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The Effect of Anion-Exchange-Treated Water Containing Phosphonic Acid and Benzotriazole on Copper Corrosion Resistance

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Abstract

Copper tubes have high thermal conductivity, excellent workability, and corrosion resistance. For these reasons, they are widely used in air conditioning equipment. However, copper tubes can corrode due to interactions between the material and its environment. The carbon film-dependent pitting corrosion is caused by the relationship between the carbon film on the inner surface of copper tubes and the quality of the water flowing them. Phosphonic acid (HEDP) and benzotriazole (BTA) have been reported to suppress pitting corrosion. Additionally, it has been reported that water quality components such as calcium ions (Ca^{2+}), silicate ions (SiO_4^{4-}) and bicarbonate ions (HCO_3^-) are effective. Tap water contains various ions, including chloride ion (Cl^-), sulphate ion (SiO_4^{2-}) and bicarbonate ions (HCO_3^-). Cl^- and SiO_4^{2-} are known as corrosive ions. Conversely, HCO_3^- is known as corrosion-inhibiting ions. Anion-exchange treatment is a technology for reducing corrosive ions in tap water. It has been reported that anion-exchange treated water inhibits corrosion in carbon steel pipes used within the same system as copper tubes. However, there are few reports on its corrosion-inhibiting effect on copper tubes. This study focused on the effect of anion-exchange treated water on copper pitting corrosion. The test specimens used different amounts of carbon film. The test solution used untreated water and treated water, with both containing HEDP and BTA. Corrosion potential and anodic polarization measurements were performed on these specimens. In corrosion potential measurement, the corrosion potential continued to rise in untreated water and treated water, regardless of the amount of carbon film. The increase in potential was suppressed with treated water compared to untreated water. After corrosion potential measurements, greenish-blue corrosion products were observed only in untreated water. In anodic polarization measurements, the current density of untreated water tended to show a sharp increase on the noble potential side, regardless of the amount of carbon film. In contrast, this trend was not observed in treated water. Based on these results, it is considered that the treated water containing HEDP and BTA inhibits carbon film-dependent pitting corrosion regardless of the amount of carbon film.

Keywords

Copper, Carbon Film, pitting Corrosion, Anion Exchange-Treated Water, Benzotriazole, Phosphonic Acid

1. Introduction

Copper tubes have high thermal conductivity, excellent workability, and high corrosion resistance. Therefore, copper tubes are widely used in heat exchangers for air conditioning and refrigeration units. A carbon film forms on the inner surface of the copper tube during the manufacturing process. In this process, processing oil adheres to the inner surface of the tube due to heat treatment, forming a carbon film. In general, the amount of carbon film on copper is shown by the residual carbon amount (mg/m^2). Carbon film induces pitting corrosion in copper tubes. This pitting corrosion is called carbon film-dependent pitting corrosion [1]-[3]. Corrosion inhibitors such as phosphonic acid (HEDP) and benzotriazole (BTA) have been reported to be effective in suppressing carbon film-dependent pitting corrosion [4] [5]. Furthermore, it has been reported that the presence of calcium ions (Ca^{2+}), silicate ions (SiO_4^{4-}), and bicarbonate ions (HCO_3^-) in solutions containing the above corrosion inhibitor inhibits pitting corrosion [6]-[8].

Tap water is mainly used as the makeup water for circulating water in air conditioning systems. Tap water contains various components including calcium ions (Ca^{2+}), silicate ions (SiO_4^{4-}), chloride ions (Cl^-), sulfate ions (SiO_4^{2-}), and bicarbonate ion (HCO_3^-). According to laboratory-scale corrosion studies, it is considered that Cl^- and SiO_4^{2-} are corrosive and that HCO_3^- inhibits corrosion. This study focused on the corrosivity of water obtained by removing corrosive ions as Cl^- and SiO_4^{2-} in tap water using an anion exchange resin. Resin is regenerated with solutions containing sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) [9]-[11]. Anion exchange water (treated water) was obtained by passing tap water through the anion exchange resin. In this process, treated water is obtained when the SiO_4^{2-} and Cl^- ions in tap water are replaced with HCO_3^- ions. That is, treated water is rich in HCO_3^- and poor in Cl^- and SiO_4^{2-}.

