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Mechanistic study of the reduction of copper oxides in alkaline solutions by electrochemical impedance spectroscopy

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Abstract

Electrochemical impedance spectroscopy was used to study the mechanism by which copper oxides are reduced in alkaline solutions. For the reductions of CuO and Cu_2O, 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 solution alkalinity and the kind of alkali hydroxide. However, the electrochemical impedance for Cu_2O reduction was considerably affected by the kind and concentration of alkali hydroxide. The diameter of the capacitive loop, i.e., the charge-transfer resistance (R_{ct}), was increased with increase in solution alkalinity. It should also be noted that R_{ct} was increased in the order of KOH < NaOH < LiOH. These dependences were consistent with the good separation between the reduction potentials of CuO and Cu_2O in chronopotentiometric and voltammetric measurements with strongly alkaline electrolytes containing Li^+. The inductive loop observed for the Cu_2O reduction at higher concentrations of KOH (>6 M) and LiOH (>0.2 M) suggested the existence of an intermediate species (probably CuOH). The specific inhibitory effect of Li^+ ions on the reduction of Cu_2O might be explained by a possible stabilization of CuOH by Li^+ ions.

Keywords: Copper oxides; Reduction mechanism; Electrochemical impedance spectroscopy; Inductive loop; Strongly alkaline solutions

1. Introduction

Oxide films on copper are composed of cuprous oxide (Cu_2O) 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, including X-ray photoelectron spectroscopy (XPS) [2–4], Auger electron spectroscopy (AES) [4], X-ray diffraction (XRD) [5], and infrared reflection absorption spectroscopy (IRAS) [6,7], have been used. These spectrophotometric techniques are useful for qualitative analysis but not necessarily adequate for quantitative analysis, whereas electrochemical techniques such as chronopotentiometry (CP) [1,8–11] and linear sweep voltammetry (LSV) [12–14] 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 Cu_2O and CuO formed on copper surfaces. Until recently, however, there were two different views regarding the order of reduction of oxides (see references cited in [15,16]). Our recent studies [17] have revealed that CuO is first reduced in a neutral solution (0.1 M KCl) followed by the reduction of Cu_2O. However, it has also been shown that the reductions of both Cu_2O and CuO occur simultaneously, to a greater or lesser extent, in such a neutral solution. Thus, the most frequently used electrolyte, i.e., KCl, seems to be inadequate for the selective determination of the copper oxides.

In our recently developed voltammetric method [17–21], a strongly alkaline electrolyte (i.e., 6 M KOH + 1 M LiOH) was employed to allow a perfect separation between two cathodic peaks due to the reductions of Cu_2O and CuO. The mechanism of reduction of copper oxides in the electrolyte was studied by using XRD and XPS. It was revealed that CuO is reduced to Cu prior to the reduction of Cu_2O to Cu [18]. This was also confirmed from the focused ion beam/scanning ion microscope (FIB/SIM)

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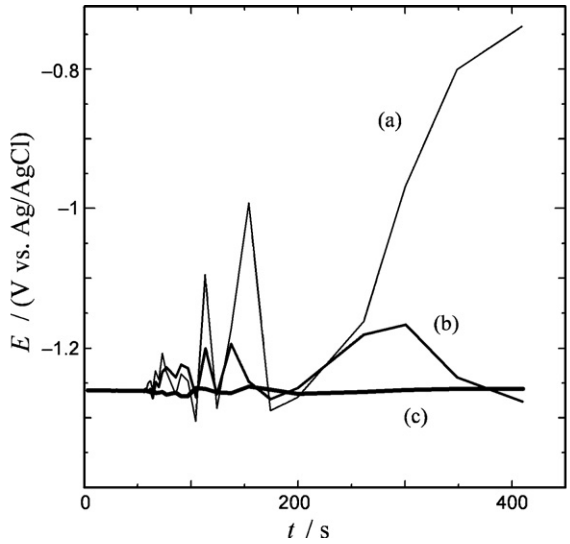

Fig. 1. dc potential–time curves recorded during EIS measurements of the Cu_2O/Cu sample in 1 M LiOH for three different ac currents: (a) 1.0 mA, (b) 0.5 mA, and (c) 0.1 mA. Before each EIS measurement, a dc current of −1.0 mA was applied to the sample for 3 min, so that the electrode potential became the reduction potential of Cu_2O, ca. ~1.2 V.

images of a Cu-duplex oxide film, which were obtained before and after the partial electrochemical reduction [17,20]. The perfect separation between the reduction peaks for Cu_2O and CuO (0.2–0.4 V depending on the samples) has been found to be not only due to the alkalinity of the solution but also to the effect of Li^+ ions. The addition of 1 M LiOH to 6 M KOH caused a significant negative shift of the reduction peak of Cu_2O [18–20]. However, mechanistic aspects of the reduction processes in such a strongly alkaline solution have not yet been resolved.

