

Mechanistic Study by Electrochemical Impedance Spectroscopy on Reduction of Copper Oxides in Neutral Solutions

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Electrochemical impedance spectroscopy was used to study the mechanism by which copper oxides are reduced in neutral solutions of alkali chloride. For the reductions of CuO and Cu₂O, a capacitive loop and also an inductive loop under certain conditions were observed in the complex plane. The electrochemical impedance for CuO reduction was not greatly dependent on the kind of alkali chloride. On the other hand, the electrochemical impedance for Cu₂O reduction was considerably affected by the kind and concentration of alkali chloride. The diameter of the capacitive loop, i.e., the charge-transfer resistance (R_{ct}), increased with increase in concentration of LiCl to 1 M. The specific behaviors of the transient decrease of R_{ct} and the emergence of the inductive loop were confirmed in 1 M LiCl. In addition, R_{ct} increased again with increase of LiCl concentration over 1 M. These dependences may be consistent with the good separation between the reduction potentials of CuO and Cu₂O in chronopotentiometric measurements. However, the reduction potential of Cu(OH)₂ shifted to lower direction in neutral solutions. The sufficient separation between the reduction potentials of Cu(OH)₂ and Cu₂O was difficult. Strongly alkaline solution containing Li⁺ ion is necessary for the simultaneous determination of Cu₂O, CuO and Cu(OH)₂ on copper surface.

1. Introduction

Copper and copper alloys are widely used in industrial fields for making electric wires, electronic components, wiring materials and many other products. Although copper is a relatively corrosion-resistant material, oxide films of various thickness are formed on copper that is exposed to air containing moisture and pollutants. Troubles such as tarnishing, soldering defect and insufficient insulation may occur according to the amount of copper oxides.

Oxide films on copper are composed of cuprous oxide (Cu₂O) and/or cupric oxide (CuO)⁽¹⁾. Selective determination of the two oxides with different properties is important for corrosion characterization.

For this purpose, surface analytical techniques such as X-ray diffraction (XRD)⁽²⁾ and X-ray photoelectron spectroscopy (XPS)^{(3), (4)} have so far been employed. These spectrophotometric techniques are very useful for qualitative analyses, but not necessarily adequate for quantitative ones, whereas electrochemical techniques such as chronopotentiometry (CP)^{(1), (5)-(11)} and linear sweep voltammetry (LSV)⁽¹²⁾⁻⁽¹⁵⁾ provide reliable information on the "quantities" of copper oxides. The CP method using neutral or weak alkaline solutions as supporting electrolytes has been the most frequently employed method for simultaneous determination of Cu₂O and CuO formed on copper surfaces. Until recently, however, there were two different views regarding the order of reduction of oxides (see references 16 and 17)). In addition, in cases of thick oxide films⁽¹⁸⁾, simultaneous determination of Cu₂O and CuO in neutral solutions is difficult to perform.

The author has developed a new voltammetric method⁽¹⁹⁾ for quantitative characterizations of copper oxide films, and has applied this method on samples in the

forms of plate^{(19), (20)}, wire⁽²¹⁾, and powder⁽²²⁾. In this method, a strongly alkaline electrolyte (i.e., 6 M KOH + 1 M LiOH) allowed a perfect separation between two cathodic peaks due to the reduction of Cu₂O or CuO. The reduction mechanism of copper oxides was revealed that CuO is reduced at once to Cu prior to the reduction of Cu₂O to Cu with the help of spectrophotometric techniques including XRD and XPS^{(18), (19)}.

Electrochemical impedance spectroscopy (EIS)^{(23), (24)} was selected for the investigation of the specific behavior that the reduction of Cu₂O was suppressed by Li⁺ in a strongly alkaline solution⁽²⁵⁾. In addition, this new method was applied for the quantitative estimation of copper sulfides⁽²⁶⁾.

