



# Production of ultrahigh purity copper using waste copper nitrate solution

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## Abstract

The production of ultrahigh purity copper (99.9999%) by electrolysis in the presence of a cementation barrier has been attempted employing a waste nitric copper etching solution as the electrolyte. The amount of copper deposited on the cathode increased almost linearly with electrolysis time and the purity of copper was observed to increase as the electrolyte concentration was increased. At some point, however, as the electrolyte concentration increased, the purity of copper decreased slightly. As the total surface area of cementation barrier increased, the purity of product increased. The electrolyte temperature should be maintained below 35 °C in the range of investigated electrolysis conditions to obtain the ultrahigh purity copper. Considering that several industrial waste solutions contain valuable metallic components the result of present study may support a claim that electrowinning is a very desirable process for their treatment and recovery.

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*Keywords:* Highly pure copper; Electrolysis; Waste etching solution; Electrowinning; Cementation barrier

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## 1. Introduction

Copper, a metal with high electrical and thermal conductivity, has good malleability and ductility. It has been commonly used for the production of wires and tubing by extrusion and drawing as well as being casted [1,2]. Presently, it is mainly used in the manufacture of the electrical conductors. There are several shapes for industrially used copper with the most common one being wire, whose production consumes about 50% of the entire use of copper. After electrodepositing copper on titanium or stainless steel cathode, copper rod is made by a wirebar process first and then by drawing this rod, copper wire is produced.

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Approximately 32% of copper wire is used for communication cables, 23% for building wires, and 19% for magnet wires. Most of the industrially employed copper has a purity of 4 N (four nines; 99.99%) and, because of its wide usage, it is usually recovered for reuse [3]. Among several methods utilized for the recovery of 4 N copper, the process that utilizes an electrochemical cell taking ingot copper made from used copper as the anode is the dominant process. It uses copper nitrate or copper sulfate solution as the electrolyte [4].

The wastewater from certain chemical processes such as ceramic coloring, mordanting, and production of preservatives, etc. contains copper nitrate or copper sulfate as the major components with the other chemical species present in trivial amounts. Therefore, with slight or no further treatment of such wastewater, it may be usable as the electrolyte solution for electrowinning process of copper. Also, if the process conditions are controlled carefully, it is considered possible to increase the purity of the recovered copper up to 5 N (five nine; 99.9999%) or even 6 N (six nine; 99.99999%) [5–7]. When the purity of copper reaches these values, its usage can be broadened due to an improvement in several physical properties. For example, the sound quality of a speaker is improved when the audio pin cable or speaker cable is made of 5 or 6 N copper. Also, the golden bonding wire being used for the manufacture of semiconductors can be replaced by copper wire of this purity, which will result in a significant economical benefit [8–10].

When the anode copper is dissolved in solution, cuprous or cupric ions are produced depending on the oxidation state of solution. If gold or silver ions exist in solution, due to their analogous chemical properties with copper ions, they behave in a similar manner to copper ions and thus can affect the purity of electrodeposited copper.

Another chemical species which can possibly influences the purity of copper is sulfur ion, since it has an affinity for the copper ion. Considering these potential problems copper sulfate solution may not be the adequate electrolyte to obtain ultrahigh purity copper [11].

In this study, production of 6 N copper has been attempted using waste copper nitrate solution from an actual process as the electrolyte solution. The major experimental variables taken were electrolysis time, electrolyte concentration, current density, and temperature. Also, the effect of cementation barrier and filtration membrane has been investigated.