Air conditioning equipment consists of many metals, such as carbon steel pipes, galvanized steel pipes, and copper tubes. There are several studies on the corrosion inhibiting effect of treated water on carbon steel [9]-[11]. They have reported that both the corrosivity of treated water is extremely low and that a passive film is formed on carbon steel in treated water. However, studies of the corrosion inhibition of treated water for copper tubes are not found.

This study investigated the effects of treated water containing HEDP and BTA on the corrosion of copper with varying amounts of residual carbon. The test specimens used both two types of copper tube with different residual carbon and copper plate without residual carbon. These were immersed in treated and untreated water, both containing HEDP and BTA. The corrosion potential was measured over time. After the test, the surface appearance was observed. In addition, anodic polarization curves of copper specimens in these waters were measured.

2. Methods

2.1. Materials

Table 1 shows the size and amount of residual carbon in test specimens. Specimens with different amounts of residual carbon were used to confirm the effect of the carbon film on pitting corrosion. Copper plate (phosphorus-deoxidized copper, JIS H 3100 C1220) and copper tubes cut parallel to the tube axis (Phosphorus-deoxidized copper, JIS H 3300 C1220, OL) were used for corrosion tests. Copper plates are processed differently from copper tubes. Copper plates are not processed using heat treatment and processing oils. Therefore, the copper plate was considered to have a residual carbon amount of 0 mg/m^2. Copper tubes A and B with different amounts of residual carbon were selected for test specimens. The residual carbon on copper tubes A and B was 5.5 mg/m^2 and 15 mg/m^2, respectively. These amounts were quantified based on the rapid filling test. The number of corrosion pits formed after exposure to H_2O_2 10 mg/L, BTA 10 mg/L, Cl^- 300 mg/L, and SiO_4^{2-} 300 mg/L solutions for 72 h. After that, the number of corrosion pits was counted. [12]. The number of corrosion pits was plotted on the approximate curve developed by Kano *et al.*, and converted to a residual carbon amount. This curve was derived from the relationship between the number of corrosion pits obtained in a rapid filling test and the amount of residual carbon collected and quantified by dissolving the inner surface of a copper tube with a mixture of nitric and hydrochloric acids. The specimens were degreased with acetone and then immersed in acid cleaning solution for 60 seconds. This method can remove the oxide films formed on the copper surface in air. The copper plate was immersed in 5 mass% nitric acid to remove oxide films. The copper tube was immersed in 3 mass% sulfuric acid. This acid can remove the oxide film on the copper tube while leaving the carbon film. After acid cleaning and rinsing with pure water, untested areas were coated with enamel resin.

2.2. Test Solutions

The solution used Tsukuba City water (untreated water) and Tsukuba City water treated with anion exchange (treated water). HEDP 2 mg/L and BTA 5 mg/L were added to these solutions and used as test solutions. The water quality of the test solutions is shown in **Table 2**.

Table 1. Sample size and residual carbon.

Sample	Size	Residual carbon
Copper Plate	Length: 100 mm ×Wide: 15 mm ×Thicness: 0.5 mm	0 mg/m^2
Copper Tube A	Length: 100 mm ×Inner diameter:15.88 mm	5.5 mg/m^2
Copper Tube B	Length: 100 mm ×Inner diameter: 15.88 mm	15 mg/m^2

Table 2. Water quality of the test solutions.

