Anodic Dissolution of Copper in Oxygenated Sulfuric Acid Solution as Examined by Rotating Ring-Disk Electrode

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\textbf{ABSTRACT}

The anodic dissolution of copper was examined in oxygenated sulfuric acid solution. A characteristic property of the anodic process is that the oxidation process \( \text{Cu} \rightarrow \text{Cu}^{2+} \) involves the detectable intermediate \( \text{Cu}^+ \), which should disproportionate into \( \text{Cu} \) and \( \text{Cu}^{2+} \) in the thermodynamic equilibrium state. On the other hand, \( \text{H}_2\text{O}_2 \) was formed during anodic dissolution in oxygenated solution by the reaction of \( \text{Cu}^+ \) with \( \text{O}_2 \). The intermediate \( \text{Cu}^+ \) and the byproduct \( \text{H}_2\text{O}_2 \) were detected in this study using a rotating ring-disk electrode. The anodic dissolution process including the role of oxygen was elucidated through the detection of \( \text{Cu}^+ \) and \( \text{H}_2\text{O}_2 \). The decrease in the activity of \( \text{Cu}^+ \) in the presence of \( \text{O}_2 \) involved a negative shift of the partial current of \( \text{Cu} \) to \( \text{Cu}^{2+} \) (or \( \text{Cu}^+ \)), and resulted in a negative shift of the corrosion potential with increasing stirring rate of the solution. In addition, \( \text{Cu}^+ \) was found to be not a transient intermediate, but rather, a thermodynamic equilibrium species. The acceleration of the corrosion rate in the presence of \( \text{O}_2 \) was elucidated successfully to be due to the couple of the partial currents for \( \text{Cu} \rightarrow \text{Cu}^+ \) and \( \text{O}_2 \rightarrow \text{H}_2\text{O}_2 \).

\textbf{Keywords :} Anodic Dissolution, Copper, Oxygen, Mixed Potential

1. Introduction

It is well known that the corrosion product of copper in sulfuric acid solution is copper(II) ions, and that the corrosion rate increases in the presence of oxygen with formation of the byproduct hydrogen peroxide.\textsuperscript{1, 2} The products of copper corrosion in oxygenated aqueous sulfuric acid solution are equimolar amounts of \( \text{Cu}^{2+} \) and \( \text{H}_2\text{O}_2 \). Anderson et al. assumed that the anodic polarization curve of copper was independent of the oxygen partial pressure.\textsuperscript{3} If the anodic partial current of copper corrosion was independent of the coexisting oxygen, the corrosion potential (mixed potential) of copper must shift to a more positive value, and also shift in the positive direction with increasing stirring rate of the solution in which the cathodic partial reaction is \( \text{O}_2 \rightarrow \text{H}_2\text{O}_2 \). However, the corrosion potential was found to shift to more negative values with increasing stirring rate of the solution (rotation speed of disk electrode). The polarization potential under constant-current electrolysis also shifted to a more negative value with increasing oxygen partial pressure. On the basis on the independence of the anodic polarization curve on oxygen, Anderson et al. accounted for these phenomena as “A Limitation to the Mixed Potential Concept…” Their terminology “limitation to the mixed potential concept” looks inadequate because anodic copper oxidation and cathodic oxygen reduction are correlated with each other in oxygenated solution.

The mechanism of the anodic dissolution of copper in oxygenated sulfuric acid solution was re-examined in this study using a rotating ring-disk electrode. The anodic partial reaction of copper oxidation and cathodic partial reaction of oxygen reduction were examined independently as described in the Theoretical section. A platinum ring-copper disk electrode was used for these experiments. Hydrogen peroxide and copper(I) ions formed at the copper disk electrode were detected independently at the platinum ring electrode. The roles of copper(I) ions in the anodic dissolution of copper and cathodic oxygen reduction in the formation of hydrogen peroxide were elucidated.