## 2. Materials and methods

### 2.1. Materials

The waste copper nitrate solution (0.6–0.8 M) generated from a practical etching process (9 Digit Materials Co. Ltd.) was employed as the electrolyte. Its content of impurities is shown in Table 1. Copper ingot cast using the used copper obtained from LG—Nikko Metal Co. was cut to form pieces with a size of 40 mm × 80 mm × 15 mm. These pieces were used as anode after slight polishing with a 600-grit sand paper. Titanium plate (>99.5%) purchased from Hyundai Titanium Co. was cut to a size of 20 mm × 80 mm × 2 mm and used as cathode after polishing with a 600-grit sand paper. One side and entire edges of this plate were coated with Teflon in order to make the copper deposit only on the non-coated side of the titanium plate. Piranha solution [12,13] prepared by mixing concentrated H<sub>2</sub>SO<sub>4</sub>

Table 1  
Chemical analysis of impurities in the raw electrolyte solution

Impurity	Concentration (mg/l)
Ag	6.5
S	0.3
Fe	0.8
Se	0.1
Te	0.1
Bi	0.1
Sb	0.1
As	0.2
Pb	0.3

and H<sub>2</sub>O<sub>2</sub> as 3:1 volume ratio was used for cleaning of cell and glassware, and distilled water (>18 MΩ) was employed for rinsing three times.

## 2.2. Experimental setup

The electrolysis cell used for the electrorefining of copper was composed of anodic and cathodic part (two-electrode system) and each part was separated by a cementation barrier (Fig. 1). A filtration membrane was located between the two electrodes when it was necessary. The cell was fabricated using acrylic resin plate (t10 mm) and immersed in a water bath equipped with an automatic temperature controller. To remove the dissolved oxygen from electrolyte and induce an agitating effect to maintain the solution in a homogeneous

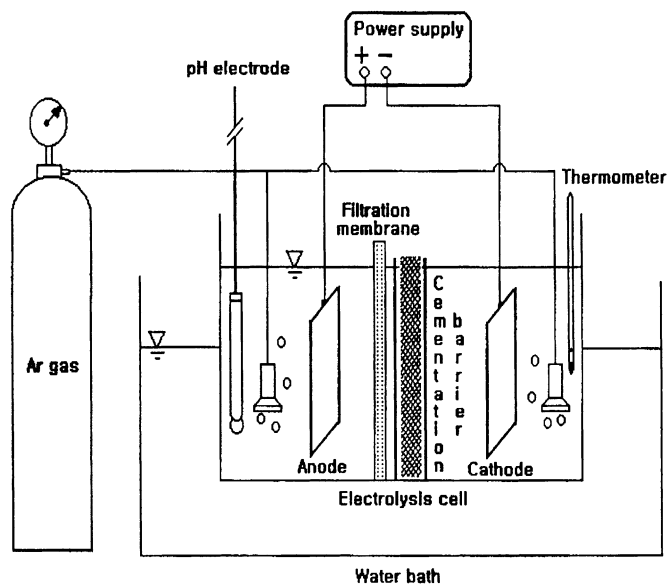


Fig. 1. Schematic diagram of the electrolysis system.

state, highly pure Ar gas (>99.999%) was continuously sparged into the solution at a flow rate of 200 ml/min at least for 30 min before electrolysis as well as during the electrorefining.

### 2.3. Electrolysis process

The pH of electrolyte was adjusted beforehand to 1.5–1.7 using nitric acid. This was the proper pH range for copper deposition using the operating current density [14]. After filtering this solution using filter paper with a mean pore size of 0.22  $\mu\text{m}$ , 100–200 mg of HCl was added per liter of solution to remove the argentous ion as precipitate and the solution was filtered again. The anode and cathode were cleaned with 0.1 M nitric acid and rinsed three times with distilled water. Copper wire (LG—Nikko Metal Co., 4 N), which was employed as the cementation barrier, was cleaned and rinsed in the same manner.

Pre-treated electrolyte (500 ml) was poured into the cell, which contained only 134 g/l of cementation barrier. The electrolyte was circulated in the direction of cathodic compartment  $\rightarrow$  pump  $\rightarrow$  anodic compartment  $\rightarrow$  cementation barrier  $\rightarrow$  cathodic compartment at a flow rate of 50 ml/min for at least 2 h prior to electrolysis to decrease the content of argentous ion further from the electrolyte by cementation. Copper wire was supported by two Teflon holders 2.5 cm apart. After circulation of the electrolyte, anode and cathode were installed in the cell 4 cm apart. The filtration membrane with an aperture size of 0.35  $\mu\text{m}$  was placed between the anode and cementation barrier when necessary. After connecting both electrodes to the power supply (Hewlett Packard, Model E3631A), electrolysis was carried out under the desired conditions. During electrolysis, the pH of the electrolyte was monitored and when pH exceeded over the optimal range, nitric acid was added to the electrolyte.

