

Effects of Inorganic Ions for Reduction and Growth of Copper Oxides

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For the quantitative characterization of copper corrosion products, the author has developed a new voltammetric method that uses a strongly alkaline solution (6 M KOH + 1 M LiOH) as the supporting electrolyte. Using this method, he investigated the growth mechanism of copper oxides (*i.e.*, Cu₂O and CuO). When copper was heated with no adherent ions supplied, both Cu₂O and CuO formed and grew. However, they showed different growth mechanisms when pre-immersed in salt solutions, and heated under high humidity. Cu₂O grew selectively when copper was pre-immersed in LiCl and LiBr solutions, most likely due to Li⁺ ions permeating into the Cu₂O layer and continuing proportionation (Cu + CuO → Cu₂O). On the contrary, CuO grew at the early stage of heating when copper was pre-immersed in a KOH solution presumably because of the high OH⁻ concentration in the water layer deposited on the copper surface.

Keywords: Copper Oxides, Voltammetry, Strongly Alkaline Electrolyte, Li⁺ Ion

1. Introduction

Beginning thousands of years ago, copper is mankind's longest used metal. Besides its relatively high corrosion resistance, copper has high electrical and thermal conductivity. Owing to these characteristics, copper and its alloys have been widely used to fabricate industrial products, coins, and artifacts. When copper is exposed to air containing moisture and pollutants, however, various corrosion products (*e.g.*, Cu₂O and CuO) are formed on copper surfaces. Copper corrosion products often have a bad influence on industrial products. For example, tarnishing via oxidation frequently reduces the commercial value of copper products.

While this is true, copper oxides have been actively utilized for various applications, such as the adhesion of a copper product and another material,⁽¹⁾ the sealing of electronic packaging,⁽²⁾ and the electrodes of solar cells.⁽³⁾ In the study of solar cells, layers of Cu₂O (bandgap: 2.1 eV)⁽⁴⁾ and CuO (bandgap: 1.35 eV)⁽⁵⁾ were prepared by cathodic deposition from aqueous solutions. For these applications as well as for corrosion management, it is important to perform qualitative and quantitative analyses on different copper species, which have different chemical properties.

A new voltammetric method for the quantitative characterization of copper oxides and other copper species^{(6),(7)} was developed. In this method, the use of a strongly alkaline electrolyte (SAE; *i.e.*, 6 M KOH + 1 M LiOH) allowed perfect separation between two current peaks due to the reduction of Cu₂O and CuO. The specific inhibitory effect of Li⁺ ions on Cu₂O reduction was discovered.

In the atmosphere, Cu(OH)₂ was the initial corrosion product formed on a copper surface. However, the surface Cu(OH)₂ layer did not grow much but dehydrated to become a layer of CuO. For further progress of corrosion, an inner Cu₂O layer was generated by the proportionation reaction between the CuO layer and the base metal Cu. The inner Cu₂O layer grew for the subsequent oxidation until the thickness reached a certain value (~35 nm). For further oxidation, the top CuO layer grew again preferentially over

the inner Cu₂O layer.⁽⁸⁾ It was difficult to generate a single layer of Cu₂O or CuO under normal atmosphere conditions.

Several preparation procedures for copper oxides have been reported.^{(9),(10)} However, no research has shown the formation mechanism of copper oxide.

This paper mainly describes the effects of inorganic ions for the growth of copper oxides. In particular, it reveals that Li⁺ ions had an inhibitory effect⁽¹¹⁾ of further oxidation of Cu₂O in addition to a specific effect on the reduction behavior of Cu₂O.

2. Experimental

2-1 Samples

For the clarification of the effect of alkali metal ions in the reduction mechanism of copper oxides, three standard samples (*i.e.*, Cu₂O/Cu^{(12),(13)}, CuO/Cu⁽¹³⁾ and CuO/Cu₂O/Cu⁽¹²⁾), each having an almost constant thickness (~1 μm) of Cu₂O and/or CuO layer(s) formed on metal Cu were prepared.