Previously, the reduction mechanism of copper oxides in 6 M KOH + 1 M LiOH was discussed in comparison with a neutral electrolyte of 0.1 M KCl^{(18), (22), (25)}. However, the comparative discussion was somewhat confusing, as the nature of above two solutions differs markedly. In this study, EIS was introduced to a mechanistic study of the reduction of copper oxides in neutral solutions focusing on the kind and the concentration of alkali metal ion. Almost all of the conventionally-prepared electrolyte solutions were 0.1 M. To the knowledge of the author, however, there has been no report on the study about the dependence of copper oxide reduction on electrolyte concentration.

2. Experimental

2-1 Copper oxide samples

A 0.71-mm diameter Dumet wire (JIS H 4541, Sumi-

tomo Electric Industries, Ltd.) for glass-to-metal seal applications was used as a Cu₂O/Cu sample⁽²¹⁾. This wire is composed of an inner layer of Fe-Ni alloy and an outer layer of Cu plating (thickness around 100 μm), the surface being thermally oxidized to form a Cu₂O layer (thickness around 1.2 μm).

A CuO/Cu sample⁽²¹⁾ was prepared in the following manner. A 0.2-mm thick oxygen-free copper sheet (JIS C15150, Mitsubishi Shindoh Co., Ltd.) was cut to a size of 5 mm by 50 mm and then treated with commercially available agents AD-331, MB-438A and MB-438B (Meltex Inc.) to form a 0.7-μm-thick film of CuO on the copper surface⁽¹⁸⁾.

A CuO/Cu₂O/Cu Cu-duplex oxide film sample was prepared from a Cu₂O/Cu sample by immersing it in 1 M NaOH for 40 hours at 30°C. The total thickness of the oxide film was determined to be around 1.4 μm⁽¹⁸⁾. It was shown by XRD that Cu₂O and CuO co-existed on the surface of a CuO/Cu₂O/Cu sample⁽¹⁸⁾. The existence of a Cu₂O or CuO film on the Cu₂O/Cu and CuO/Cu samples was also ascertained by XRD. Above three samples are called “standard samples.” In electrochemical measurements for standard samples, the surface area to be tested was usually 1.0 cm². Powder samples of Cu₂O, CuO and Cu(OH)₂ were mixed with the carbon paste (BAS Inc.) before each measurement⁽²²⁾. The ratio by weight of powder sample to carbon paste was 1:5.

2-2 Electrochemical measurements

A conventional three-electrode electrolytic cell was employed for electrochemical measurements. An Ag/AgCl (in 3 M NaCl) electrode was used as the reference electrode, to which all potentials are referred in this paper. A platinum wire was used as the counter electrode. The electrolyte solutions used were LiCl, NaCl and KCl, all of which were not deaerated. All the reagents used for preparation of the electrolyte solutions were of analytical grade. CP and LSV measurements were carried out using a model HZ-3000 electrochemical measurement system (Hokuto Denko Co. Ltd.). In CP, the current was

usually set at -1.0 mA. In LSV for powder samples, a potential sweep was performed from a rest potential to the potential for hydrogen evolution at the rate of 10 mV s⁻¹.

The electrochemical impedances were measured by using HZ-3000 and a model FRA5080 frequency response analyzer (NF Corporation). After a CP measurement for 3 minutes at -1mA, the EIS measurements were performed⁽²⁵⁾. The amplitude of the imposed current modulation was 0.1 mA, and the frequency range was from 50 mHz to 10 kHz⁽²⁵⁾. A ZSimpWin software program (Princeton Applied Research) was used for analyzing the impedance data.

3. Result and Discussion

3-1 Difference by alkali metal ion type

CP and EIS were performed in conducting a mechanistic study of copper oxide reduction by focusing on the type of alkali metal ions. Three different types of 2 M alkali chloride solution (LiCl, NaCl and KCl) were used as the supporting electrolyte. In the cases where alkali chloride solutions of only about 0.1 M are used, there is no difference in the copper oxide reduction behaviors between different kinds of alkali ions.