Produced copper was detached from the cathode and rinsed thoroughly using distilled water. Then, it was dried in a vacuum oven (Jeil Scientific, Model J-DV04) and stored in a desiccator filled with Ar gas to prevent surface oxidation before analysis.

### 2.4. Analysis

The electrodeposited copper was cut to several pieces and completely dissolved using aqua regia (3:1 volume mixture of HCl and  $\text{HNO}_3$ ) in 250 ml Erlenmeyer flask. This solution was sealed and stored in a refrigerator at 4 °C. Subsequently, its composition was analyzed using ICP-Mass Spectrometer (Perkin-Elmer, Model ELAN-6000) later.

## 3. Results and discussion

### 3.1. Cementation barrier

In order that the purity of electrodeposited copper on cathode is as high as 6 N, the total amount of impurities in it should not exceed 1 mg/l. Since copper nitrate solution was used as the electrolyte in this study, Ag may be regarded as a major impurity influencing the purity of product (Table 1). In practice, the total amount of impurities except Ag contained in the product was observed to be <0.4–0.5 mg/l based upon pre-experiments. Therefore, control of Ag content in the cathodically depositing copper is critical for the production of

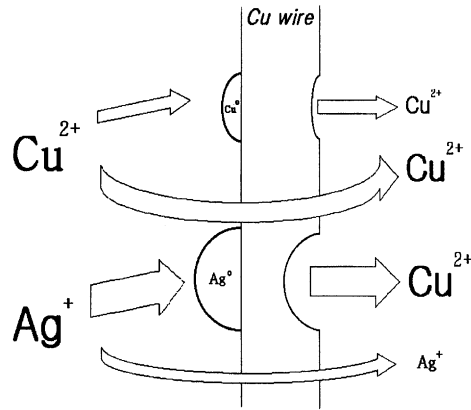


Fig. 2. Schematic of the cementation effect occurring at the barrier.

ultrahigh purity copper and application of a cementation barrier has been considered for this purpose.

The scheme for a cementation barrier is presented in Fig. 2. The cementation barrier was composed of fine copper wire to insure a high surface area and there was almost no resistance to the flow of electrolyte through the barrier during electrolyte circulation and electrolysis.

When  $\text{Cu}^{2+}$  approaches the barrier, some of the ions are reduced to metallic copper and deposited on the surface of copper wire. Simultaneously, an equivalent amount of  $\text{Cu}^{2+}$  to the deposited as copper is released to the electrolyte. However, most of  $\text{Cu}^{2+}$  ions pass the barrier without being reduced so that there is almost no change in the amount of copper ions. Compared with  $\text{Cu}^{2+}$ , most of  $\text{Ag}^+$  can be reduced to its metallic form on the wire surface in the course of passing through the barrier since silver is more noble than copper. As for copper, an equivalent amount of  $\text{Cu}^{2+}$  corresponding to the reduced silver will be dissolved into electrolyte from the wire as shown in Eq. (1).



Thus, only a small portion of the  $\text{Ag}^+$  is capable of passing through the barrier. The silver ions originally present in the electrolyte will be treated by cementation during prior circulation and most of the silver ions dissolved from the anode in the course of electrolysis are also anticipated to be removed from solution in the same manner.

