Highly Selective Determination of Copper Corrosion Products by Voltammetric Reduction

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A new voltammetric method using a strongly alkaline electrolyte (SAE; *i.e.*, 6 M KOH + 1 M LiOH) as the supporting electrolyte was developed for the quantitative characterization of copper corrosion products. Conventional chronopotentiometric method using 0.1 M KCl as the electrolyte has been most frequently used for selective determination of copper oxides (Cu_2O and CuO) formed on copper surfaces. However, there have been two serious problems. One is the conflicting view regarding the order of reduction of the oxides, and the other is the poor separation between Cu_2O and CuO. In 2001, the author successfully employed SAE to achieve a perfect separation of the reduction peaks of the two oxides. It was then found that the oxides were reduced in SAE according to a thermodynamic order, *i.e.,* "$CuO \rightarrow Cu_2O$." It has also been shown that the developed method with SAE can be applied to analyse various corrosion products including Cu_2S, $Cu(OH)_2$, and also patinas. Use of the developed method has allowed researchers to clarify the mechanism of the atmospheric corrosion of copper.

1. Introduction

In 2015, the author was awarded the Technical Achievement Award by the Japan Society for Analytical Chemistry, for the study on "Highly Selective Determination of Copper Corrosion Products by Voltammetric Reduction." In 2001, the first report[1] on this study was published in *Journal of the Electrochemical Society*. After continuing the study, a review article[2] was published in *Analytical Sciences* in 2012. A series of the author's study has shown that the use of a strongly alkaline electrolyte (SAE; 6 M KOH + 1 M LiOH), which is completely different from conventional ones, enables us to determine copper corrosion products quantitatively. A wide application of this method in copper corrosion analysis is quite promising.

2. Background of Investigation of the New Electrochemical Method

Copper is the metal that has been used longest by mankind for thousands of years. Besides its relatively high corrosion resistance, copper has characteristics of high electrical and thermal conductivities. Therefore, 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 are formed on copper surfaces. It is generally known that cuprous oxide (Cu_2O) forms at an early stage of the corrosion process. Upon further oxidation, a new top layer of cupric oxide (CuO) grows preferentially over the Cu_2O layer. Eventually, corrosion products on copper change to a stable patina. In addition, copper sulfides, mainly cupric sulfide (Cu_2S), are formed on copper surfaces in air containing H_2S or in a solution containing S^{2-} ions.

Copper corrosion products often have a bad influence on industrial products. Tarnishing by oxidation frequently reduces the commercial value of copper products. Other problems have also been reported. Since the corrosion products formed on copper have different properties, their qualitative and quantitative analyses are important for clarification of the corrosion mechanism and for corrosion protection. For selective analysis of copper corrosion products, surface analytical techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) have been extensively employed. These spectroscopic techniques are very useful for qualitative analysis, but are not necessarily adequate for quantitative analysis. Electrochemical techniques provide more reliable information on the "quantities" of copper corrosion products. Chronopotentiometry (CP) using a neutral or weak alkaline electrolyte such as 0.1 M (M = mol dm^{-3}) KCl or 0.1 M Na_2CO_3 has been most frequently applied for quantitative analysis of copper oxides (Cu_2O and CuO) or cuprous sulfide (Cu_2S). However, this conventional method has serious problems including (1) an obscurity about the reduction order of copper oxides and (2) a poor separation between the reduction potentials of Cu_2O and CuO. The first report[3] in this area for the use of CP, published in 1937, claimed that the reduction of Cu_2O occurred firstly, followed by the reduction of CuO, however, no convincing evidence was presented.[4]

On the basis of the above-mentioned background, the author carried out this study to develop a more reliable method for quantitative determination of copper corrosion products. The method selected was voltammetry, which provides, under appropriate measurement conditions, peak-like signals that are easy to analyze.

3. Developed New Voltammetric Method

3-1 Estimation of copper oxides

So far, mainly two oxides (*i.e.*, Cu_2O and CuO) have been analyzed by conventional electrochemical methods. For the development of the new voltammetric

method, the study was focused on the reduction order and the peak separation of two oxides.