Figure 1 shows potential-time curves plotted by CP for Cu₂O/Cu, CuO/Cu, and CuO/Cu₂O/Cu samples in three different electrolyte solutions: 2 M KCl, 2 M NaCl, and 2 M LiCl. When an oxide-free copper surface is dedicated to the CP measurement, the measured potential should immediately shift to the hydrogen evolution potential (around -1.3 V). **Figure 1A(c)** shows that for a CuO/Cu₂O/Cu sample, two distinct potential plateaus were observed when 2 M LiCl was used. The first and second plateaus should correspond to the reduction of CuO and Cu₂O, respectively. This was supported by the plotted curves for Cu₂O/Cu and CuO/Cu samples,

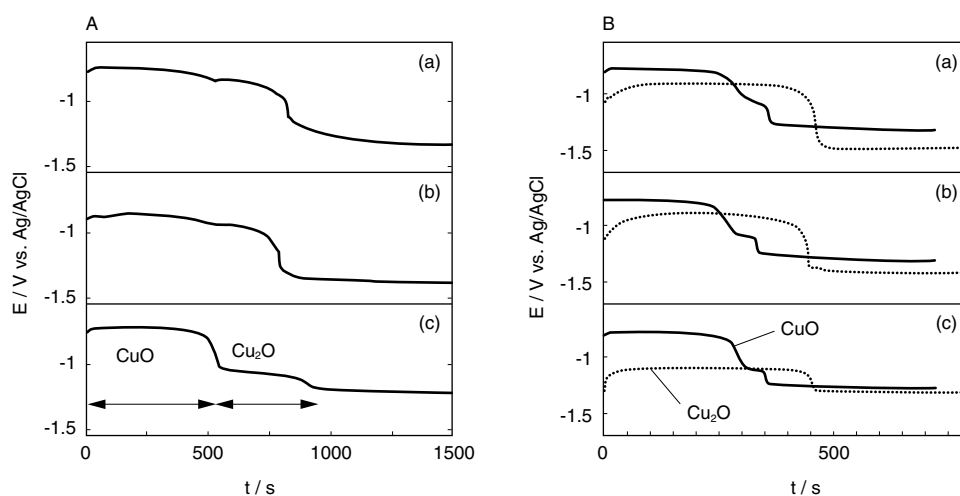


Fig. 1. Potential-time curves recorded by CP for (A) CuO/Cu₂O/Cu samples and (B) CuO/Cu samples (solid lines) and Cu₂O/Cu samples (dashed lines). Applied current: -1.0 mA. Electrolyte solution: (a) 2 M KCl, (b) 2 M NaCl, and (c) 2 M LiCl.

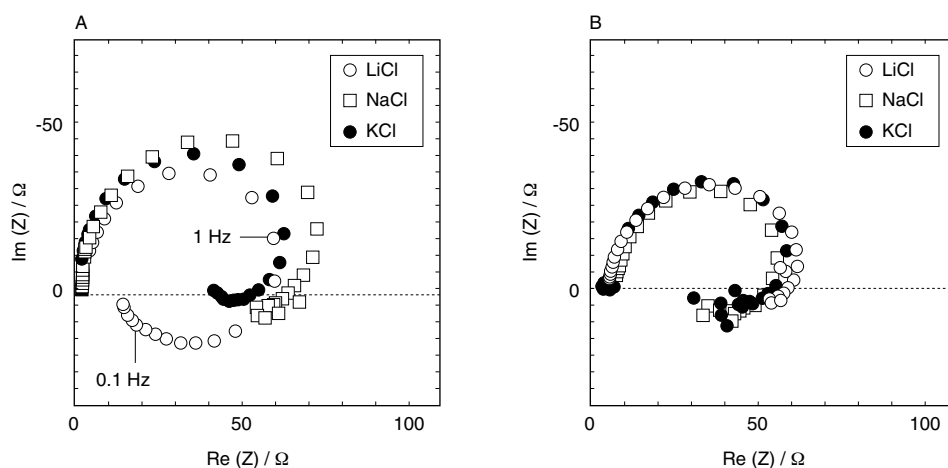


Fig. 2. Electrochemical impedances of (A) $\text{Cu}_2\text{O}/\text{Cu}$ samples and (B) CuO/Cu samples in 2 M LiCl, 2 M NaCl and 2 M KCl. DC current: -1.0 mA, AC current: 0.1 mA

which are shown in **Fig. 1B(c)**. The last potential plateau observed in every measurement is due to hydrogen evolution. When 2 M KCl or 2 M NaCl was used, the deviation of two reduction potential plateaus was smaller than that observed when 2 M LiCl was used.