Oxide-free copper plates (0.5 mm thick: 99.99% purity) were used for the copper substrate for the growth of oxide layers. Each copper plate was cut into 20 × 50 mm pieces and then etched in 3 M sulfuric acid, followed by rinsing successively with distilled water. Copper plates were heated at 300°C in a muffle furnace, or immersed in various inorganic solutions for 1 hour and then subjected to heating in a temperature/humidity-controlled chamber at 80°C and relative humidity (RH) of 90%.

2-2 Electrochemical measurement

A conventional three electrode electrolytic cell was employed for voltammetric measurements. An Ag/AgCl (in 3 M NaCl) electrode was used as the reference electrode, to which all potentials are referred to in this paper. A platinum wire was used as the counter electrode. Unless otherwise noted, the electrolyte solution used was SAE (6 M KOH + 1 M LiOH), which was not deaerated. All of the reagents used for the preparation of the electrolyte solutions were of

analytical grade. Linear sweep voltammetric (LSV) measurements were carried out using an electrochemical measurement system (Hokuto Denko Co. Ltd., Japan, HZ-5000). A potential sweep was performed from a rest potential to the potential for the hydrogen evolution at various sweep rates in consideration of the thickness of the film of copper oxides. The measurement area was 1.0 or 2.0 cm².

3. Result and Discussion

3-1 Effect of Li⁺ ions in reduction of copper oxides

Adequate separation of the reduction potentials of Cu₂O and CuO was successfully achieved in SAE as a supporting electrolyte.⁽⁶⁾

Figure 1 shows current–potential curves obtained by LSV for three standard samples. As clearly demonstrated in

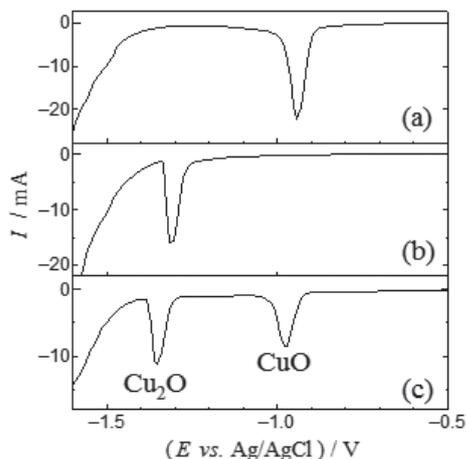


Fig. 1. Current–potential curves recorded by LSV for (a) Cu₂O/Cu, (b) CuO/Cu, and (c) CuO/Cu₂O/Cu samples. Measurement area: 1.0 cm². Scan rate: 1 mV/s.

the figure, CuO is firstly reduced, prior to the reduction of Cu₂O. The mass of each oxide layer can be calculated using Faraday's Law from each peak area, *i.e.*, the quantity of electricity required for the reduction of the oxide layer. A highly selective determination of Cu₂O and CuO can be performed using SAE.

Figure 2A⁽¹⁴⁾ shows current–potential curves recorded by LSV for the Cu₂O/Cu and CuO/Cu in 1.0 M of alkali hydroxides (*i.e.*, LiOH, NaOH, and KOH).

As can be seen in the figure, the reduction of Cu₂O is thermodynamically easier in the order of KOH > NaOH > LiOH. On the other hand, the reduction potential of CuO is hardly affected by the kind of alkali hydroxide, as also shown in Fig. 2A. As a result, a good separation of the reduction potentials of Cu₂O and CuO could be achieved in 1.0 M LiOH (see Fig. 2B). Also, when KOH is used, the reduction potential of Cu₂O shifted to lower values with an increase in KOH concentration.⁽¹⁵⁾ A sufficient separation between the two reduction potentials is achieved with LiOH rather than with KOH. It has thus been found that, although the solution alkalinity has a definitive effect, Li⁺ ions have a specific effect on the reduction behavior of Cu₂O. Taking into consideration the solubility of reagents, SAE has been proposed as the best electrolyte for the selective determination of copper oxides.