3-1-1 Reduction order of two oxides

In order to study comprehensively the performance of the developed method, the author prepared three standard samples (*i.e.*, Cu_2O/Cu[5], CuO/Cu[5] and $CuO/Cu_2O/Cu$[6]), which are schematically shown in Fig. 1. The thickness of copper oxide films in each sample was standardized to around 1 μm. To the author's knowledge, there have been only a few studies, in which the reduction mechanism of copper oxides was investigated by using standard samples. However, the previous standard samples were composed of a rather thin and not fully identified oxide layer.[7],[8]
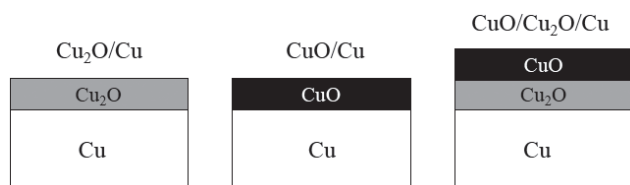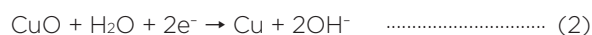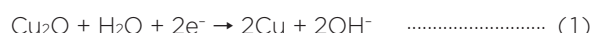

Fig. 1. Schematic representation of the cross-sections of three standard samples

A good separation of the reduction potentials of Cu_2O and CuO could be achieved in SAE as a supporting electrolyte.[1] Figure 2A shows current–potential curves obtained by linear sweep voltammetry (LSV) with SAE for three standard samples. As clearly demonstrated in the figure, CuO is firstly reduced, prior to the reduction of Cu_2O. It should be noted here that the LSV measurements were made without deaeration of the electrolyte, because the voltammograms are not entirely changed by deaeration. The reduction current of dissolved oxygen appears to be very low compared with the reduction currents of the copper oxides. Thus, a highly selective analysis of Cu_2O and CuO can be performed using SAE. On the other hand, when 0.1 M KCl is used, no clear separation was found as shown in Fig. 2B. In order to determine which oxide is first reduced in 0.1 M KCl, the author prepared several copper samples with enough amounts of Cu_2O and CuO. After partial reduction of copper oxides in 0.1 M KCl, copper surfaces were analyzed by XRD etc. It was cliarified that the reduction of CuO also occured first, followed by the reduction of Cu_2O, in 0.1 M KCl.

3-1-2 Quantitative capability of voltammetry using SAE

On the basis of the results shown in Fig. 2A, it can be considered that the respective two oxides are reduced according to:

$$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$CuO + H_2O + 2e^- \rightarrow Cu + 2OH^- \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Thus, CuO as well as Cu_2O is reduced to metal Cu in one step. If CuO was reduced in two steps, *i.e., via* the intermediate Cu_2O, a reduction peak for Cu_2O would be observed in the voltammogram for CuO in panel (a) of Fig. 2A. The mass of each oxide layer can be calculated using Farady's law from each peak area, *i.e.*, the quantity of electricity required for the reduction of the oxide layer. If the oxide density is equal to the theoretical one, the mass gain can be converted to the average thickness of the oxide layer. In order to investigate the quantitative capability of the voltammetry using SAE, an inert gas fusion analysis was applied for determining the amounts of oxygen in Cu_2O/Cu and CuO/Cu samples.[5] Since their values converted to the weights of Cu_2O and CuO showed close agreement with those obtained by voltammetry, it was concluded that accurate amounts of copper oxides can be obtained by voltammetry using SAE.
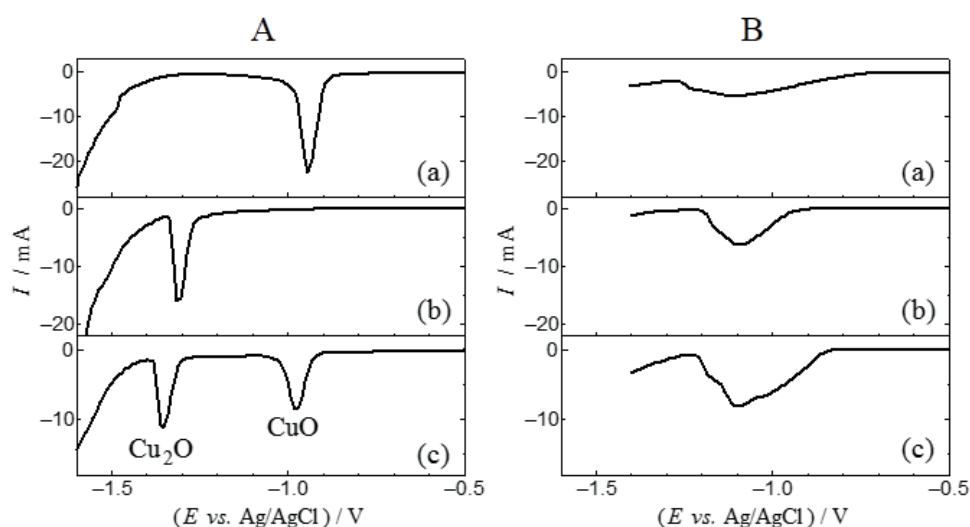