Although the short plateaus were ascertained around 300 seconds on time–potential curves of a CuO/Cu sample in **Fig. 1B**, no details were known on this behavior. These short plateaus were not detected when 1 M alkali hydroxide solutions were used⁽²⁵⁾.

Figure 2 shows the electrochemical impedances for the reductions of CuO/Cu and $\text{Cu}_2\text{O}/\text{Cu}$ samples in 2 M LiCl, 2 M NaCl, and 2 M KCl. The DC potential was kept constant for $I_{\text{DC}} = -1$ mA and $I_{\text{AC}} = 0.1$ mA, suggesting that a certain part of the Cu_2O or CuO film remained unreduced at least for the measurement time.

In every case, a large semi-circular arch appeared in the upper part of the complex plane, indicating the influence of the double-layer capacitance (C_{dl}). The diameter of the arch in the high frequency range can be recognized as the charge-transfer resistance (R_{ct}) in the reduction of copper oxides. As also shown in **Fig. 2A**, a characteristic inductive loop was observed in the low frequency range for the reduction of a $\text{Cu}_2\text{O}/\text{Cu}$ sample in 2 M LiCl. This loop probably indicates the existence of some reaction intermediate.

As seen in **Fig. 2B**, the electrochemical impedance of a CuO/Cu sample is hardly affected by the kind of alkali chloride used as the supporting electrolyte. This result is in harmony with the CP data shown in **Fig. 1B**. On the other hand, the impedance of a $\text{Cu}_2\text{O}/\text{Cu}$ sample (**Fig. 2A**) was strongly affected by the kind of alkali metal ion. Thus, it was shown that Li^+ ions had a reducing effect on R_{ct} , i.e., an inhibitory effect on the reduction of Cu_2O . The inductive loop was also most prominent for 2 M LiCl and rather ambiguous for 2 M NaCl and 2 M KCl.

For the reduction of Cu_2O by water vapor⁽²⁷⁾, CuOH

Table 1. Comparison of electrode impedance parameters for reduction of Cu_2O in LiCl and KCl solutions with different concentrations.

Electrolyte		R_{sol} (Ω)	R_{ct} (Ω)	C_{dl} (mF)	P (Ω)	L (H)
Cu_2O	2 M LiCl	0.8	67	1.8	17	32
	2 M NaCl	1.1	88	1.0	(120)	(37)
	2 M KCl	0.8	83	0.9	(72)	(16)
CuO	2 M LiCl	4.9	60	1.0	(252)	(130)
	2 M NaCl	5.8	55	1.0	(67)	(31)
	2 M KCl	4.9	58	0.9	(98)	(44)
Cu_2O	0.1 M LiCl	19	71	0.8	(374)	(33)
	0.5 M LiCl	4.0	92	1.1	(750)	(741)
	1 M LiCl	3.0	145	1.6	(91)	(224)
	2 M LiCl	0.8	67	1.8	17	32
	4 M LiCl	1.3	87	1.9	29	64
	6 M LiCl	0.9	108	1.8	31	82
	0.1 M KCl	14	69	0.5	(154)	(13)
	1 M KCl	1.9	83	0.6	(95)	(16)
	2 M KCl	0.8	83	0.9	(58)	(21)
	3 M KCl	0.6	81	0.9	(61)	(22)

