Enhanced fabrication of hybrid Cu–Cu$_2$O nanostructures on electrodes using electrochemical migration

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Abstract
Cu, Cu$_2$O and CuO nanostructures have characteristic physical properties, and are used in a variety of fields such as lithium ion batteries, solar batteries and gas sensors. Recently, various techniques for the nanostructures fabrication have been studied for these applications. It has been reported that electrochemical migration (ECM) causes insulation deterioration on the printed circuit boards in high-humidity and high-temperature conditions. Previous investigations of the suppression of ECM revealed that eluted Cu ions grew as dendrites. A considerable number of studies have investigated the suppression of ECM, but the beneficial use of ECM has not been studied extensively. The use of ECM has become the subject of increasing interest because ECM is a low-cost and green fabrication technique, and the reaction requires only DC voltage and water without any metal salts and hydroxides. Some attempts have been made to fabricate hybrid Cu–Cu$_2$O nanostructures using ECM. However, it has been reported that the growth of dendrites between electrodes ceases because the dendrites create a short-circuit. Thus, proper fabrication has not yet been achieved. This study aimed to enhance the fabrication of hybrid Cu–Cu$_2$O nanostructures using ECM. In this study, we changed the path length of the dendrites’ growth, and improved the fabrication process through evaluation of the results.

Keywords: Electrochemical migration, Nanostructure, Performance evaluation, Electrode shape, Fabrication

1. Introduction
Cu, Cu$_2$O and CuO nanostructures show characteristic physical properties, including a remarkably high surface-to-volume ratio, and these nanostructures have been used in a variety of applications, including lithium ion batteries (Ikeda and Narukawa, 1983, Novák et al., 1985 and Poizot et al., 2000) and solar batteries (Anandan et al., 2005 and Dahrul et al., 2016). Various techniques for the fabrication of these nanostructures have been investigated, including hydrothermal synthesis (Li et al., 2004 and Jiang et al., 2014).

Electrochemical migration (ECM) causes insulation deterioration for printed circuit boards in high-humidity and high-temperature environments. A considerable number of studies have investigated the suppression of ECM, with the aim of preventing electronic device failure (Minzari et al., 2011 and Zhong et al., 2013), and these studies have reported that the precipitation grows as dendrites (Krumbein, 1988, Liu et al., 2011 and Medgyes et al., 2016). Attempts have also been made to exploit precipitation because ECM is a low-cost and green fabrication technique in which the reaction is caused simply by DC voltage and water without any metal salts or hydroxides (Nakajima et al., 2015).

An experimental system for using ECM was proposed by Aoki et al. (2016). In this experimental system, the use of larger electrodes and a larger distance between the electrodes (compared with those used in insulation breakdown experiments (Krumbein, 1988, Reid et al., 2005 and Mendes et al., 2009)) for ECM allowed the fabrication of hybrid Cu–Cu$_2$O nanostructures. The other study reported that the anode with Cu–Cu$_2$O nanostructures has high performance.
of lithium ion batteries (Ni et al., 2013), and hence it was expected that hybrid Cu–Cu₂O nanostructures by ECM contributed to higher performance of lithium ion batteries if the large-scale and sustainable fabrication was realized. However, it was confirmed in a suppression study of printed circuit boards (Zhou et al., 2013) that for this fabrication process, in which DC voltage was applied, the electrical resistance (ER) between the electrodes decreased drastically. In relation to the ER reduction, it was reported that the growing dendrites reached the anode electrode, and stop their growth due to the formation of a short-circuit (Zhou et al., 2013). Therefore, it seems that the same characteristic problem occurred in the experimental system investigated by Aoki et al. (2016), and that it remains difficult to fabricate sustainable and large-scale hybrid Cu–Cu₂O nanostructures.

Our preliminary study (Fukaya et al., 2017) focused on the electrode shape to solve this problem. The reason for this was that the dendrites grew preferentially on the interface between the reaction cell and the water, as confirmed through the observation of the ECM behavior. It was presumed that the period required for the formation of a short-circuit was extended by increasing the path length of the dendrite growth. Preliminary results were reported previously showing that changing the electrode shape enabled the extension of the ECM period (Fukaya et al., 2017). However, although the effect of the path length was implied, the effect of changing the electrode shape on the path length was not investigated in detail.