Fig. 2. Current–potential curves recorded by LSV for (a) Cu_2O/Cu, (b) CuO/Cu, and (c) $CuO/Cu_2O/Cu$ samples. Measurement area: 1.0 cm². Electrolyte solution: (A) SAE and (B) 0.1 M KCl. Scan rate: 1 mV s⁻¹.

3-1-3 Effects of electrolyte

As described above, SAE was found to be a very favorable electrolyte for the selective determination of Cu_2O and CuO, compared with conventional electrolytes such as 0.1 M KCl. There are two principal factors related to the advantages of SAE[9], i.e., (1) Li^{+} ions and (2) high alkalinity.

Figure 3A shows current–potential curves recorded by LSV for the Cu_2O/Cu and CuO/Cu in 1.0 M of alkali hydroxides (LiOH, NaOH, and KOH). As can be seen in the figure, the reduction of Cu_2O is thermodynamically easier in the order of KOH > NaOH > LiOH. A similar dependence has been observed when alkali chlorides (LiCl, NaCl, and KCl) are used as the supporting electrolytes[10], although neutral solutions are inadequate for the analysis of real samples containing patinas.[10] On the other hand, as also shown in Fig. 3A, the reduction potential of CuO is hardly affected by the kind of alkali hydroxide. As a result, a good separation of the reduction potentials of Cu_2O and CuO could be achieved in 1.0 M LiOH (see Fig. 3B). Also when KOH is used, the reduction potential of Cu_2O is shifted to lower values with an increase in KOH concentration.[9] A sufficient separation between the two reduction potentials may be achieved for KOH concentrations of > 6 M. However, a much higher concentration than that of LiOH is required for KOH. It has thus been found that, though the solution alkalinity has a definitive effect, Li^{+} ions have a specific effect on the reduction behavior of Cu_2O.

Taking into consideration the solubility of reagents, we have then proposed "6 M KOH + 1 M LiOH" as the best electrolyte for the selective determination of copper oxides.