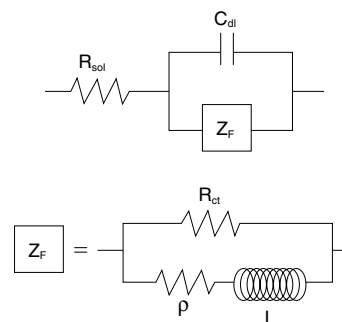
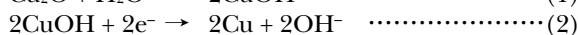


Fig. 3. Equivalent circuit of electrode impedance.⁽²⁸⁾⁻⁽²⁹⁾

has been suggested to be an intermediate. In a similar manner, the author tentatively assumes the following reaction scheme for the reduction of Cu₂O:



As described above, the electrochemical impedances for the reduction of Cu₂O in 2 M LiCl showed not only a capacitive but also an inductive loop in the complex plane. Analogous inductive loops were reported for a faradaic impedance of the dissolution of Fe in sulfuric acid⁽²⁸⁾ and the electrocrystallization of Ni or Co⁽²⁹⁾. By consulting the literature, the author assumed a circuit equivalent to that shown in Fig. 3 for the reductions of copper oxides. As shown in Fig. 3, the equivalent circuit involves a faradaic impedance (Z_F), which is connected to C_{dl} in parallel and to R_{sol} in series. Then, Z_F consists of a charge-transfer resistance (R_{ct}) in parallel with the series connection of a faradaic resistance (ρ) and a self-inductance (L):

$$\frac{1}{Z_f} = \frac{1}{R_{ct}} + \frac{1}{\rho + j\omega L} \quad \dots\dots\dots(3)$$

where *j* is the imaginary unit and ω is 2π*f* (*f* being frequency). The overall impedance of the electrochemical cell can be written as^{(28), (29)}

$$Z = R_{sol} + \left[\frac{1}{Z_f} + j\omega C_{dl} \right]^{-1} \quad \dots\dots\dots(4)$$

Using Eqs. (3) and (4), non-linear least squares curve fitting was performed for the impedance data shown above. As an example, the electrochemical impedance for a Cu₂O/Cu sample in 2 M LiCl is shown in Fig. 4. As can be seen in the figure, the simulated or calculated plots fitted well to the measured plots. The parameters, C_{dl}, R_{sol}, R_{ct}, ρ and L, were then evaluated as adjusting parameters, being shown in Table 1. Similar analyses with the equivalent circuit in Fig. 3 could be performed also for the impedance data under other conditions. Except

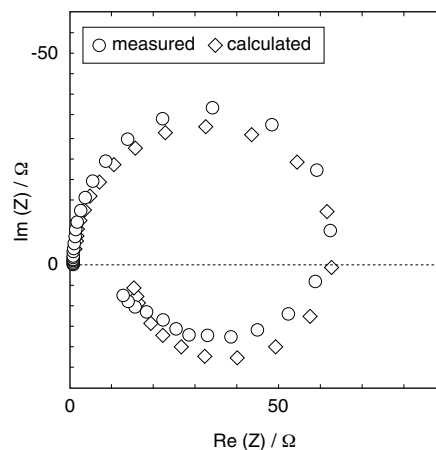


Fig. 4. Electrochemical impedance of Cu₂O/Cu sample in 2 M LiCl. Open circles: measured values, open diamonds: calculated values. DC current: -1.0 mA, AC current: 0.1 mA.

for a case where 2 M LiCl was used for the reduction of a Cu₂O/CuO sample, ρ and L were shown with a parenthesis because the existence of inductive loops was ambiguous.