Compositions	Units	Test solutions	
		Untreated Water	Treated Water
pH (25˚C)	-	7.7	7.8
Electric conductivity	mS/m	27.5	22.9
Total hardness	mg $CaCO_3$/L	71	72
Ca hardness	mg $CaCO_3$/L	45	45
Alkalinity (pH 4.8)	mg $CaCO_3$/L	45	127
Cl^-	mg/L	35.6	<0.3
SiO_4^{2-}	mg/L	28.5	<0.2
NO_3^-	mg/L	2.8	<0.1
SiO_2	mg/L	6	6
HEDP	mg/L	2	2
BTA	mg/L	5	5

2.3. Corrosion Potential Measurement

A schematic drawing of the test apparatus is illustrated in **Figure 1**. A 500 ml beaker was used as the test vessel. The test solution was added to a volume of 500 ml and stirred at 300 rpm at room temperature. Furthermore, this test was conducted under open-air conditions to evaluate changes in the corrosion potential of copper in the test environment. The immersion period was set at 7 days, and the corrosion potential was measured over time. The corrosion potential was measured using a digital multimeter (Keysight: 34,070 A). The saturated Ag/AgCl (SSE) reference electrode was used. The test area was set to 3 cm^2. The measurements were performed in triplicate. After testing, the specimens were examined for surface observation and composition analysis using a digital microscope (KEYENCE: VHX-5000) and an SEM equipped with EDX (Hitachi High-Technologies: S-4300).

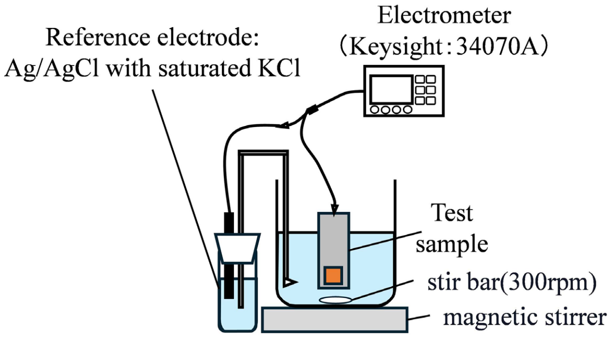

Figure 1. Schematic of corrosion potential measurement apparatus.

2.4. Anodic Polarization Curve Measurement

A schematic drawing of the test apparatus is illustrated in **Figure 2**. A 500 ml beaker was used as the test vessel. The test solution was added to a volume of 500 ml and stirred at 300 rpm at room temperature. The measurement was conducted by deoxidizing the test solution using nitrogen gas. The purpose of this was to remove the effects of oxygen and evaluate the reaction of copper under the test environment. The polarization curve was measured using a potentiostat (HZ-7000; Hokuto Denko, Tokyo, Japan). The sweep speed was set to 20 mV/min. The specimens were used as the working electrode, the reference electrode was a saturated Ag/AgCl (SSE), and platinum was used as a counter electrode. The test area was set to 1 cm^2. Measurements were performed in triplicate.

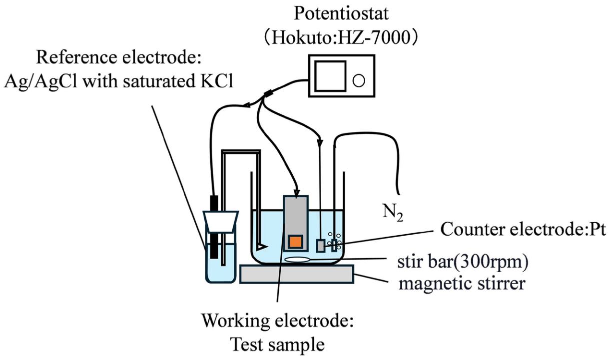

Figure 2. Schematic of anodic polarization curve measurement apparatus.

3. Results and Discussion

3.1. Corrosion Potential Measurement

The measurement results of the corrosion potential are shown in **Figure 3** and **Figure 4**. This shows the average of three measurements.