2. Theoretical Basis

When the electrode reactions of different redox reactions occur at the same electrode, the overall current-potential curve is composed of the sum of each partial current. This principle is known as the “additive property of partial currents.” Let us take, for example, the oxidation partial reaction \( \text{Cu} \rightarrow \text{Cu}^+ + 2e^- \) and the reduction partial reaction \( 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \). The oxidation potential and reduction potential of copper metal in sulfuric acid medium is the simple sum of the oxidation partial-potential curve of copper and the reduction of \( \text{H}^+ \). At the corrosion potential (mixed potential), the net current is zero and the corrosion rate of copper is estimable from the exchange current at which the absolute value of the oxidation partial current is equal to the reduction partial current.

The anodic and cathodic partial reactions are as follows for copper corrosion in oxygenated sulfuric acid solution,

\begin{align*}
\text{Cu} \rightarrow 2\text{e}^- & \rightarrow \text{Cu}^+ \quad \text{(a)} \\
\text{Cu} \rightarrow \text{e}^- & \rightarrow \text{Cu}^+; \text{Cu}^+ \rightarrow \text{Cu}^{2+} \quad \text{(a')} \\
\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2\text{O}_2 \quad \text{(b)}
\end{align*}

If anodic electron transfer were a simple two-electron transfer as in Eq. (a), the additive property of partial currents (a) and (b) would hold. If the electron-transfer rate of \( \text{Cu} \rightarrow \text{e}^- \rightarrow \text{Cu}^+ \) were faster than \( \text{Cu} \rightarrow 2\text{e}^- \rightarrow \text{Cu}^{2+} \) and the succeeding chemical step of \( \text{Cu}^+ \) with \( \text{O}_2 \) were rather slow, \( \text{Cu}^+ \) would be included as a transient intermediate in the solution bulk. In this case, the partial current of the electron-transfer steps (\( \text{Cu} \rightarrow \text{e}^- \rightarrow \text{Cu}^+ \) ) would be independent of oxygen...
and the Tafel plot would be similar to that in nitrogen-saturated solution. On the other hand, if the succeeding chemical reaction of Cu⁺ with O₂ were sufficiently fast, the activity of Cu⁺ would decrease and the anodic partial current would shift in the negative direction in the presence of oxygen, and electron transfer from Cu⁺ to O₂ would occur immediately adjacent to the electrode surface. The electron transfer would appear as if it occurred through the electrode. The overall current-potential curve differs from the sum of the partial currents, and is apparently inconsistent with the additive property of partial currents.

The authors assumed that the partial reactions (a) and (b) were not independent, but interacted with each other. Figure 1(A) shows the schematic anodic and cathodic partial currents (dotted lines) in an oxygen-free atmosphere, i.e., nitrogen-saturated solution. In this case, the cathodic partial reaction is hydrogen evolution. If the oxygen partial pressure increased and there were no interaction between Eqs. (a) and (b), the whole reaction scheme would be as depicted in Process I of Fig. 1(B). In this case, the anodic partial current would be independent of coexisting oxygen, and only the cathodic partial current would increase (bold dotted line). If this assumption were true, the partial current of copper dissolution must be independent of coexisting oxygen, and the corrosion potential must shift to O₂ + 2e⁻ → H₂O₂.

Our significant finding in this study was that the Tafel plot shifted considerably in the negative direction in the presence of oxygen at an intermediate current density, and converged to a straight line at a high current density, showing a convex curve. The Tafel slope above the convergence point was consistent with that in nitrogen-saturated solution. The absolute value of the current at the convergence point was consistent with the limiting diffusion current of oxygen reduction, as will be discussed in the text. Accordingly, Process II does not contradict the principle of the additive property of partial currents. Rather, Process II will be consistent with this principle if the fast interaction between Cu⁺ and H₂O₂ is taken into consideration.

3. Experimental

3.1 Ring-disk electrode

The disk electrode was copper electroplated on a platinum disk and the ring electrode was platinum. The disk radius was 0.385 cm, the ring inner radius was 0.396 cm, and the outer radius was 0.492 cm. The collection efficiency of this ring-disk electrode was 0.382. Copper plating on the platinum disk was carried out in 0.01 mol dm⁻³ copper(II) sulfate solution with 1 mol dm⁻³ nitric acid at a current density of 20 mA cm⁻², which gave a bright copper plating and reproducible voltammetric measurements. The thickness of the copper plating was about 10 µm. The rotation speed was 2,500 rpm unless otherwise stated. The current axis is shown as the apparent current, and not the current density. All voltammetric measurements were referred to the saturated calomel electrode (SCE).