3-2 Influence of alkali metal ion concentration

The influence of the concentration of alkali metal ion was also investigated. Figure 5 shows the time-potential curves of (A) CuO/Cu₂O/Cu samples and (B) Cu₂O/Cu samples, which were obtained in different concentrations of LiCl (0.1 to 4 M) or KCl (0.1 to 3 M). As seen in Fig. 5A(b), the second plateau indicating the reduction potential of Cu₂O was shifted to lower potentials with increase in LiCl concentration. Because the first plateau indicating the reduction potential of CuO, was shifted only slightly to lower potentials, a sufficient separation between the two plateaus was achieved for LiCl concentrations larger than 1 M. However, the sepa-

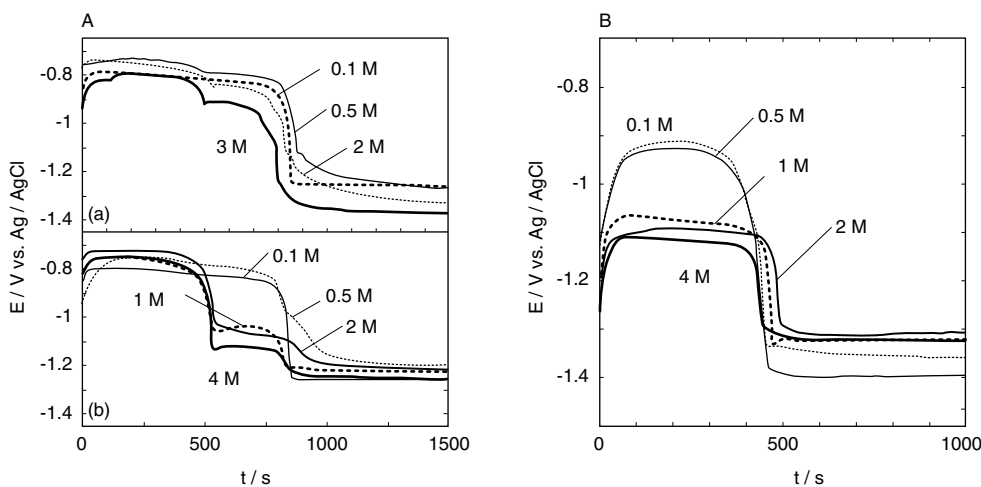


Fig. 5. (A) Potential-time curves for CuO/Cu₂O/Cu samples, which were obtained for (a) KCl and (b) LiCl solutions of different concentrations. (B) Potential-time curves for Cu₂O/Cu samples, which were obtained for LiCl solutions of different concentrations. Applied current: -1.0 mA.

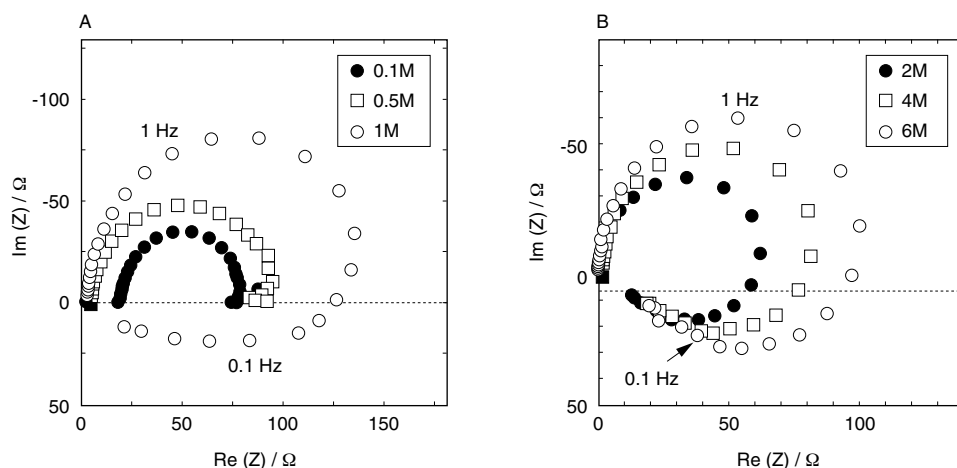


Fig. 6. Electrochemical impedances of $\text{Cu}_2\text{O}/\text{Cu}$ samples in solutions of different concentrations ((a) 0.1 to 1 M, (b) 2 to 6 M). DC current: -1.0 mA. AC current: 0.1 mA.

ration of the two plateaus was insufficient in KCl. As seen in **Fig. 5B**, the reduction potential of Cu_2O is similar to that of the second plateau of a $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}$ sample for various concentrations of LiCl.