### 3.2. Electrolysis time

Fig. 3 shows the variation of copper deposition with electrolysis time. It can be seen that about 5.5 and 18.6 g of copper were cathodically deposited after 15 and 72 h electrolysis, respectively. The amount of deposited copper is almost linearly proportional to the electrolysis time and this can be explained by Faraday's law [15]:

$$W = \frac{Ite_q}{F} \quad (2)$$

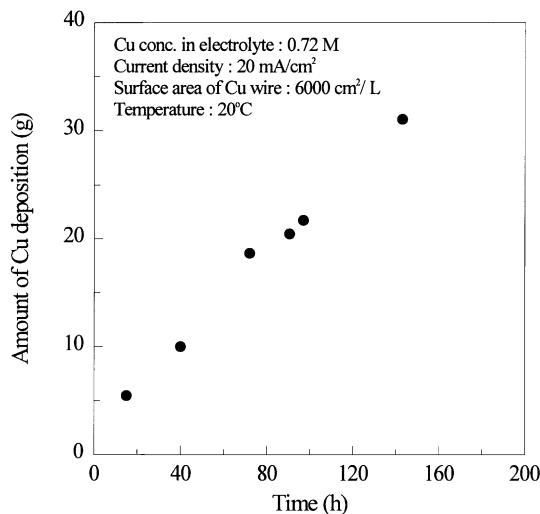


Fig. 3. Change in the amount of copper deposition according to the electrolysis time.

where  $W$  is the mass of material deposited on (or dissolved from) electrode (g),  $I$  the current flowed through the interface between electrode and electrolyte (A),  $t$  the time of current flow (s),  $e_q$  the equivalent of material deposited (or dissolved),  $F$  the Faraday constant (96,500 C/mol).

From the above equation, one concludes that the mass of deposited material is expected to be in proportion to current flowing time under a condition of constant current flow.

### 3.3. Effect of $\text{Cu}^{2+}$ concentration on the purity of deposited copper

The molar concentration of copper in the waste solution was in the range of 0.6–0.8 M. Electrolysis was conducted for electrolytes with different copper concentrations, and the purity of product and content of Ag impurity were measured (Fig. 4). It has been shown that purity of the product is as high as 6N for the entire range of copper concentrations. Purity increases with the concentration of electrolyte up to 0.74 M but it decreases slightly above this concentration. The amount of Ag impurity changes in the opposite manner.

The reason for increase in purity of product as electrolyte concentration rises is presumably found in the increase of the activity of copper ions, which results in the increased electrodeposition of copper on cathode. The small decrease of purity at higher concentrations is thought to be due to the increased potential coming from the increase of copper concentration, which possibly results in the slight increase in silver deposition. Electrolysis under the same conditions was also carried out for different (shorter and longer) electrolysis times. The variation in the purity of product and content of Ag impurity with electrolyte concentration showed a nearly similar trend (results not shown here).

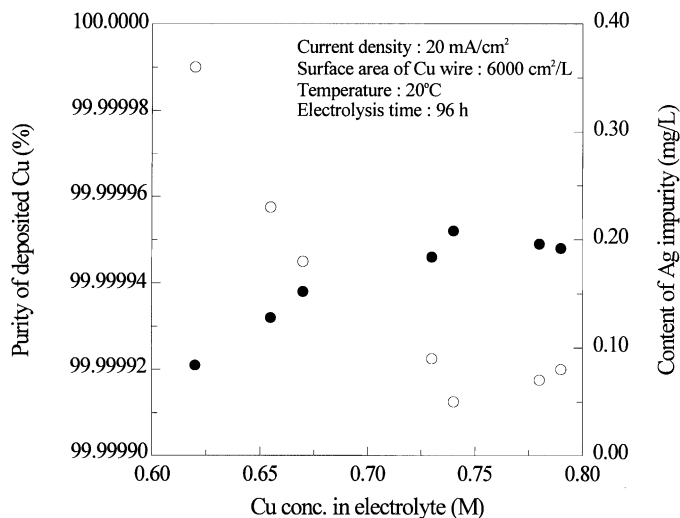


Fig. 4. Change in the purity of deposited copper (●) and content of Ag impurity (○) according to the  $\text{Cu}^{2+}$  concentration in electrolyte.