3.2 Chemicals

High-purity water was obtained using a Milli-Q Reagent Grade Water System (Millipore Corporation), and had a resistivity of 18 MΩ cm⁻¹. All measurements were performed in 2 mol dm⁻³ sulfuric acid solution prepared with the high-purity water. All
chemicals used were Fisher Certified Reagents and used without further purification. Three kinds of solution were prepared by saturating with nitrogen gas, air, and oxygen gas. Deoxygenation by nitrogen gas was confirmed from the residual current of oxygen reduction at the platinum disk electrode. For comparison, the voltammetric property of copper was examined in a solution containing hydrogen peroxide.

4. Results and Discussion

The most important purpose of this study was the elucidation of the role of copper(I) ions and oxygen on copper corrosion in oxygenated sulfuric acid solution on the basis of “the principle of the additive property of partial currents.” Equations (1)–(8) indicate the overall electrochemical and chemical reactions related to copper corrosion in oxygenated sulfuric acid solution. The standard electrode potentials of the important reactions are listed with each equation.

- Anodic reactions:
  \[
  \begin{align*}
  \text{Cu} - e^- & \rightarrow \text{Cu}^{2+}; \quad E^o = +0.521 \text{V} \\
  \text{Cu}^+ - e^- & \rightarrow \text{Cu}^{2+}; \quad E^o = +0.153 \text{V} \\
  \text{Cu} - 2e^- & \rightarrow \text{Cu}^{2+}; \quad E^o = +0.337 \text{V}
  \end{align*}
  \]

- Disproportionation reaction:
  \[
  2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+} \quad K = [\text{Cu}^+]^2/[\text{Cu}^{2+}] = 5.8 \times 10^{-7}
  \]

- Cathodic reactions:
  \[
  \begin{align*}
  2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 \\
  \text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{H}_2\text{O}_2; \quad E^o = +0.682 \text{V} \\
  \text{H}_2\text{O}_2 + 2\text{e}^- + 2\text{H}^+ & \rightarrow 2\text{H}_2\text{O}; \quad E^o = +1.77 \text{V} \\
  \text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O}; \quad E^o = +1.23 \text{V}
  \end{align*}
  \]

- Chemical reaction:
  \[
  2\text{Cu}^+ + \text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O}_2
  \]

Generally, these equations are indicated using the equal (=) sign. This sign is replaced by an arrow to reveal the corrosion process. Note that the standard electrode potentials in the literature were ideal ones, and the observed values that were measured in real solution using a saturated calomel electrode (SCE) contain inherent errors.

It should be noted that the overall cathode reaction in the presence of oxygen should be Eq. (8) and the final product would be \( \text{H}_2\text{O} \). However, it has been proved that the products in the early stage of open-circuit corrosion were equimolar amount of \( \text{Cu}^{2+} \) and \( \text{H}_2\text{O}_2 \). Figure 2 in Ref. 3, and Eq. (6) was selected as the representative cathode reaction in this study.

4.1 Corrosion potential of copper

The corrosion potential (mixed potential) of the rotating copper-disk electrode was measured to verify the effect of oxygen diffusion on the corrosion of copper, and the result is shown in Fig. 2. A similar relation was measured under constant-current electrolysis as shown in Fig. 3. The corrosion potential in Fig. 2 shifted in the positive direction in the order \( \text{O}_2 \rightarrow \text{air} \rightarrow \text{N}_2 \) irrespective of the rotation speed, as suggested by the simple mixed-potential concept\(^3\) with the exception of \( \text{H}_2\text{O}_2 \).

The corrosion potential in nitrogen-saturated solution is determined by the couple of anodic copper dissolution and cathodic oxygen reduction, as given by Eqs. (3) and (6). In this case, the difference in diffusion rate between copper ions and oxygen would be competitive.