On the other hand, the reduction potential of CuO was almost the same for different kinds of alkali metal ion and different concentrations.

The data of EIS measurements is shown in this and the following sections. **Figure 6** shows the electrochemical impedances for the reductions of $\text{Cu}_2\text{O}/\text{Cu}$ samples in various concentrations of LiCl. R_{ct} increased with increase in concentration of LiCl to 1 M. The specific behaviors of the transient decrease of R_{ct} and the emergence of an inductive loop were confirmed in 1 M LiCl. In addition, R_{ct} increased again with LiCl concentration increase over 1 M. These behaviors seem to relate to the reductive potential of Cu_2O in **Fig. 5B**. An intermediate probably suppresses the reduction of Cu_2O with increase in LiCl concentration.

Figure 7 shows the electrochemical impedances for the reductions of (A) CuO/Cu samples in various concentrations of LiCl (0.1 to 4 M) and (B) $\text{Cu}_2\text{O}/\text{Cu}$ samples in various concentrations of KCl (0.1 to 3 M). The obvious dependence on alkali metal ion concentration was not ascertained.

In the reduction of Cu_2O , among parameters C_{dl} , R_{sol} , R_{ct} , ρ and L shown in **Table 1**, C_{dl} became larger with the increase of LiCl concentration to 2 M. It probably means that the time required for charging an electrochemical double-layer capacitor increase with the increase of LiCl concentration. In addition, R_{ct} and L grew larger with the increase of LiCl concentration over 2 M. It is assumed that the incorporation of Li^+ into Cu_2O and the generation of a reaction intermediate had taken place, leading to the suppression of the reduction of Cu_2O .

3-3 Analysis of powder sample

Powder samples of Cu_2O , CuO and $\text{Cu}(\text{OH})_2$ were measured by CP or LSV using 0.1 M KCl and 4 M LiCl as

supporting electrolytes. Time-potential curves and current-potential curves were shown in **Fig. 8**.

As can be seen in the figure, an insufficient separation between the reduction peaks of Cu_2O and CuO was obtained using 0.1 M KCl. In addition, the reductive reaction of $\text{Cu}(\text{OH})_2$ was ascertained in lower potential than that of the reductive reaction of Cu_2O . On the other hand, 4 M LiCl enabled a sufficient separation between the reduction peaks of Cu_2O and CuO . But the reductive potential of $\text{Cu}(\text{OH})_2$ was almost equal to that of Cu_2O . The existence of $\text{Cu}(\text{OH})_2$ is likely to further complicate the problematic situation.

Selective determination of Cu_2O and CuO by CP or LSV using 4 M LiCl is possible if only Cu_2O and CuO are formed on Cu. However, it is easily assumed that $\text{Cu}(\text{OH})_2$ coexists with copper oxides on samples exposed to outdoor conditions.

For the selective determination of $\text{Cu}(\text{OH})_2$ and copper oxides, the use of a strongly alkaline electrolyte (i.e., 6 M KOH + 1 M LiOH) is more appropriate⁽³⁰⁾. The potential at which the reduction of $\text{Cu}(\text{OH})_2$ occurred was somewhat higher than that of CuO reduction^{(22), (26)}. This corresponds to the thermodynamic scale of potentials⁽³¹⁾.

4. Conclusions

The mechanism of reduction of copper oxides in neutral solutions was studied by electrochemical techniques, including EIS, and the following conclusions were drawn.

1. The reduction of CuO is hardly affected by the kind and concentration of alkali chloride used as the supporting electrolyte. On the other hand, the reduction of Cu_2O is easier suppressed larger in 2 M LCl than in 2 M KCl or 2 M NaCl.