3-2 Normal heating without pre-immersion

In the absence of corrosive gases, the major corrosion products of copper are its oxides (*i.e.*, Cu₂O and CuO). In the atmosphere, Cu₂O is first formed, followed by the formation of CuO and its growth by further oxidation.^{(6),(8)} Figure 3 shows current–potential curves for the copper plates heated at 300°C for 10–30 minutes. The peaks of Cu₂O and CuO appeared and grew together. In the initial stage of corrosion, however, Cu₂O seems to have formed before CuO, because Cu₂O was the main oxide species formed by heating at a lower temperature, *i.e.*, 250°C for 10 minutes (data not shown). The corrosion behavior at higher temperatures such as 300°C was relatively simple. The corrosion products were only CuO and Cu₂O.

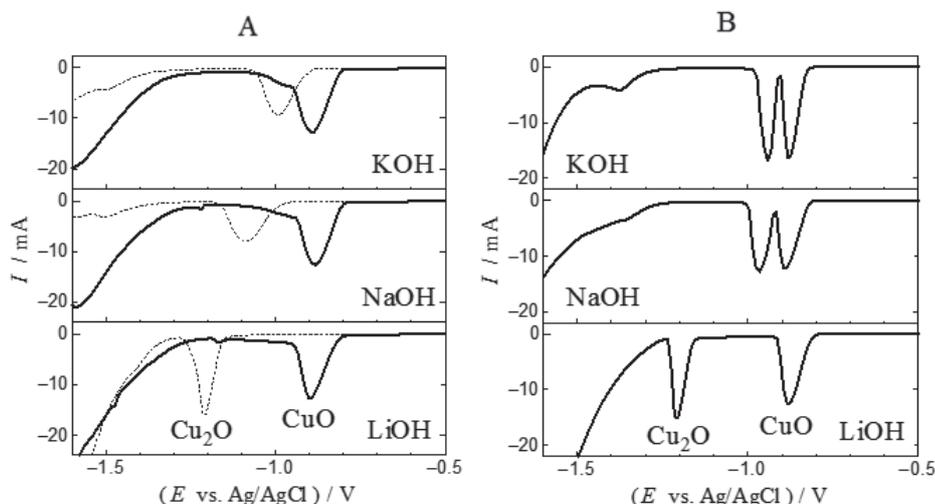


Fig. 2. Current–potential curves recorded by LSV for (A) Cu₂O/Cu (dashed line) and CuO/Cu (solid line) and (B) CuO/Cu₂O/Cu in 1.0 M of three alkali hydroxides. Measurement area: 1.0 cm². Scan rate: 1 mV/s.

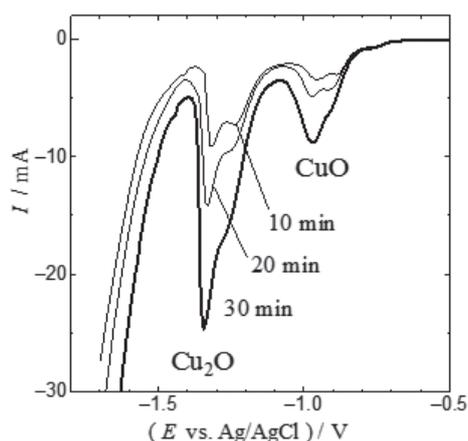


Fig. 3. Current-potential curves recorded by LSV for copper plates heated at 300 °C for 10, 20, 30 min. Measurement area: 2.0 cm². Scan rate: 10 mV/s.

Figure 4 shows current-potential curves recorded by LSV for copper plates heated at 80 °C and RH 90%.⁽⁸⁾

A current peak is observed around -0.8 V for the sample treated for a short period (*i.e.*, 10 minutes). Referring to the results for standard powder samples,⁽⁸⁾ the peak may be ascribed to the reduction of Cu(OH)₂. Prolonging the treatment period around 30 minutes, the reduction peak of Cu₂O appeared at -1.3 to -1.4 V and then grew with an increase in the treatment period around 1 day. The limiting thickness of the Cu₂O layer is likely the result from the competition of the proportionation reaction ($\text{Cu} + \text{CuO} \rightarrow \text{Cu}_2\text{O}$)⁽¹⁶⁾ and the CuO formation ($\text{Cu}_2\text{O} + (1/2)\text{O}_2 \rightarrow 2\text{CuO}$). The threshold value of the Cu₂O-layer thickness (~35 nm) probably depends on unknown factors that govern the kinetics of the competing reactions.