The corrosion potential of copper in oxygenated solution should shift in the positive direction with increasing rotation speed if the anodic dissolution of copper were independent of the oxygen partial pressure, because the diffusion of oxygen to the electrode surface would be rate-determining. Thus, the experimental finding suggested that the partial reaction of anodic copper dissolution had some relation with the reduction of oxygen. Figure 3 shows the rotation-speed dependence of the electrode potential under constant-current electrolysis at 0.2 mA. The order of the electrode potential inverted under electrolysis, and the observed potential in an oxygen atmosphere was more negative than that in a nitrogen atmosphere.

The negative-direction shift with increasing rotation speed and the inverse order of corrosion potential between the oxygen-free and oxygenated solutions can be accounted for as follows. The oxygen that diffused to the electrode surface contributed more predominantly to the reduction in the activity of copper(I) ions than to the increase in the cathode reaction to form \( \text{H}_2\text{O}_2 \). The rotation-speed dependence in Fig. 2 and inverse relation in Fig. 3 seem inconsistent with the prediction of Andersen et al., who suggested that the rate-determining step was the diffusion of oxygen to the electrode surface to increase the cathodic reaction.\(^3\)

The role of \( \text{H}_2\text{O}_2 \) is briefly accounted for as follows. The open circles in Fig. 2 show the rotation-speed dependence of the copper disk electrode in 2 mmol dm\(^{-3}\) \( \text{H}_2\text{O}_2 \) under a nitrogen atmosphere. In this case, the cathodic process is the reduction of \( \text{H}_2\text{O}_2 \) to water.
molecules, as given in Eq. (7). It should be noted that the reaction rate of Cu$^+$ and H$_2$O$_2$ was rather slow and the anodic partial current of copper dissolution was not affected by hydrogen peroxide. Thus, the additive property of the anodic partial current of Cu → Cu$^{2+}$ and cathodic partial current of H$_2$O$_2$ → H$_2$O would hold. The corrosion potential in the solution containing H$_2$O$_2$ shifted in the positive direction, as suggested by Process I in Fig. 1. The rotation-speed dependence was also positive, as shown in Fig. 2. The positive tendency of the corrosion potential revealed that the diffusion of H$_2$O$_2$ was rate-determining.

4.2 Independent detection of Cu$^+$ and H$_2$O$_2$

Prior to the examination of the anodic polarization curve of copper, the hydrogen peroxide and copper(I) ions formed on the disk electrode were assessed on the platinum ring electrode. Figure 4 shows the current-potential curve of the rotating platinum ring electrode in the solution containing hydrogen peroxide. On freshly prepared platinum, which was prepared by oxidation at +1.5 V vs. SCE for 5 min followed by reduction at +0.4 V for 5 min, a current maximum was observed at +1.0 V (open circles). The maximum current, approximately the limiting current, was proportional to the concentration of dissolved hydrogen peroxide. The current value was invariant over one hour of measurement and independent of the oxygen partial pressure. On the other hand, oxidized platinum at +0.7 V (preceded by oxidation at +1.5 V for 5 min) was inactive to H$_2$O$_2$, and the oxidation current at +0.7 V was negligible. Contrary to the oxidation of hydrogen peroxide, the oxidation of copper(I) ions was independent of the electrode pretreatment, and a steady limiting diffusion current was observed from +0.7 to +1.0 V.

From these two preparatory experiments, it was found that the current measured at +1.0 V on a freshly prepared platinum electrode involved the sum of the partial currents of the oxidation of H$_2$O$_2$ and Cu$^+$. The current is indicated by $i_{D}(+1.0)$ V. The current at +0.7 V on oxidized platinum was for Cu$^+$ only, and is indicated by $i_{D}(+0.7)$ V.

4.3 Detection of Cu$^+$ during the anodic dissolution of copper

This study of the reduction process Cu$^{2+}$ → Cu$^+$ → Cu in the solution containing a sufficient amount of Cl$^-$ showed a well-defined two-step current-potential curve. The standard electrode potentials of Cu$^+/Cu$ and Cu$^{2+}/Cu^+$ are +0.137 and +0.562 V vs. NHE, respectively, in a solution with a Cl$^-$ concentration of 1 mol dm$^{-3}$. The potential sequence is consistent with the valence sequence. This was a good example for the study with the rotating ring-disk electrode.