Here, the fabrication of hybrid Cu–Cu₂O nanostructures using ECM is investigated, focusing on the electrode distance and shape, and evaluating the performance to demonstrate the sustainable and large-scale fabrication of hybrid Cu–Cu₂O nanostructures.

2. Theoretical background

In metals, ECM involves the movement and precipitation of metallic atoms of electrodes in contact with an insulating material, inside and at the surface of the insulating material (Kohman et al., 1955 and Fujishiro et al., 2007). The existence of water between the electrodes is a key factor. The metal at the anode is eluted as metal ions by the voltage applied between the electrodes. Next, the eluted metal ions move to the cathode electrode under the influence of the Coulomb force produced by the electric field. When the metal ions reach the cathode electrode, the eluted metal ions receive electrons and precipitate due to reduction. It has become clear that ECM is the phenomenon causing these three reactions sequentially.

The metal elution occurs at the interface between the anode electrode and the water, as oxidation during which the metal emits electrons. Taking the case of Cu dealt with in this study, a lytic reaction occurs at the anode electrode under self-oxidation as

\[
\text{Cu} \rightarrow \text{Cu}^+ + e^- \quad \text{(1)}
\]

It is obvious that the elution process of Cu⁺ ions has the lower activation energy than that of Cu²⁺ ions (Medgyes et al., 2012). At the same time, water oxidation occurs at the anode as

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 2e^- \quad \text{(2)}
\]

Cu⁺ ions then combine with OH⁻ ions to form Cu(OH), which is not stable and decomposes to Cu₂O and H₂O as

\[
2\text{Cu}^+ + 2\text{OH}^- \rightarrow 2\text{Cu(OH)} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad \text{(3)}
\]

In the parallel, the reduction process in which the metal is precipitated occurs at the cathode as

\[
\text{Cu}^+ + e^- \rightarrow \text{Cu} \quad \text{(4)}
\]

Also, water reduction to give hydroxide ions at the cathode is likely to occur continuously during the electrolysis as

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(5)}
\]

With the lapse of time, the metal ions elute to pure water. The metal elution and precipitation mainly occur. Consequently, migrated Cu⁺ ions are deposited in form of Cu and Cu₂O, and these then grow as dendrites towards the anode electrode (Harsányi, 1995).

3. Experimental procedure

The ECM tests were carried out using a water-drop test, in the experimental system as illustrated in Fig. 1(a). Two 80-μm-thick Cu foils were used as the anode and cathode electrodes. In order to investigate the effect of the electrode distance and path length on the precipitation of the hybrid Cu–Cu₂O nanostructures, two electrode shapes were used: Electrode A had a shape that contacted with the bottom of the reaction cell, and Electrode B had a shape that provided a
distance of 5 mm between the electrode and the bottom of the reaction cell, as shown in Fig. 1(b). The FR-4 reaction cell and spacer were cleaned using ultrasonication, and were then dried in air. Deionized water with a specific electrical resistivity of more than 8 MΩ cm was added dropwise to the reaction cell, and a DC voltage of 20 V was applied between electrodes using a power supply (GP035-5 Takasago Ltd.).

In the present study, we performed two types of experiments. The effect of changing the electrode distance was investigated under condition (i) using Electrode A, as shown in Table 1. The electrodes were set at a distance of 19.25 mm, larger than the distance of 9.25 mm used in the preliminary study (Fukaya et al., 2017). Increasing the electrode distance also increases the path length of the dendrite growth. Next, the performance of changes in the path length was investigated under the condition (ii) with 9.25 mm electrode distance shown in Table 1. The reason for setting the electrode distance with 9.25 mm is that the concentration of the electric field by the surface roughness affects the formation of dendrites at a distance of less than 9.25 mm. The ECM tests were carried out using Electrode A-1 to -5 and B-1 to -5, and the mass of Electrode A-3 to -5 and B-3 to -5 as an example were measured before and after each experiment because the mass of the hybrid Cu–Cu2O nanostructures was a measure of the fabrication performance using ECM. The path length for Electrode B, where the dendrites along the reaction cell, was 10 mm longer than for Electrode A (see Fig. 1(c)). Under the same electric field, the effect of the path length by different electrode shapes was investigated. It is noted that the area of Electrode A touching the water was the same as the area of Electrode B touching the water.