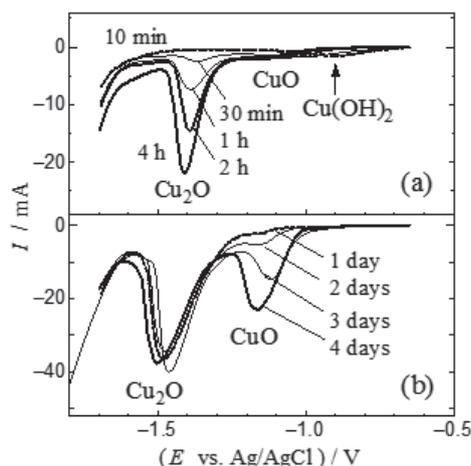


Fig. 4. Current-potential curves recorded by LSV for copper plates heated at 80 °C and RH 90% for (a) 10 min–4 h and for (b) 1–4 days. Measurement area: 2.0 cm². Scan rate: 100 mV/s. Scan rate: 100 mV/s.

3-3 Growth mechanism of copper oxides after pre-immersion in salt solutions

Copper plates were prepared by pre-immersion in various salt solutions, followed by heating in air at 80 °C and RH 90%. The formation kinetics of each oxide film followed the parabolic rate law with a few exceptions.⁽⁶⁾ The effects of pre-immersion of copper samples in various 0.1 M sodium salt solutions (*i.e.*, NaCl, Na₂SO₄ and NaNO₃) on the growth of oxide layers were studied.⁽¹⁷⁾ The growth rate of copper oxides on a copper surface was fastest with pre-immersion in 0.1 M NaCl. As seen in Fig. 4 as well, there was a time lag after the initiation of Cu₂O formation before the CuO began to grow. In the case of pre-immersion in NaNO₃, CuO grew selectively.

Based on the specific effect of Li⁺ ions on the reduction behavior of Cu₂O, other salts were used for pre-immersion. Figure 5 shows current-potential curves recorded by LSV for copper plates heated at 80 °C and RH 90%. Three 0.1 M salt solutions (*i.e.*, KCl, LiCl and Li₂SO₄) were used for pre-immersion. In Fig. 5(a), both Cu₂O and CuO grew with the heating period. On the contrary, Cu₂O selectively grew in (the case of using) LiCl solution for pre-immersion. About 1 μm of Cu₂O layer was confirmed after a heating period of 3 days. In Fig. 5(c), reduction peaks of copper oxides were not detected on this current scale. The difference was observed in oxidation performance on copper surfaces between LiCl and Li₂SO₄. This must have been due to the difference in complex forming power between chloride ions and sulfate ions.

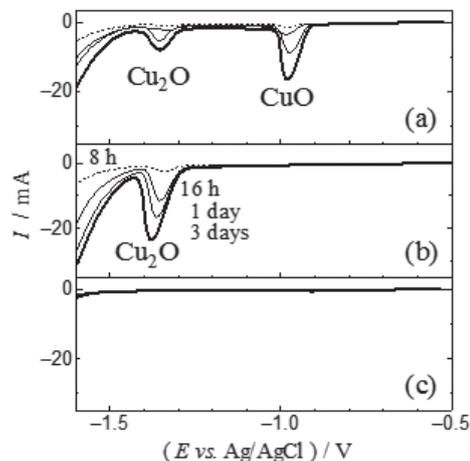


Fig. 5. Current-potential curves recorded by LSV for samples prepared by pre-immersion of copper plates in (a) 0.1 M KCl, (b) 0.1 M LiCl, and (c) 0.1 M Li₂SO₄, followed by heating in air at 80 °C and RH 90% for 8, 16 h and 1 day, and 3 days. Measurement area: 2.0 cm². Scan rate: 2 mV/s.