For untreated water, the corrosion potential of all test specimens increased sharply immediately after immersion. Subsequently, the corrosion potential continued to increase gradually. Untreated water contains corrosive ions such as Cl$^-$ and SiO_4^{2-}. It is considered that these corrosive ions promoted corrosion reactions, causing the corrosion potential to rapidly increase. These reactions formed an oxide film on the surface of the test specimen, which is suggested to have caused the corrosion potential change to become more gradual.

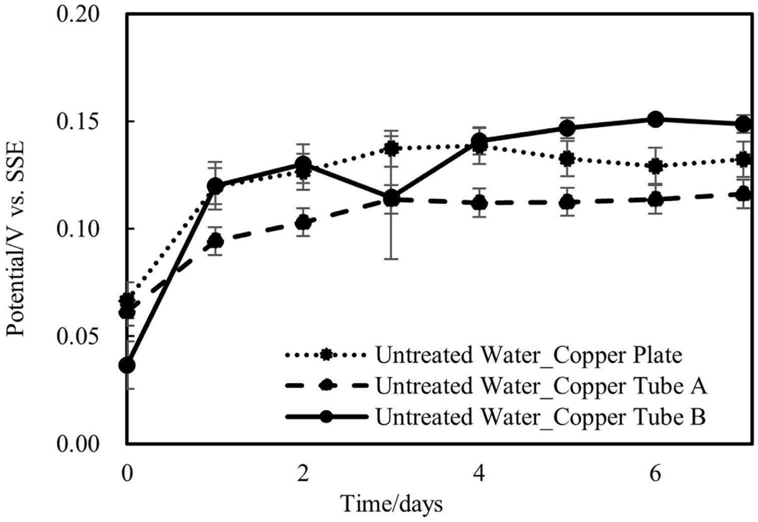

Figure 3. Time-Dependent changes in the corrosion potential of test specimens in test solutions of untreated water. (Stirred at 300 rpm, under room temperature, open-air conditions.)

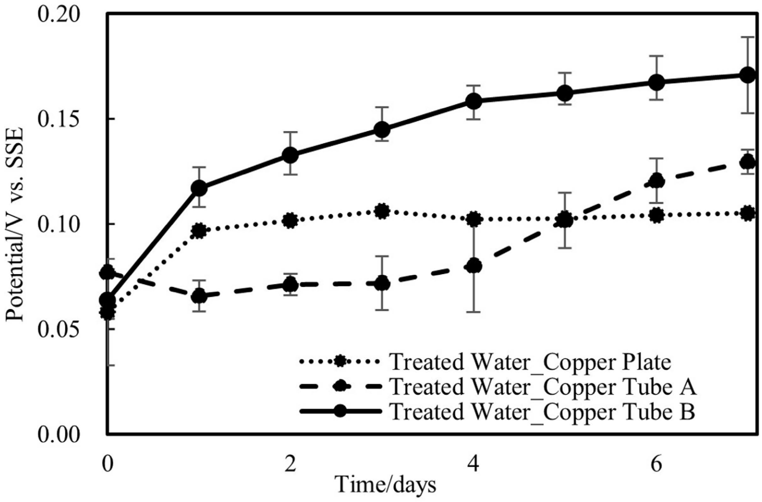

Figure 4. Time-Dependent changes in the corrosion potential of test specimens in test solutions of treated water. (Stirred at 300 rpm, under room temperature, open-air conditions.)

Yamada *et al.* reported that the carbon film formed unevenly on the inner surface of the copper tube [1]. It has also been reported that the coated carbon film areas act as the cathode, while the uncoated copper substrate areas act as the anode [3]. Copper tube A has a low residual carbon amount, suggests that the cathode area on the test surface is small and unevenly distributed. Therefore, it is considered that the initial corrosion potential rise during immersion was smaller for copper tube A than for the copper plate and copper tube B. On the other hand, copper tube B has a high residual carbon amount relative to the test area and a large cathode area. For this reason, it is considered that cathodic reactions proceeded rapidly immediately after immersion, causing the corrosion potential to rise sharply.