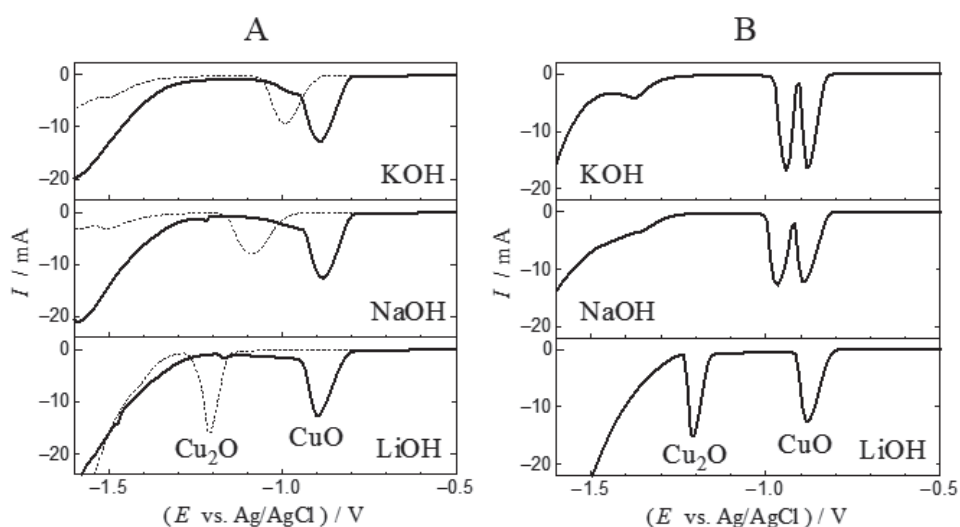Figure 4A shows electrochemical impedances for reduction of the Cu_2O/Cu sample in the three different

Fig. 3. Current–potential curves recorded by LSV for (A) Cu_2O/Cu (dashed line) and CuO/Cu (solid line) and (B) CuO/Cu_2O/Cu in 1.0 M of three alkali hydroxides. Scan rate: 1 mVs[−1].
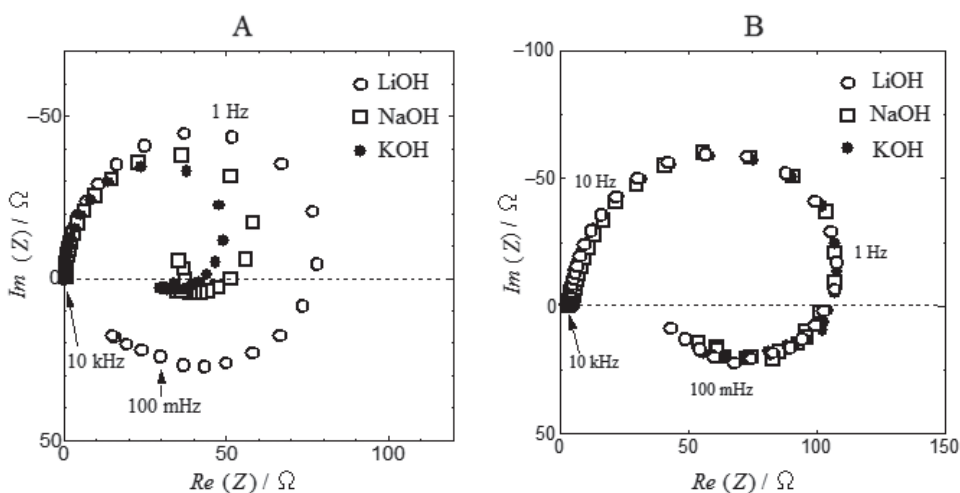

Fig. 4. Electrochemical impedances of (A) Cu_2O/Cu and (B) CuO/Cu in 1.0 M LiOH, 1.0 M NaOH, and 1.0 M KOH. DC current: −1.0 mA. AC current: 0.1 mA.

alkali hydroxides.[9] In each case, a capacitive loop is observed in the upper part of the complex plane. The diameter of the capacitive loop corresponds to the charge–transfer resistance (R_{ct}) for the reduction of Cu_2O. The value of R_{ct} increased with increase in the solution alkalinity. It should also be noted that R_{ct} was largest for LiOH and decreased in the order of LiOH > NaOH > KOH. Thus, it has been shown that Li+ ions have an increasing effect on R_{ct}, *i.e.*, an inhibitory effect on the reduction of Cu_2O. As also shown in Fig. 4, a characteristic inductive loop[11] was observed in the low-frequency range for most measurements. This loop probably indicates the existence of some reaction intermediate. The specific inhibitory effect of Li+ ions on Cu_2O reduction might be explained by a possible stabilization of CuOH by Li+ ions.