Figure 6 shows current-potential curves recorded by LSV heated at 80 °C and RH 90%. Two 0.1 M salt solutions (*i.e.*, BrCl and LiCl) were used for pre-immersion. As shown in Fig. 6 (a), Cu₂O grew selectively when using LiCl for pre-immersion as well. Bromide ions probably possess complex forming power in the same manner as chloride

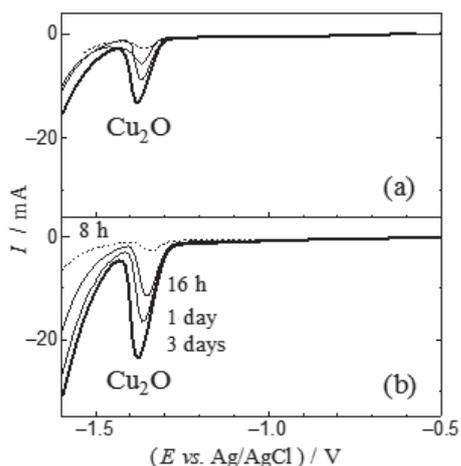


Fig. 6. Current-potential curves recorded by LSV for samples prepared by pre-immersion of copper plates in (a) 0.1 M BrCl and, (b) 0.1 M LiCl, followed by heating in air at 80°C and RH 90% for 8, 16 h and 1 day, and 3 days. Measurement area: 2.0 cm². Scan rate: 2 mV/s.

ions. However, the amounts of Cu₂O were half compared with using LiCl.

Figure 7 shows current-potential curves recorded by LSV for copper plates heated at 80°C and RH 30%, 60%, 90%. 0.1 M LiCl was used for pre-immersion. Under low RH conditions, the Cu₂O-layer did not grow too much.

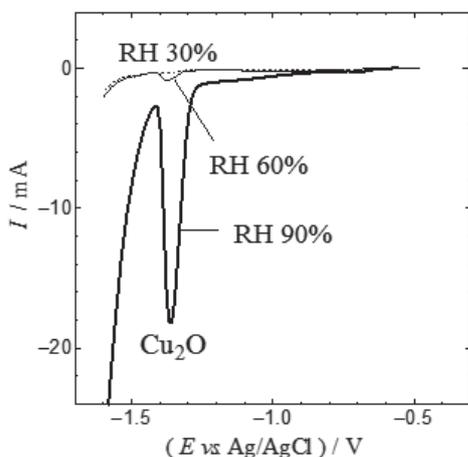
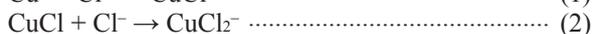
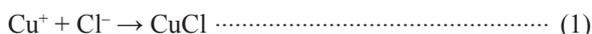


Fig. 7. Current-potential curves recorded by LSV for copper plates heated at 80°C and RH 30, 60, 90% for 2 days. Measurement area: 2.0 cm². Scan rate: 2 mV/s.

In the presence of chloride ions, dissolved species of monovalent Cu⁺ would react with Cl⁻ to form CuCl, which is more stable than CuOH. CuCl would dissolve in the solution as a Cu chloride complex ion, and at the same time would yield Cu₂O through hydrolysis. This reaction seemed to be accelerated under high humidity conditions.



Current-potential curves in Fig. 4 show that CuO grew rapidly when the Cu₂O-layer was more than a certain level under normal heating treatments. On the contrary, Cu₂O grew selectively when a 0.1 M LiCl solution was used for pre-immersion. As the ionic radius of Li⁺ ions is very small, Li⁺ ions probably entered the Cu₂O-layer, and then could continue the proportionation reaction (Cu + CuO → Cu₂O) by the high ion conductivity of inserting Li⁺ ions.