On the other hand, the standard electrode potentials of Cu$^+/Cu$ and Cu$^{2+}/Cu^+$ are +0.521 and +0.153 V, respectively, in the absence of Cl$^-$ for example, in sulfuric acid solution. According to the contradictory sequence between the standard electrode potential and valence state, copper(I) ions have been considered as a thermodynamically unstable intermediate, and thus, it has been considered to be a transient intermediate in anodic copper dissolution.

The most determinate point is that the copper(I) ions detected in this study are thermodynamically stable species that obey the Nernst equation. A definite experimental proof was the detection of copper(I) ions on the ring electrode either in the oxidation of copper metal to copper(II) ions or in the reduction of copper(II) ions to copper metal. Figure 5 shows the anodic polarization curve of the copper disk (open circles) and ring current at +0.7 V for the corresponding disk potentials (open triangles). The ring current at +0.7 V shows the oxidation of copper(I) ions. On the other hand, copper(I) ions were detected by Nekrasov during the reduction of copper(II) ions. They found an oxidation current of copper(I) ions at the ring electrode (Fig. 2-B in Ref. 6). The concentration ratio of [Cu$^{2+}$]/[Cu$^+$] was estimated from the peak-current potential (~+0.38 V vs. NCE) and its standard electrode potential +0.153 V vs. NHE [Eq. (2)]. The estimated [Cu$^{2+}$]/[Cu$^+$] ratio was about 6.3. On the other hand, the experimental [Cu$^{2+}$]/[Cu$^+$] ratio was about 5.3, as estimated from the ratio of the disk current of Cu$^{2+}$ to the ring current of Cu$^+$ and the collection efficiency. These results are consistent if inherent errors of the standard electrode potential in the real solution are taken into consideration. The consistency suggested that the equilibrium of Cu$^{2+}$ + e$^-$ = Cu$^+$ was held at the disk electrode and copper(I) ions detected on the ring electrode were thermodynamically stable species that satisfied the Nernst equation.

Let us consider the copper(I) ions detected in the anodic dissolution of copper shown in Fig. 5. The anodic polarization curve of the copper disk and corresponding ring current at +0.7 V (oxidation current of transient copper(I) ions) showed a similar exponential property. The ratio of the ring current to the disk current, $i_{D}(+0.7)/i_{P}$, is illustrated simultaneously (closed squares). The ratio $i_{D}(+0.7)/i_{P}$ decreased almost linearly as the disk potential became positive. The decrease in $i_{D}(+0.7)/i_{P}$ indicated that the concentration ratio [Cu$^{2+}$]/[Cu$^+$] adjacent to the disk electrode surface increased with increasing electrode potential. The decreasing property was predicted from the factor (RT/nF) in the Butler-Volmer relation (difference in n), and the exponential property of current held in two anodic dissolution reactions: Cu $\rightarrow$ e$^-$ $\rightarrow$ Cu$^+$ (n = 1) and Cu $\rightarrow$ 2e$^-$ $\rightarrow$ Cu$^{2+}$ (n = 2). The concentration of copper(I) ions and the ratio [Cu$^{2+}$]/[Cu$^+$] during the anodic dissolution of copper were estimated from the

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**Figure 4.** Current-potential curves of H$_2$O$_2$ on platinum ring electrode. ◆ anodic scan and ○ cathodic scan. Sampling point: A (+0.7 V) for Cu(I) and B (+1.0 V) for (Cu(I) + H$_2$O$_2$).