Fig. 1 Schematic illustrations of (a) the experimental system used for the ECM tests, (b) the copper electrode shapes (the area of Electrode A touching the deionized water was the same as the area of Electrode B touching the deionized water) and (c) the differences between Electrode A and B.
4. Results and discussion
4.1 ECM test at large electrode separation

This experiment aimed to clarify the efficiency of fabricating hybrid Cu–Cu$_2$O nanostructures with a large electrode separation. The mass of cathode Electrode A hardly increased and the dendrites did not form a short-circuit, although the ECM behavior was confirmed by the change in the ER.

In the case of the ECM tests, it is believed that the ER confirmed the ECM behavior as a result of the following mechanism, as illustrated in Fig. 2. (I) Cu ions eluted from the anode electrode into the deionized water, and the increase in the concentration of Cu ions drastically decreased the ER. (II) The Cu ions eluted from the anode moved under the influence of the Coulomb force, and precipitated as hybrid Cu–Cu$_2$O nanostructures at the cathode. The nanostructures grew in the form of dendrites extending from the cathode electrode. (III) The dendrites formed a short-circuit between the electrodes, and a large amount of current flowed in the dendrites. Thus, the dendrites stopped growing, and the ER rapidly decreased.

It was inferred that the effect of the electric field on the ion behavior in steps (I) and (II) decreased with increasing electrode distance. These results indicated that ECM at large electrode separations was not appropriate for the fabrication of hybrid Cu–Cu$_2$O nanostructures.

![Fig. 2 Schematic of electrical resistance (ER) as a function of time.](image)

Table 1 Experimental conditions.

| Experimental condition | Resistivity of deionized water [M$\Omega$ cm] | Volume of dropwise [ml] | Applied voltage [V] | Electrode distance [mm] |
|------------------------|---------------------------------------------|-------------------------|---------------------|------------------------|
| (i)                    | 8                                          | 6.9                     | 20                  | 19.25                  |
| (ii)                   | 8                                          | 5.3                     | 20                  | 9.25                   |
4.2 Evaluation of the performance of Electrode A and B, focusing on the path length of dendrite growth

The fabrication of hybrid Cu–Cu$_2$O nanostructures on an electrode is accompanied by the growth of dendrites. Here, we considered a way to fabricate larger-scale hybrid Cu–Cu$_2$O nanostructures by controlling the dendrite growth. As described in Section 4.1, the large-scale fabrication of hybrid Cu–Cu$_2$O nanostructures requires ECM to be induced with a small electrode separation. Here, we evaluated the performance of Electrode A and B with 9.25 mm electrode distance. The ECM behavior of Electrode A and B also consisted of three steps as set out above. Here, the ratio ER/ER$_{LM}$ was introduced to explain the change in ER, as shown in Fig. 3, where subscript of LM represents the local minimum. The electrical resistance (ER$_{LM}$) was assumed to be a reference value at which the Cu ions initially precipitated as Cu and Cu$_2$O (as shown in Fig. 2). In Fig. 3, the ER/ER$_{LM}$ ratio for Electrode A is shown by dotted curves, and that of Electrode B is shown by solid curves. In the present study, we defined the period for the formation of a short-circuit as the value below ER/ER$_{LM}$ of 0.5. The ER/ER$_{LM}$ ratio for Electrode A decreased rapidly and the period for the formation of a short-circuit was 0.6 ± 0.1 h. In contrast, the decrease in ER/ER$_{LM}$ for Electrode B occurred and the period for the formation of a short-circuit was 1.3 ± 0.2 h. Figure 3 indicated that ECM occurred for a longer period for Electrode B.