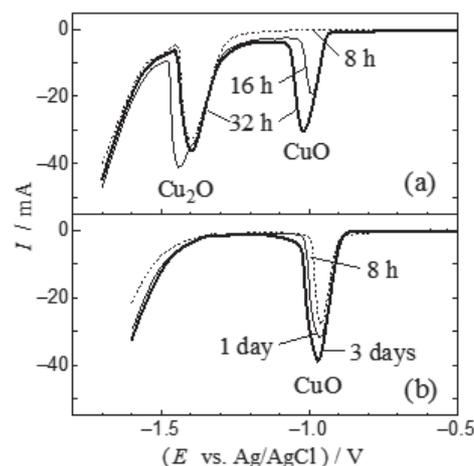
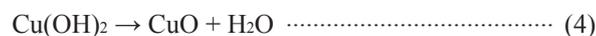


Fig. 8. Current-potential curves recorded by LSV for copper plates (A) incubated in 1 M NaOH at 30°C for 8-32 hours, and (B) prepared by pre-immersion in (a) 0.1 M NaOH, followed by heating in air at 80°C and RH 90% for 8 hours, 1 day, and 3 days. Measurement area: 2.0 cm². Scan rate: (A) 10 mV/s, (B) 2 mV/s.

Figure 8 (a) shows the current-potential curves recorded for the copper plates incubated in 1 M NaOH at 30°C for 8-32 hours. Cu₂O grew with an increase in the immersion period around 8 hours. However, the reduction peak of Cu₂O at around -1.4 V was almost constant in height for the immersion periods of 8-32 hours. It was speculated that with heating treatment of more than 8 hours, the oxide film had a homogeneously covered CuO-layer (CuO/Cu₂O/Cu⁽¹²⁾) in which the inner Cu₂O-layer was stabilized. After the growth of Cu₂O stopped, a CuO-layer grew rapidly, as can be seen in the figure. After 16 hours of incubation, the copper surface became black.

Figure 8 (b) shows current-potential curves recorded by LSV for heated copper plates previously immersed in 0.1 M NaOH. Differing from the current-potential curves in Fig. 8 (a), CuO grew selectively for increasing heating periods. The early start of CuO formation was probably due to a high OH⁻ concentration in the water layer deposited on the Cu surface and the resultant quick saturation of Cu(OH)₂. Cu(OH)₂ is converted by dehydration to CuO according to the reaction



As mentioned above, Cu₂O or CuO grew selectively

on copper surfaces heated under high humidity conditions (e.g., 80°C + RH90%) on copper plates previously immersed in specific salt solutions.

4. Conclusion

A new voltammetric method using SAE as the supporting electrolyte was mainly applied for the investigation of the growth mechanism of copper oxides. Effects of various adherent inorganic ions were studied, and the following conclusions were drawn.

1. Under normal heating treatments using no adherent ions on a copper surface, both Cu₂O and CuO formed and grew. It was difficult to generate a single layer of Cu₂O or CuO. At an early stage of the oxidation of copper, Cu₂O grew selectively. However, the growth of the inner Cu₂O layer appeared to stop after a certain time lag under the given conditions. Instead, the surface CuO layer grew rapidly.
2. Different growth mechanisms of copper oxides under a high humidity condition using various salts for pre-immersion of copper plates were shown. Cu₂O grew selectively on copper surfaces due to adherent Li⁺ ions and halogen ions (i.e., Cl⁻ and Br⁻). Li⁺ ions probably enter in the Cu₂O-layer, and then could continue the proportionation reaction inhibiting the growth of CuO. In the case of using a KCl solution, both Cu₂O and CuO grew. On the contrary, CuO grew selectively from the early stage of heating on copper plates pre-immersed in a KOH solution. This behavior was perhaps due to the high OH⁻ concentration in the water layer deposited on the copper surface.

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Technical Term

- *1 Voltammetry: Voltammetry is one of the most applied electrochemical method for analyzing redox reactions on a working electrode. By sweeping a potential of the electrode, a current responding to the potential is measured.

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