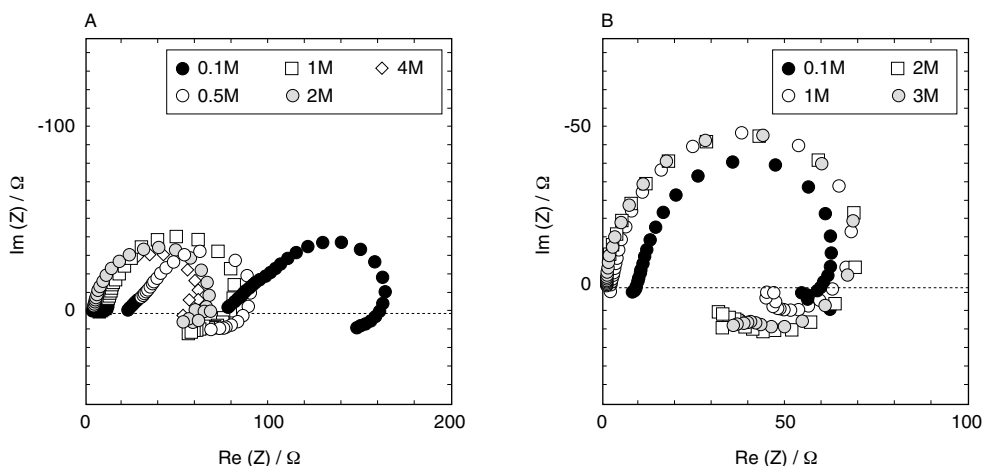


Fig. 7. Electrochemical impedances of (A) CuO/Cu samples in LiCl solutions of various concentrations (0.1 to 4 M) and (B) Cu₂O/Cu samples in KCl solutions of various concentrations (0.1 to 3 M). DC current: -1.0 mA, AC current: 0.1 mA.

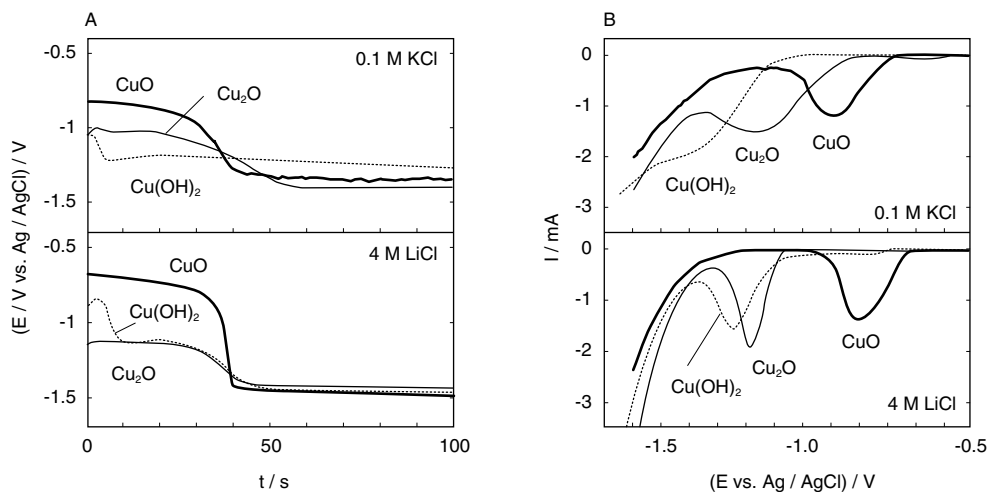


Fig. 8. (A) Time-potential curves recorded by CP for powder samples. Applied current: -1.0 mA. (B) Current-potential curves recorded by LSV for powder samples. Scan rate: 10 mV s⁻¹. Electrolyte solution: 0.1 M KCl or 4 M LiCl.

2. The equivalent circuit for the reduction of Cu₂O in higher concentrations of LiCl (higher than 1 M) involves a self-inductance, which suggests the existence of an intermediate (a possible candidate being CuOH).
3. The specific inhibitory effect of Li⁺ ions on the reduction of Cu₂O might be explained by a possible stabilization of the intermediate (CuOH) by Li⁺ ions.

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