![Fig. 3](image-url)  
**Fig. 3** The ratio of electrical resistance (ER) to reference value of electrical resistance (ER$_{LM}$) vs. time for Electrode A and B.

Table 2 The correlation among the path length, the period required for the formation of a short-circuit and the average mass of precipitated nanostructures.

| Electrode shape | The path length [mm] | The period required for the formation of a short-circuit [h] | The average mass of precipitated nanostructures [mg] |
|-----------------|----------------------|----------------------------------------------------------|--------------------------------------------------|
| Electrode A     | 9.25                 | 0.6±0.1                                                  | 0.200±0.033                                      |
| Electrode B     | 19.25                | 1.3±0.2                                                  | 0.360±0.081                                      |
The ECM performance was evaluated by comparing the mass of the hybrid Cu–Cu$_2$O nanostructures for Electrode A and Electrode B. Table 2 shows the correlation among the path length, the period required for the formation of a short-circuit and the average mass of precipitated nanostructures. The hybrid Cu–Cu$_2$O nanostructures at Electrode B indicated a greater degree of precipitation than that for Electrode A due to increase in the path length. When the path length is doubled, the period required for the formation of a short-circuit is doubled. Hence, the mass of precipitated nanostructures is doubled. Figure 4 shows SEM images of the hybrid Cu–Cu$_2$O nanostructures at cathode Electrode (a), (b) A-5 and (c), (d) B-5. It was presumed that Cu$^+$ ions also grew as the dendrites at the gap of precipitated nanostructures through the long period required for the formation of a short-circuit. Therefore, the dendrites grew densely.

Also, the uniformity of the hybrid Cu–Cu$_2$O nanostructures was correlated with the period required for the formation of a short-circuit. Figure 5 shows the photographs of cathode Electrode (a) A-5 and (c) B-5, and the optical images of the hybrid Cu–Cu$_2$O nanostructures at the center of cathode Electrode (b) A-5 and (d) B-5. Comparing the photographs, the hybrid Cu–Cu$_2$O nanostructures at cathode Electrode B formed with the uniformity. However, the hybrid Cu–Cu$_2$O nanostructures slightly precipitated at the corner of cathode Electrode B, as shown in Fig. 6(a). It seems that the concentration of the electric field affects the precipitation behavior of the hybrid Cu–Cu$_2$O nanostructures. We performed the finite element analysis (FEA) by using the commercial software program Femtet (Murata Software Co., Ltd.). The electrical potential 20 V was applied between the anode and cathode as the boundary condition and the relative dielectric constant of water is 80.4. Figure 6(b) shows the FEA result for Electrode B, which indicates the concentration of the electric field at the corner. It is presumed that the concentration of the electric field preferentially forms dendrites growing from the cathode to anode, but does not contribute to precipitation of nanostructures on the cathode surface.

![Fig. 4 FE-SEM images of (a), (b) the hybrid Cu–Cu$_2$O nanostructures at cathode Electrode A-5 and (c), (d) the hybrid Cu–Cu$_2$O nanostructures at cathode Electrode B-5.](image-url)
Fig. 5 (a) The photograph of cathode Electrode A-5, (b) the optical image of the hybrid Cu–Cu$_2$O nanostructures at the center of cathode Electrode A-5, (c) the photograph of cathode Electrode B-5 and (d) the optical image of the hybrid Cu–Cu$_2$O nanostructures at the center of cathode Electrode B-5.

Fig. 6 (a) The optical image of the hybrid Cu–Cu$_2$O nanostructures at the corner of cathode Electrode B-5 and (b) the distribution of the absolute value of the electric field at the corner of cathode Electrode B based on the 3D FEA.

5. Conclusions

In this study, ECM tests under various experimental conditions were performed to realize the sustainable and large-scale fabrication of hybrid Cu–Cu$_2$O nanostructures. The results of this study show that the optimal experimental conditions were provided by increasing the path length for dendrite growth by changing the electrode shape. Consequently, more hybrid Cu–Cu$_2$O nanostructures were precipitated on the electrode, and this result indicates the possibility of the sustainable and large-scale fabrication of hybrid Cu–Cu$_2$O nanostructures using ECM.

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