For treated water, the corrosion potential on the copper plate and the copper tube B increased sharply immediately after immersion. Following this, the corrosion potential became stabilized. For copper tube A, the corrosion potential changed gradually, immediately after immersion. Both copper plates and copper tubes A and B showed a tendency for the corrosion potential rise to be suppressed during the initial immersion phase, compared to untreated water. In treated water, corrosive ions are replaced by corrosion-inhibiting ions, reducing the concentration of the corrosive ions. For this reason, this suggests that corrosion reactions on all specimens are suppressed, resulting in a lower potential increase compared to untreated water. In particular, for copper tube A, the reduction in the concentration of corrosive ions suppressed localized corrosion reactions, resulting in little change to the corrosion potential immediately after immersion.

3.2. Surface Observation and Analysis

The results of surface observation and analysis are shown in **Figure 5**. In untreated water, greenish-blue corrosion products were observed, regardless of the residual carbon amount. However, in the treated water, greenish-blue corrosion products were not observed, regardless of the residual carbon. **Figure 6** shows SEM images and the results of the EDX analysis for areas where corrosion products were observed and where they were not observed. In the corrosion products, 1.6 mass% of Cl was detected. In the copper base metal areas without corrosion products, Cl was not detected. The area beneath the corrosion was not observed to be pitted. This is considered to be due to the short test period. It has been reported that pitting corrosion of copper tubes progresses due to the influence of Cl^- [13]. Kano *et al.*'s EDX analysis of the pitting area confirmed the accumulation of Cl [14]. Although no pitting was observed directly beneath the corrosion products, the EDS analysis detected Cl^- in the corrosion products. These results are considered consistent with the early stages of pitting corrosion and suggest indications of pitting corrosion occurrence.

3.3. Anodic Polarization Curve Measurement

The results of the anodic polarization curve measurements are shown in **Figure 7** and **Figure 8**. The measurement was performed three times. A similar trend was observed in all these measurements. The data from one of these measurements are shown. For untreated water, the current density increased sharply starting around −0.05 V vs. SSE, regardless of the amount of residual carbon. It then stabilized near 0 V vs. SSE, and the current density gradually increased. Subsequently, for all specimens, the current density increased sharply again starting from around +0.2 to 0.3 V vs. SSE. The polarization potential at which the current density sharply increases again is defined as the Break down potential (BDP). The BDP increased in the order copper tube B < copper tube A < copper plate, and a higher amount of residual carbon tended to cause it to occur on the less noble potential side.

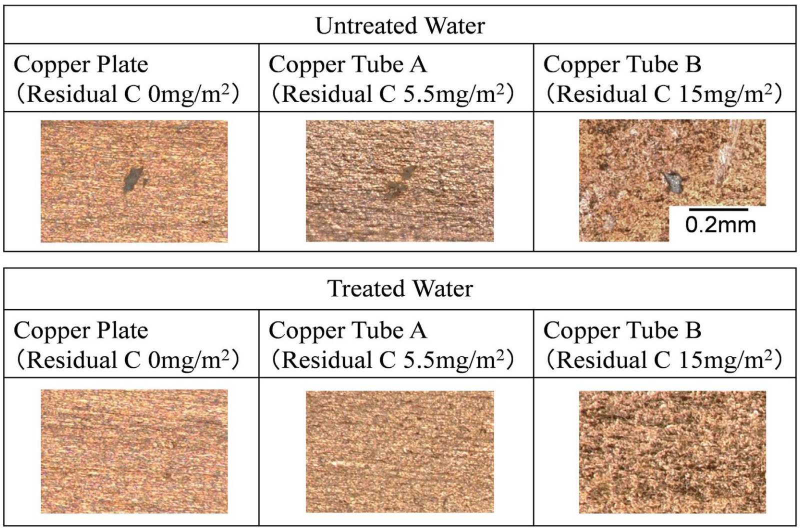

Figure 5. The surface of the copper plate and copper tubes A and B after the corrosion potential was measured with untreated water and treated water.