**Figure 5.** Current-potential curve of Cu-disk in nitrogen atmosphere and Cu(I) detection on ring electrode. ◆ disk current of Cu dissolution $i_{D}$, △ ring current of Cu(I) oxidation at +0.7 V vs. SCE, and ○ ratio $i_{D}(+0.7)/i_{P}$.
standard electrode potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^2^+, which are +0.337 and +0.153 V vs. NHE, respectively, assuming that the equilibrium Cu^{2+} + 2e^- = Cu was maintained during anodic dissolution. The concentration of copper(II) ions at 0.0 V vs. SCE in Fig. 5 (corresponding to +0.241 V vs. NHE) was estimated from the Nernst equation to be 6 x 10^{-4} mol dm^{-3}. The concentration of copper(I) ions at the same potential was estimated by similar procedure, and it was 2 x 10^{-3} mol dm^{-3}. The [Cu^{2+}]/[Cu^{+}] concentration ratio should be about 30 if the Nernst equilibrium of these electrode reactions hold during anodic dissolution. On the other hand, the experimental concentration ratio [Cu^{2+}]/[Cu^{+}] was seven times smaller than that estimated from the Nernst equation. This difference is significant even though the inherent errors of the standard electrode potential in the real solution were taken into consideration.

The result in Fig. 5 suggested that the electrode reaction of Cu → Cu^{+} + e^- was fast enough to establish Nernst equilibrium during anodic dissolution. On the other hand, the reaction of Cu → Cu^{2+} + 2e^- was slow, the activation overpotential of anodic dissolution was high, and the surface concentration of Cu^{2+} would be lower than expected from the Nernst equation. Thus, the difference in the electron-transfer rate between Cu^{2+} and Cu^+ resulted in the low [Cu^{2+}]/[Cu^{+}] concentration ratio. In fact, the Tafel slope (dE/d log i = aRT/nF) in Fig. 8 under nitrogen atmosphere was 50 mV and transfer coefficient α was estimated to be 0.6 for n = 2. If the electron transfer process in the dissolution reaction were very fast (so-called reversible) and diffusion-controlled, the slope would be 30 mV for n = 2.

The rotation-speed dependence of the ring current was examined to investigate the disproportionation reaction of copper(I) ions during the transfer from the disk electrode to the ring electrode. The following discussion involves qualitative analysis, because the theory of the rotating-ring-disk electrode for such an electrode reaction including a disproportionation reaction [Eq. (4)] has not yet been established. Figure 6 shows the rotation-speed dependencies of i_D and i_D([+0.7]) at a constant disk potential of +10 V vs. SCE. The plot of i_D was linear and had a significant intercept. The intercept must show a slow electron-transfer rate (so-called irreversible) compared with the diffusion of copper ions to the solution bulk. On the other hand, the plot of i_D([+0.7])/i_D was almost proportional to w^{1/2}, and the intercept was almost negligible. The regression equation was

i_D([+0.7])/i_D = 0.0010w^{1/2} + 0.006 \quad (R^2 = 0.990) (10)

The detection of copper(I) ions was carried out in the limiting-current range (Fig. 4). Thus, the proportional property with the negligible intercept suggested that copper(I) ions formed at the disk electrode were stable with a rather long life and diffused to the ring electrode without any accompanying disproportionation reaction.

4.4 Ring-disk current in oxygenated solution

The formation of Cu^+ and H_2O_2 was examined more closely in oxygenated solution. The ring current at +1.0 V [i_D([+1.0])] indicates the sum of the oxidation currents of H_2O_2 and Cu^+, and the ring current at +0.7 V [i_D([+0.7])] indicates the oxidation of Cu^+.

The closed circles in Fig. 7(A) show the ratio of i_D([+1.0])/i_D in an air-saturated solution, and those in (B) show that in an oxygen-saturated solution. The ratio decreased monotonously as the disk potential became more positive, and reached almost zero at +80 mV in Fig. 7(A). At negative potentials lower than -25 mV, the ratio exceeded the collection efficiency of 0.382, and went to infinity at the corrosion potential (-80 mV) and i_D = 0. The apparent large collection efficiency could be accounted for as follows. The disk current i_D around the corrosion potential included the negative current of oxygen reduction, and the apparent i_D must be smaller than that ascribed to the copper oxidation. The plot of i_D([+0.7])/i_D([+1.0]) in Figs. 7(A) and 7(B) will be discussed in detail jointly with the Tafel plot in the next section.