On the other hand, the electrochemical impedance of CuO (Fig. 4B) was hardly affected by the kind of alkali hydroxide. These results are in harmony with the LSV data shown in Fig. 3A. When LiOH is used, a sufficient separation of the reduction peaks for Cu_2O and CuO can be achieved at concentrations of > 0.2 M.
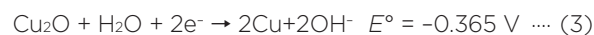
3-2 Analysis of copper sulfides

Researchers in the field of copper corrosion have been interested in copper sulfides besides copper oxides. Among the various copper sulfides, Cu_2S is the most common corrosion product. Like copper oxides, copper sulfides cause various discolorations of copper surfaces, depending on the thickness of the sulfide layer.[12]

Figure 5 shows current–potential curves for commercially available powder samples of Cu_2O, CuO, Cu_2S, and $Cu(OH)_2$, which were recorded using two different electrolytes: (a) 0.1 M KCl and (b) SAE.

The powder samples were prepared by kneading into a carbon paste and sticking the paste onto a glassy

carbon disk electrode.[13] In the same manner as that for the above-shown plate samples (*e.g.*, in Fig. 2), the reduction peaks of the powder Cu_2O and CuO samples were more clearly separated in SAE than in 0.1 M KCl. In contrast, the reduction peaks of Cu_2S were not greatly affected by the kind of electrolyte.

The peak for Cu_2S emerged at a slightly higher potential than that of Cu_2O in SAE. The order of the observed reduction potentials was inconsistent with that predicted from thermodynamic consideration. The reduction reactions for Cu_2O and Cu_2S are expressed as follows:

$$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \quad E° = -0.365 \text{ V} \quad \cdots (3)$$

$$Cu_2S + 2e^- \rightarrow 2Cu + S^{2-} \qquad E° = -0.898 \text{ V} \quad \cdots (4)$$

The electrochemical impedance of Cu_2O reduction depended appreciably on the type of electrolyte. In SAE, R_{ct} was incomparably greater than that in 0.1 M KCl. This suggested that the reduction of Cu_2O was strongly suppressed in SAE. Meanwhile, the values of R_{ct} for Cu_2S reduction were comparable in the two types of electrolytes.[14] This behavior was compatible with the small difference in the reduction potential of Cu_2S in the two electrolytes (Fig. 5). Since the reduction of Cu_2O was selectively and strongly suppressed in SAE, the reduction order of Cu_2O and Cu_2S was inverted depending on which electrolyte was used.

3-3 Growth mechanism of copper oxides

In the absence of corrosive gases such as H_2S, major corrosion products of copper in the air are its oxides (*i.e.*, Cu_2O and CuO). It has been reported that Cu_2O is first formed, followed by the formation of CuO by further oxidation.[1],[15] The types of adherent anions influenced the different growth mechanisms of copper oxides.[16] Besides the oxides, copper hydroxides {mainly, $Cu(OH)_2$} may be formed in air. However, no electrochemical method for analyzing the formed $Cu(OH)_2$ layer has been reported. The author successfully employed the voltammetric method with SAE to clarify the growth mechanism of copper oxides and $Cu(OH)_2$ for atmospheric corrosion.

Figure 6 shows current-potential curves recorded by LSV with SAE for copper plates heated at 80°C and relative humidity (RH) 90%.[15] A current peak is observed around –0.8 V for the sample treated for a short period (*i.e.*, 10 min). Referring to the results for standard powder samples in Fig. 5 (b), one may be ascribed to the reduction of $Cu(OH)_2$. Prolonging the treatment period up to more than 30 min, the reduction peak of Cu_2O appeared at –1.3 to –1.4 V and then grew with an increase in the treatment time up to at least 1 day. The limiting thickness of the Cu_2O layer might result from the competition of the proportionation reaction (Cu + CuO → Cu_2O)[17] and the CuO formation ($Cu_2O + (1/2)O_2 \rightarrow 2CuO$).