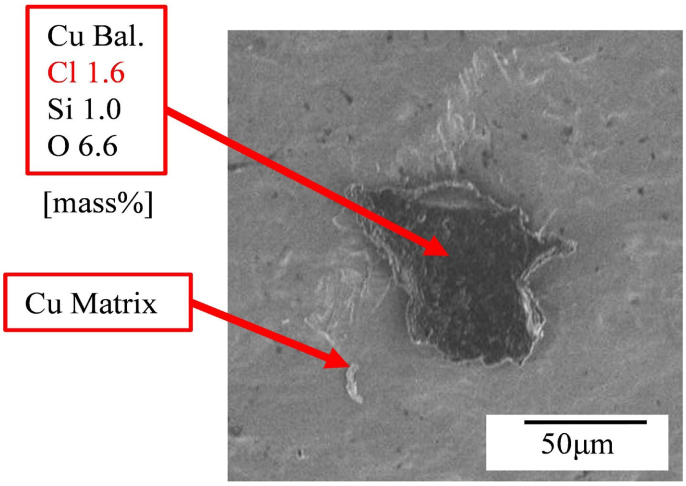

Figure 6. SEM image and the EDX analysis of copper tube B after measurement of corrosion potential with untreated water.

For treated water, the current density increased sharply from around −0.05 V vs. SSE, regardless of the residual carbon amount. Subsequently, for all specimens, the current density stabilized near 0 V vs. SSE. The BDP could not be observed, and the current density could be different.

3.4. The Effects of Treated Water for Carbon Film-Dependent Pitting Corrosion

In solutions containing HEDP and BTA, a composite film forms on the copper surface [5]. Corrosive ions, such as Cl^- and SiO_4^{2-}, act on this composite film, destroying it and inducing pitting corrosion. In untreated water, corrosion products were identified in Section 3.2 and BDP was identified in Section 3.3. Furthermore, as the residual carbon amount increased, BDP was observed on the less noble potential side. It is considered that corrosive ions in untreated water destroy composite films and that with a higher residual carbon amount, the film is more easily damaged. On the other hand, no corrosion products were observed in treated water. Furthermore, BDP was not identified and the current density continued to rise gradually. In treated water, through anion exchange treatment, the concentration of corrosive ions decreases, while the concentration of corrosion-inhibiting ions increases. Therefore, it is suggested that corrosive ions were prevented from damaging the composite film. Furthermore, HCO_3^- acts as a pH buffer and helps maintain the film. In treated water containing water treatment chemicals, it is considered that a film composed of Cu_2O, HEDP, and BTA forms on the copper surface [5] [15]. The presence of HCO_3^- in the treated water is considered to contribute to the formation of a more stable composite film. The effect of HCO_3^- on this film formation is to be investigated in future studies. Furthermore, these results were obtained under the HEDP and BTA concentration and water quality conditions in this study. If these conditions differ, the effects on corrosion could be different. Therefore, further investigations under various water quality conditions are required.