In this study, electrochemical impedance spectroscopy (EIS) [22–24] was newly introduced to a mechanistic study of the reduction of copper oxides. The EIS method has been frequently applied to the analysis of corrosion of metals [25] and also to studies of copper for its corrosion rate [26], antiseptics [27–29], and plating [30]. To our knowledge, however, there has been no report on analysis of the reduction of copper oxides by means of EIS.

2. Experimental

2.1. Copper oxide samples

Dumet wire (JIS H 4541, Sumitomo Electric Ind., 0.71-mm Ø) for glass-to-metal seal applications was used as a Cu_2O/Cu sample [20]. This wire is composed of an inner layer of Fe–Ni alloy and an outer layer of Cu plating (ca. 100-μm thick), the surface being thermally oxidized to form a Cu_2O layer (ca. 1.2-μm thick).

A CuO/Cu sample [20] was prepared in the following manner. An oxygen-free copper sheet (0.2-mm thick; JIS C15150, Mitsubishi Shindo Co. Ltd.) was cut to the size of 5 mm × 50 mm and then treated with commercially available solutions (AD-331, MB-438A, MB-438B; Meltex Inc.) to form a 0.7-μm thick film of CuO on the copper surface [31].

A sample of Cu-duplex oxide films, which is called a $CuO/Cu_2O/Cu$ sample, was prepared from the Cu_2O/Cu sample by immersing it in 1 M NaOH for 40 h at 30 °C. The total thickness of the oxide film was determined to be ca. 1.4 μm [17]. It was shown by XRD that Cu_2O and CuO co-existed on the surface of a $CuO/Cu_2O/Cu$ sample [17]. The existence of a Cu_2O or CuO film on the Cu_2O/Cu and CuO/Cu samples was also ascertained by XRD.

In electrochemical measurements for the samples, the surface area to be tested was usually $1.0\,cm^2$.

2.2. Electrochemical measurements

A conventional three-electrode electrolytic cell was employed for electrochemical measurements. The Cu_2O/Cu, CuO/Cu, or $CuO/Cu_2O/Cu$ sample served as the working electrode. 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 not deaerated. All of the reagents used for preparation of the electrolyte solutions were of analytical grade. CP and LSV measurements were carried out using an electrochemical measurement system (Hokuto Denko Co. Ltd., Japan; model HZ-3000). The current density in CP was usually set at $1.0\,mA\,cm^{-2}$ and the sweep rate in LSV was set at $1\,mV\,s^{-1}$. The electrochemical measurements were started within 1 min after the immersion of each sample into the electrolyte solution. EIS measurements were performed by using the HZ-3000 system equipped with a frequency response analyzer (NF Co., Japan; model FRA5080). Prior to each EIS measurement, a CP measurement with −1.0 mA was performed for 3 min so that the sample electrode was kept at the reduction potential for Cu_2O or CuO. Then an ac current modulation of 0.1 mA was superimposed on the dc current of −1.0 mA at frequencies from 10 kHz to 50 mHz, and the ac voltage response was analyzed by the frequency analyzer. Commercially available software, ZSimpWin (Princeton Applied Research), was used for modeling of the obtained impedance data. This software utilizes the “downhill simplex method” based on a trial-and-error method to find the best fit for a given set of data and the chosen equivalent circuit. The parameters providing the closest fit to a model are obtained by minimizing the statistical function defined as the sum of the squares of the residuals.

In a previous paper [20], we examined the reproducibility of the voltammetric measurements by using the standard Cu_2O/Cu and CuO/Cu samples; the relative standard deviations were 3.5% and 7.0%, respectively.

3. Results and discussion

3.1. Measurement conditions for EIS

A preliminary experiment was performed to find an appropriate value of alternating current (I_{ac}) for the EIS measurements. Fig. 1 shows the dc potential–time curves that were recorded during EIS measurements of the Cu_2O/Cu sample for three different I_{ac} values: 1 mA, 0.5 mA, and 0.1 mA. Before each EIS mea-