The threshold value of the Cu_2O-layer thickness probably depends on unknown factors that govern the kinetics of the competing reactions.
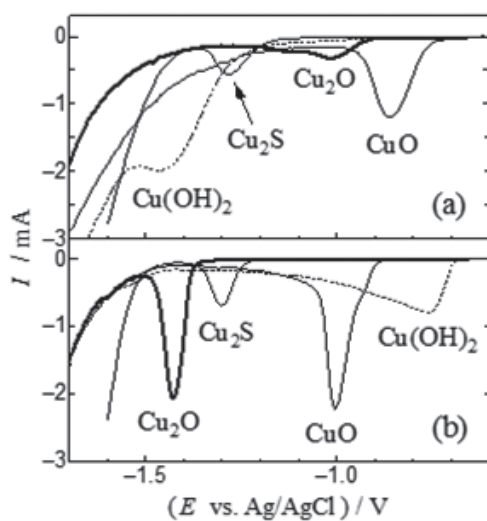

Fig. 5. Current–potential curves recorded by LSV for powder samples. Electrolyte solutions:
(a) 0.1 M KCl, (b) SAE. Scan rate: 10 mVs⁻¹. Similar data were reported in ref. 13.
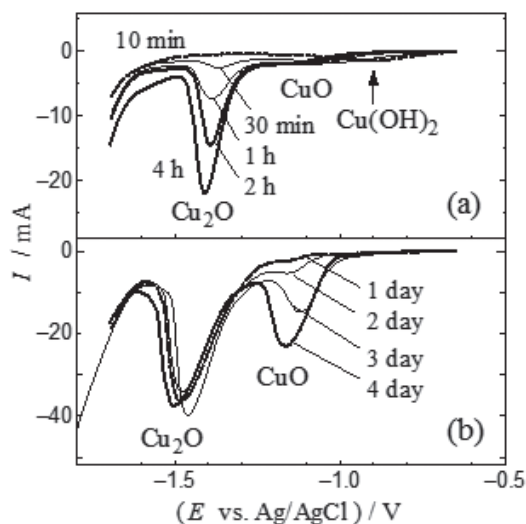
Fig. 6. Current–potential curves recorded by LSV for copper plates heated at 80 °C and RH 90% for (a) 10 min–4 h and for (b) 1 day–4 day. Electrolyte solution: SAE. Scan rate: 100 mV s^{-1}

3-4 Analysis of Patina

"Patina" is the general term for "rusts of copper" produced by long-term exposure to air[18], and it is basic copper minerals which includes basic copper chlorides, sulfides, carbonates, and others. Basic copper sulfates are the main chemical species of the patinas on the Statue of Liberty in New York. The peak of patinas obtained by LSV with SAE is similar to that of Cu(OH)$_2$.[2] However, patinas is difficult to be reduced in 0.1 M KCl.[19] By immersing patinas in SAE, the species are changed to Cu(OH)$_2$.

Figure 7 shows current–potential curves for an electric copper wire of 2 mm-ø (*ca.* 1 cm), which was wired in the air for about 20 years. As shown by the solid line, the well-defined cathodic peak at –1.4 V showed the presence of Cu$_2$O, whereas the broad cathodic peak appearing at a less negative potential showed the presence of another corrosion product(s). In order to identify the corrosion product(s), XRD measurements were performed for the wire samples not reduced and partially reduced by stopping the voltammetric potential scan at –1.2 V (see the current–potential curve shown by a dotted line in Fig. 7A). For the non-reduced sample shown in Fig. 7B (a), besides Cu$_2$O, two basic copper sulfides, *i.e.*, brochantite (Cu$_4$SO$_4$(OH)$_6$) and posnjakite (Cu$_4$SO$_4$(OH)$_6 \cdot$H$_2$O) were identified. For the partially-reduced sample shown in Fig. 7 (b), however, no XRD peaks for the basic copper sulfides were observed. Therefore, the broad cathodic peak at around –0.85 V may be ascribed to the reduction of basic copper sulfides.