### 3.4. Effect of current density

In electrolysis process, the current density is known to be a critical factor influencing both the quality and quantity of the product. If the current density is too low, the amount of product will decrease. Too high a current density will result in the deterioration in the quality of product. In this study, the effect of current density on the purity of product was examined at 20 °C and 72 h electrolysis using 0.69 M electrolyte (Fig. 5). Under these conditions, the purity of the deposited copper decreased, as the current density was raised.

Increased current density will result in an increase in potential, which may result in the increase of the electrodeposition of impurities along with copper ions. For the utilized conditions, the purity of product is below 6N when the current density is increased more than 40 mA/cm<sup>2</sup>. It seems important to keep the current density in a relatively lower value range to obtain ultrahigh purity copper.

Actually, the variation of potential with current density was found to be linear for an electrolyte with somewhat different copper concentration (Fig. 6). The electrical resistance can be estimated from the slope of the regression line which connects the experimental points.

The efficiency of current has been estimated to evaluate the productivity of electrolysis along with quality of product. The efficiency of current is defined as:

$$E(\%) = \frac{D_a}{D_t} \times 100 \quad (3)$$

where  $D_a$  and  $D_t$  are the mean actual and the theoretical amount of deposition, respectively.  $D_t$  can be calculated using Eq. (2). The change of current efficiency according to the applied

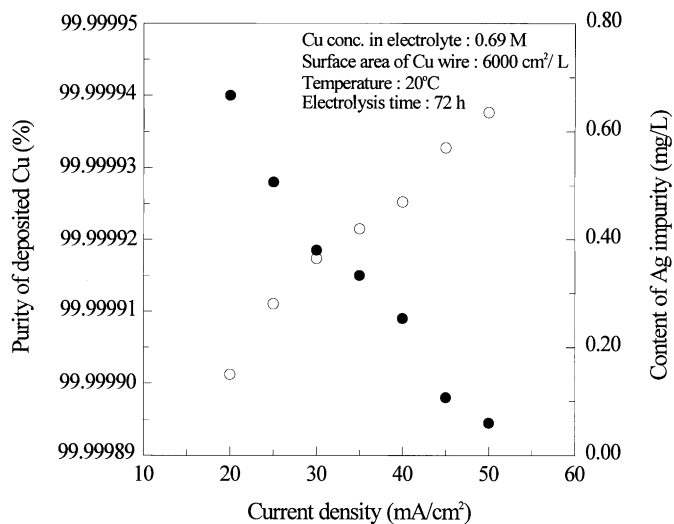


Fig. 5. Change in the purity of deposited copper (●) and content of Ag impurity (○) according to the current density.

current density in the same electrolysis conditions as in Fig. 5 is represented in Fig. 7. As can be seen, the current efficiency becomes high as the current density increases.

Therefore, it will be more economical to increase current density in a practical electrolysis process. However, since content of impurities in the product also increases with current density, optimal operating condition should be determined considering both of these aspects.

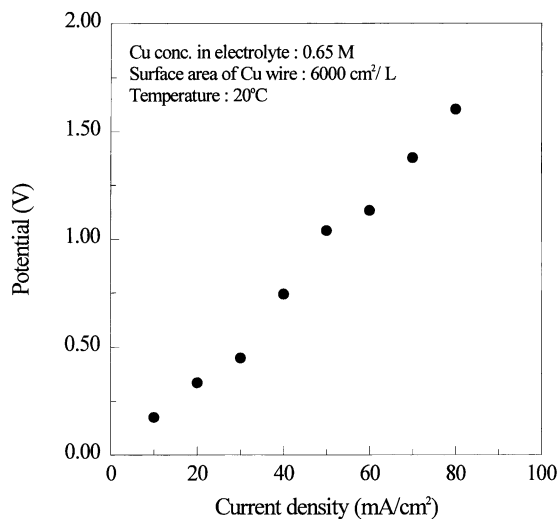


Fig. 6. Relation between potential and current density.



