○) and 0.05 M H$_2$SO$_4$ (●) solutions, respectively, when the potential was negatively swept from +1.0 to +0.1 V.

Figure 5.9 shows that the potentials where the ORR current started to flow on the Pt surface in HClO$_4$ (○) and H$_2$SO$_4$ (●) solutions were almost the same. This result indicates that the adsorption of oxygen on the Pt surface was not significantly inhibited by sulfate at the Pt surface.

In the HClO$_4$ solution (○), $\Delta m$ started to increase at ca. +0.60 V where the Pt surface oxide was partially reduced. $\Delta m$ increased as the potential became more
negative and reached its maximum at ca. +0.5 V. \( \Delta \Delta m \) started to decrease when the potential became more negative and reached almost 0 at ca. +0.1 V where the diffusion-limited current was observed. This result suggested that the adsorption of oxygen on the Pt surface occurred with the desorption of \( \text{ClO}_4^- \), which was considered weakly adsorbed on the metal electrode surface, similar to the adsorption of oxygen on Au surface. In contrast to the \( \text{H}_2\text{SO}_4 \) (●) solution, \( \Delta \Delta m \) decreased when the adsorption of oxygen occurred at ca. +0.60 V where the coverage of sulfate was kept at a maximum (constant) in the solution without oxygen [9, 28] and slightly increased at potentials more negative than +0.2 V where the diffusion-limited ORR current was observed. The adsorbed \( \text{SO}_4^{2-} \) on the Pt surface appeared to be replaced by oxygen as mentioned previously [33], which was not observed on the Au surface, i.e., the adsorption of oxygen on the Au surface was strongly inhibited by \( \text{SO}_4^{2-} \) and occurred with the desorption of \( \text{SO}_4^{2-} \).

### 5.4 Conclusion

The effect of sulfate anion on the potential-dependent adsorption of oxygen on the Pt electrode surface was studied by EQCM. The present study showed that the adsorption of oxygen was first observed at identical potentials (i.e., ca. +0.60 V) in solutions with and without sulfate. The inhibition of the sulfate anion on the adsorption of oxygen was not significantly observed on the Pt electrode surface. In the \( \text{HClO}_4 \) solution, the adsorption of oxygen on the Pt surface was analogous to that observed on the Au surface, i.e., oxygen was apparently adsorbed on the surface with the desorption of anion. The adsorbed \( \text{SO}_4^{2-} \) appeared to be replaced by oxygen on the Pt surface in \( \text{H}_2\text{SO}_4 \) solution, which was different from that observed for the Au surface in chapter 4. This discrepancy can be attributed to the stronger interaction between oxygen and Pt compared with that between oxygen and Au.
5.5 References

Chapter 6

GENERAL CONCLUSION AND FUTURE PROSPECTS

1. General Conclusion

The effects of pH, anion, and electrode materials on the adsorption and reduction of oxygen in aqueous solutions were studied in this thesis.

In chapter 3, the effect of pH on the ORR was investigated using RDE on Au(111) surface with an HM configuration. The overpotential for a given ORR current decreased with increasing pH. The Tafel slope observed in this study shifted from ca. −130 mV dec$^{-1}$ to ca. −80 mV dec$^{-1}$ when the electrolyte solution was changed from acidic to alkaline solution, indicating that the rds was changed from $O_2 + e^- \rightarrow O_2^-$ to $HO_2 + e^- \rightarrow HO_2^-$. At pH < 4, the Tafel slope was larger than −120 mV dec$^{-1}$, suggesting that the adsorption of oxygen may partially contribute to the rds. Furthermore, the direct evidence of oxygen adsorption is still limited. Further study on the adsorption of oxygen is necessary to understand fully the mechanisms of ORR.

In chapter 4, the effect of pH and sulfate (SO$_4^{2-}$) anion on the adsorption of oxygen on Au surface was investigated by EQCM. The adsorption of oxygen on the Au surface was first observed at potentials more positive than the potential at which the ORR started to occur. The amount of adsorbed oxygen increased and reached its saturation value as the potential became more negative in all the solutions in this study. The adsorption of oxygen on the Au electrode surface started at ca. +0.82 V in perchlorate solution (SO$_4^{2-}$-free) and at ca. +0.60 V in the sulfate solution, showing the inhibition of the adsorption of oxygen by strongly adsorbed sulfate anions. In all the SO$_4^{2-}$-free solutions at various pH values in this study, the
adsorption of oxygen started at a potential where the surface oxide was partially reduced and the mass change difference between the results obtained in the Ar- and O$_2$-saturated solution reached its saturation value at each pH level when the surface oxide was fully reduced. The maximum mass change difference increased with increasing pH and reached its constant level when the pH $> 11.4$. In this study, 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 the Pt electrode surface was investigated by EQCM. The adsorption of oxygen was first observed at ca. +0.60 V where the surface oxide was partially reduced and the ORR current was flowed both in the perchlorate and sulfate solutions. The inhibition of the sulfate anion on the adsorption of oxygen was not significantly observed on the Pt surface compared with that observed on the Au electrode surface. However, the adsorption of oxygen on the Pt surface caused an increase in mass in the perchlorate solution and a decrease in mass in the sulfate solution. It was proposed that the adsorbed sulfate was replaced by oxygen on the Pt surface. The effect of anion on the adsorption of oxygen on the Pt surface is different from that observed on the Au surface discussed in chapter 4. This discrepancy can be attributed to the stronger interaction between oxygen and Pt compared with that between oxygen and Au.

2. Future Prospect

This thesis emphasized the importance of the ORR mechanism in improving the performance of the fuel cell system. The processes of oxygen adsorption, electron transition, and desorption of intermediates/products are involved in ORR.

In this thesis, the effects of anion, pH, and electrode materials on the adsorption of oxygen, which is considered the first step in ORR, were systematically studied.
In the future, the reduction of oxygen will be studied to contribute in clarifying the mechanism of ORR. Finally, enhance the performance of fuel cell systems.
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Sheng-Fu Tong
Tsukuba
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