When brochantite is immersed in SAE, SO$_4^{2-}$ ions in patina are exchanged with OH$^-$, and then converted to Cu(OH)$_2$.[19] As a result, the current–potential curve of brochantite in SAE is similar to that of Cu(OH)$_2$. Same behaviors were confirmed for other patinas. Obvious peaks seemed not to be obtained in 0.1 M KCl because this exchange reaction did not occurred. SAE is an efficient electrolyte for the analysis of patinas by extremely-high alkalinity of SAE.

In recent publications, the author has described the recommended procedure and its instructions[20],[21] for voltammetric determination of copper corrosion products.

4. Conclusion

Based on the results of the voltammetric study of copper corrosion, the following conclusions have been reached:
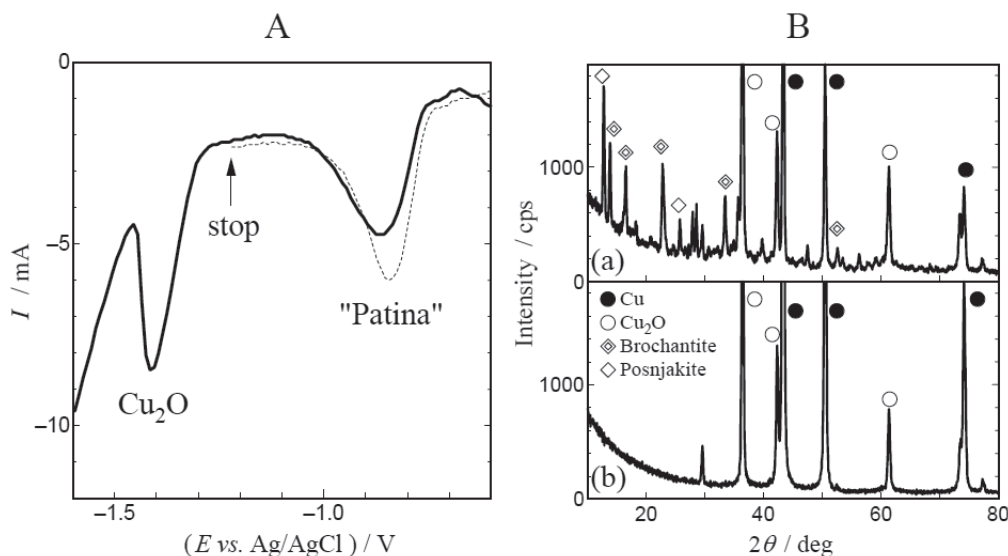

Fig. 7. (A) Current–potential curves recorded by LSV for an electric copper wire. For the curve shown by a dotted line, the voltammetric scan was stopped at –1.2 V. Sweep rate: 1 mVs^{-1}. (B) XRD patterns for the wire samples (a) not reduced and (b) partially reduced by stopping the voltammetric scan as shown by the dotted line in panel (A).

1) Using SAE, a perfect separation can be achieved between the reduction peaks of Cu_2O and CuO.

2) Using a conventional neutral electrolyte (0.1 M KCl), the reduction peaks of the two oxides are overlapped. This has probably led to the two conflicting views about the reduction order of the oxides.

3) The good separation between the reduction peaks of Cu_2O and CuO in SAE can be ascribed mainly to the specific inhibitory effect of Li^+ ions on the Cu_2O reduction.

4) The developed method can also be applied to the selective detection of Cu_2S and $Cu(OH)_2$ in the case of coexistence of copper oxides.

5) The developed method has been successfully applied to clarify the mechanism for atmospheric corrosion of copper, in which $Cu(OH)_2$ plays an initial key role.

6) The possibility for further application to the analysis of patinas were suggested. The fast exchange reaction presumably occurred between SO_4^{2-} or CO_3^{2-} ions in patinas and OH^- ions in SAE, so that the reduction peak of patina could be observed at potentials close to that of $Cu(OH)_2$.

5. Acknowledgements

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