4.5 Shift of corrosion potential and polarization curve in oxygenated solution

It is well known that the equilibrium potential of an electron-transfer reaction depends on the succeeding chemical processes. If the chemical reaction is sufficiently fast, a decrease in the activity of the electron-transfer product will occur. For example, the electrode potential of Cu^{2+}/Cu shifts significantly in the negative direction in the presence of complexing agents such as NH_3, and that of Ag^+/Ag shifts in the presence of Cl^-}. According to the negative shift of the electrode potential, the polarization curve shifts in the negative direction. For example, the polarization curve of the anodic dissolution of copper shifts negatively in the presence of NH_3, and that of mercury shifts in the presence of Cl^-}. In addition, a limiting current will appear, corresponding to the concentration of complexing agents. The effect of the oxygen partial pressure in Figs. 2 and 3 is attributable to the decrease in activity of the copper(I) ions, as will be discussed below.

Tafel plots of the rotating copper disk electrode measured in nitrogen-, air-, and oxygen-saturated solutions are shown in Fig. 8. The plot measured in hydrogen peroxide solution is illustrated for comparison. Under the nitrogen atmosphere, the Tafel plot gave a
To account for this phenomenon, the authors have assumed that a thin reaction layer is formed from the disk to the ring electrode, in which Cu⁺, O₂, and H₂O₂ coexist. The thickness of the reaction layer is determined either by the diffusion of oxygen from the solution bulk or by the reaction rate of Eq. (9). Such a reaction-layer model assures the constant activity of copper(I) ions near the electrode surface from the disk to ring electrodes.

With the reaction-layer model, a saturation curve in the ring current of \( i_R(0.7)/i_R(1.0) \) would be accountable. Then, the constant activity of copper(I) ions at the high current range would give a straight Tafel plot in Fig. 8 (higher than +60 mV in air-saturated solution), and the plot would show a more negative shift of about 10 mV compared to that in the nitrogen-atmosphere, as seen in Fig. 8.

The above mentioned phenomenon was observed similarly in oxygen-saturated solution. However, the current rise in \( i_R(0.7)/i_R(1.0) \) appeared more strongly from a more negative potential (+0.0 mV) than in the air-saturated solution [open triangles in Fig. 7(B)], in spite of the fact that \( i_R(0.7)/i_R(1.0) \) must be suppressed more strongly with increasing oxygen partial pressure. The stronger increase in the oxygen-saturated solution could be attributed to the fact that \( i_R(0.7) \) included the oxidation current of H₂O₂ and a false increase in the concentration of copper(I) ions was observed.

5. Conclusion

It is well known that copper(I) ions undergo a disproportionation reaction in sulfuric acid solution to form metallic copper(0) and copper(II) ions. However, these three species exist in equilibrium, and the amount of copper(I) ions is detectable electrochemically in such an equilibrium state based on the Nernst equation. The fundamental conclusion of this study is that the copper(I) ions detected at the ring electrode in nitrogen-saturated solution are an equilibrium species that satisfy the Nernst equation. Figure 5 in this study and Fig. 2-B in Ref. 6 provide definite experimental proof of this conclusion. The dissolved oxygen decreases the activity of copper(I) ions to form Cu²⁺ and H₂O₂, and increases the anodic dissolution rate of copper in oxygenated solution. Acceleration of the chemical corrosion rate with zero external current can be accounted for by a similar mechanism.

The mixed-potential concept is deduced from the fundamental principle of the additive property of the partial currents of each electrode reaction. It should be noted that such an additive property is established only if the partial reactions do not interact with one another. The acceleration of copper dissolution in the presence of oxygen is ascribed to the decrease in the activity of copper(I) ions due to their reaction with oxygen. Thus, the oxidation of copper and the reduction of oxygen interact with each other in the process of the anodic dissolution of copper in oxygenated sulfuric acid solution. The dissolved oxygen causes a decrease in the activity of copper(I) ions, shifts the polarization curve in the negative direction, and results in the apparent inconsistency with the additive property of partial currents.

References