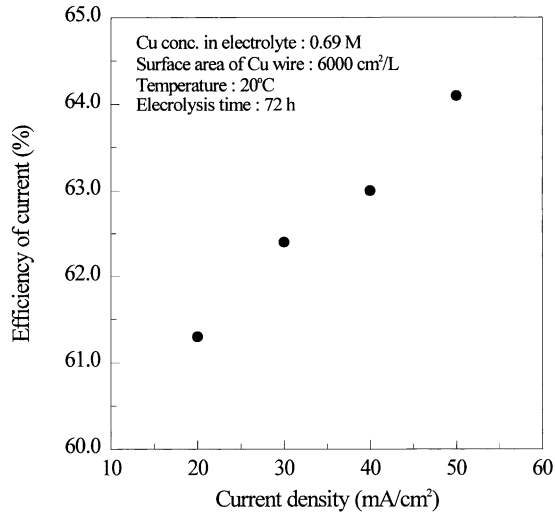


Fig. 7. Change in the efficiency of current depending on current density.

### 3.5. Influence of surface area of cementation barrier

The total surface area of copper wire, which works as the cementation barrier, is considered to have a direct effect on the purity of the product since the amount of Ag impurity passing through cementation barrier will decrease as barrier's surface area increases. Fig. 8

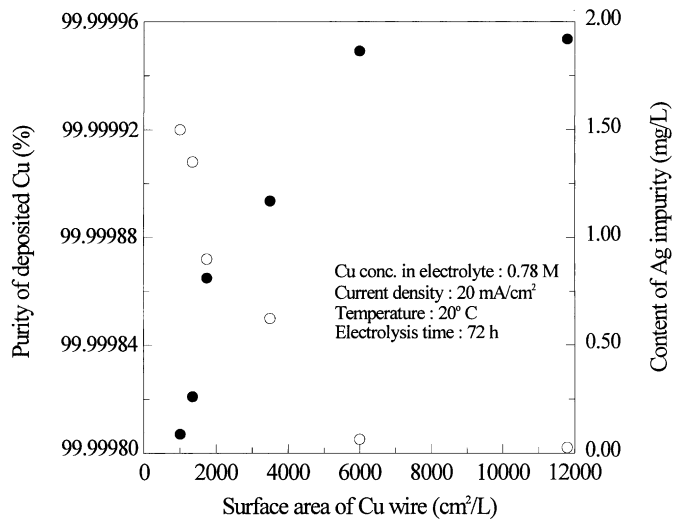


Fig. 8. Variation in the purity of deposited copper (●) and content of Ag impurity (○) with surface area of copper wire.

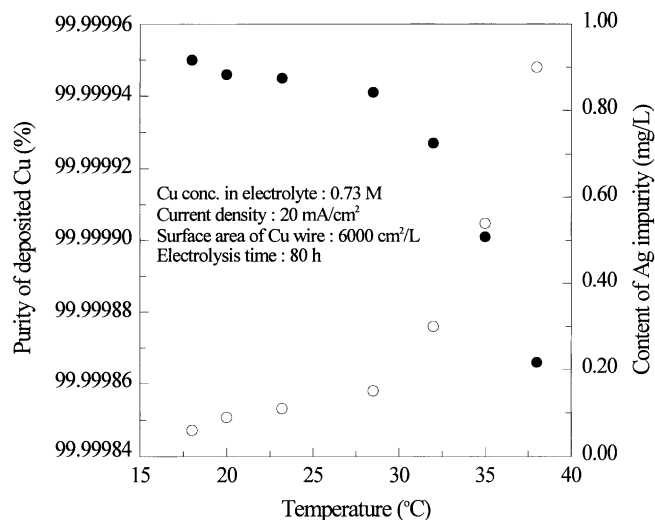


Fig. 9. Variation in the purity of deposited copper (●) and content of Ag impurity (○) with electrolysis temperature.

shows the effect of surface area of the cementation barrier on the purity of deposited copper. The surface area of the cementation barrier was varied using copper wire with different diameters but at a constant concentration of 134 g/l based on an assumption that the copper wire was in the shape of long cylinder. From the results, it can be seen that purity of product increases with surface area up to 6000 cm<sup>2</sup>/l and is almost constant above this value. For the applied electrolysis condition, 6 N purity was ensured when the barrier's surface area was greater than ca. 5000 cm<sup>2</sup>/l.