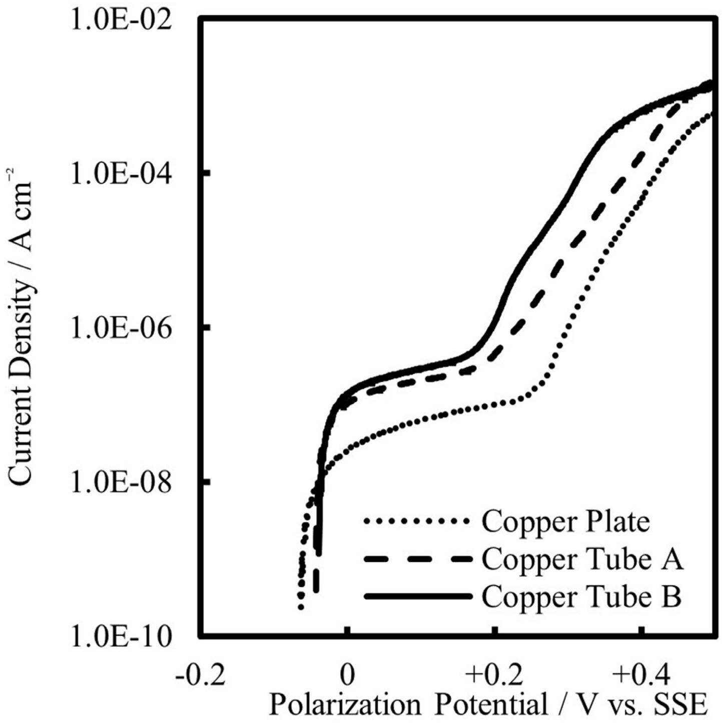

Figure 7. Anodic polarization curves of test specimens in test solutions of untreated water (sweep speed 20 mV/min, stirred at 300 rpm, at room temperature, deoxidized by nitrogen gas.)

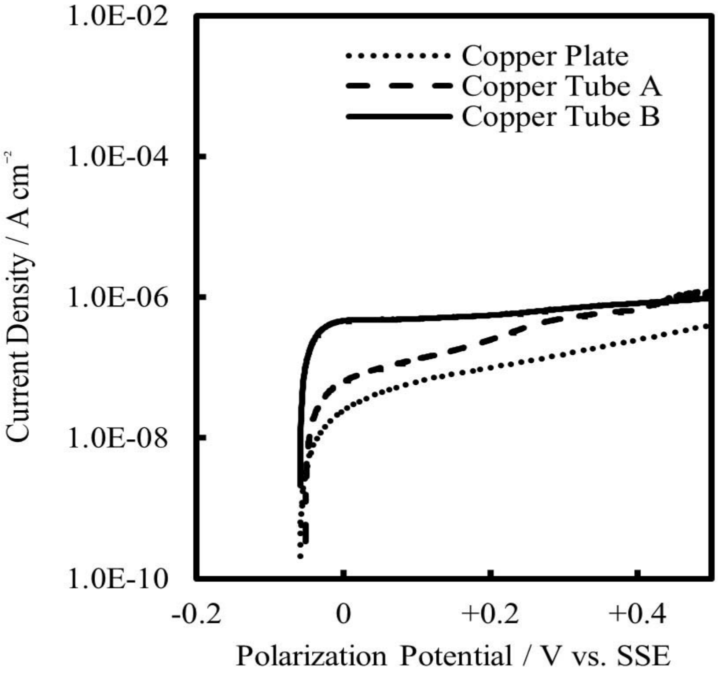

Figure 8. Anode potential curves of test specimens in test solutions of treated water. (Sweep speed 20 mV/min, stirred at 300 rpm, at room temperature, deoxidized by nitrogen gas.)

4. Conclusions

This study investigated the effects of anion-exchange-treated water containing HEDP and BTA on copper pitting corrosion. As a result, the following findings were obtained.

1) In the corrosion potential measurements, the corrosion potential increased and then stabilized for both untreated and treated water, regardless of the residual carbon amount. After the immersion test, greenish-blue corrosion products were observed on the surface of the untreated water test specimens. In contrast, no corrosion products were observed on the surface of the treated water specimens.

2) In the anodic polarization curve measurement of untreated water and treated water, untreated water showed a tendency for current density to increase sharply at the noble potential side, regardless of residual carbon amount. In the treated water, a rapid increase in current density was not observed on the noble potential side.

3) Based on these results, it is considered that corrosion is suppressed in the treated water regardless of the residual carbon amount. Furthermore, the treated water contains high concentrations of corrosion-inhibiting ions; it is considered that these ions caused a dense composite film consisting of HEDP and BTA to form on the copper surface. In the next phase, research will focus on the effects of HCO_3^- on this film.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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