The meaningful aspect of the cementation barrier can be found not in its weight but in its surface area, so that in actual electrolysis, it is thought that one can reduce the amount of copper wire by employing a finer wire as the cementation barrier.

### 3.6. Influence of electrolysis temperature and filtration membrane

Like most chemical reactions, the electrodeposition of copper was also considered to be influenced by temperature. Thus, the effect of temperature on the purity of the product and its Ag content was investigated (Fig. 9). An increase in temperature reduces the purity, especially above 30 °C. As the temperature rises, the diffusivity of impurities increase, which presumably results in the decrease of purity. When the electrolyte temperature was greater than 35 °C, it was impossible to obtain 6 N copper. Considering that a conventional electrolysis process, such as electroplating or electrorefining is operated at approximately 60 °C [16], the electrolysis process to obtain ultrahigh purity copper is a *cool* electrolysis process.

The role of the cementation barrier is a chemical screening of dissolved impurities through redox reaction. However, solid impurities such as fine slime occurring at the anode, which possibly can be included in the cathodic deposition during electrolysis, are not blocked

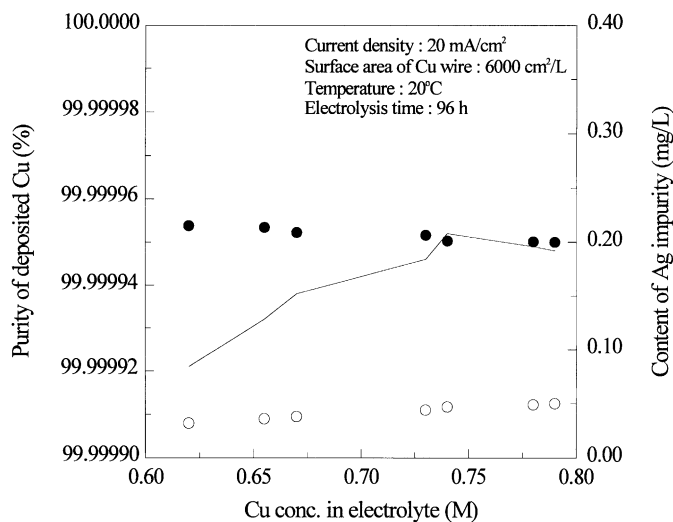


Fig. 10. Comparison of the purity of deposited copper in the absence (—) and presence (●) of filtration membrane. Also shown is the change in content of Ag impurity (○) with  $\text{Cu}^{2+}$  concentration in electrolyte in the presence of filtration barrier.

by this method. Therefore, along with the chemical screening, application of filtration membrane as a physical screen has been attempted in the present study (Fig. 10).

Compared with the results of experiments conducted in the absence of membrane, the purity of product is observed to increase especially when the electrolyte concentration is relatively low. Also, the content of the Ag impurity remains at a very low level for the entire concentration range of electrolyte utilized. The reason for the specific effectiveness of filtration membrane viewed at lower concentration range is not clear presently, however, it can be suggested that application of filtration membrane is effectual for the acquisition of electrodeposition product with a stable quality in the conditions of fluctuating electrolyte concentration.

#### 4. Conclusions

It has been shown that it is possible to produce 6N copper by electrolysis by using a cementation barrier with copper etching solutions as the electrolyte. Usage of waste process solution as the electrolyte for the production of ultrahigh purity copper is important for resource recovery. Considering the large amount of industrial waste solution containing metallic ions, employment of this waste as the electrolyte for obtaining high purity metal after simple pretreatment will provide several benefits such as reduction of the amount of waste solution, materials reuse, energy savings, and so on. As a further study, an investigation of increased current efficiency and evaluation of the feasibility to scale up the process is planned.

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