

Controlling the oxidation of organic brightener during electroplating using an ion-exchange membrane

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Abstract—The effect of an ion-exchange membrane combined with a dimensionally stable anode on the oxidation rate of organic brightener and electroplating performance was investigated. The oxidation rate of the brightener was measured by analyzing the total organic carbon content in the plating solution. The oxidation rate increased rapidly as the current density increased when there was no ion-exchange membrane. However, when an ion-exchange membrane was present, the oxidation rate of the brightener was significantly reduced by Neosepta CMX and CMS cation-exchange membranes. The CMS monovalent selective cation-exchange membrane in particular was the most effective in reducing organic brightener oxidation, regardless of the current density. Through-hole printed circuit board electroplating was more precise with an ion-exchange membrane than with no membrane. These results confirmed that the electroplating performance was improved by the presence of an ion-exchange membrane on the anode, effectively inhibiting the oxidation of organic brightener.

Key words: Printed Circuit Board, Electroplating, Brightener, Oxidation, Ion-exchange Membrane

INTRODUCTION

A printed circuit board (PCB) is a circuit formed by copper plating on a phenolic or epoxy resin panel. PCBs play an important role in the electronics industry by electrically connecting electronic components and holding them in place [1-3]. They are a basic component of all electronics products. PCBs now come with narrower wiring widths and increased density, requiring a sophisticated and complicated manufacturing process. Multilayer PCB technology is used to increase the wiring density by laminating wired layers [4-6].

Drilling and plating processes are used to connect the wires on each layer of multilayer PCBs. Drilling is used to process the via holes on the board once the lamination has been completed. The wiring on each layer is connected through the via holes, and plating is necessary to connect the non-conductive internal walls of the via holes [7,8]. When electroless plating is used, it is difficult to make the plating thicker, and the electrical conductivity is lower than for normal electroplating. To resolve these problems, the via holes are generally electroplated to a thickness of 20-30 μm after the electroless plating process is complete [9].

In conventional plating, the board to be plated is placed on a cathode and a copper ball is installed on an anode to supply copper ions. The plating occurs once direct current is applied. In an alternative method, a dimensionally stable electrode is used as the anode, and copper ions are added to the plating solution. Both methods have the common problem that the organic brightener added to enhance the plating performance during the plating is oxidized on the surface of the anode and changes the composition of the plating solution [10], which reduces the plating performance. This requires discard-

ing the plating solution and replacing it with fresh solution [11], producing large amounts of waste plating solution and increasing the expense [12-18]. The continual supply of new plating solution and expensive organic brightener also contributes to the cost of plating.

For this reason, processing the via holes and plating the area around the holes affects the PCB performance and productivity. A new plating process must be developed because it is difficult to inhibit the oxidation of organic brightener and resolve the problems associated with the existing plating process.

This paper describes a modified plating process that uses an ion-exchange membrane to inhibit the oxidation of organic brightener that occurs while plating the PCB via holes. The amount of oxidized organic brightener was measured after using a dimensionally stable anode (DSA) combined with an ion-exchange membrane. The effects on the organic brightener and plating performance of the PCB via holes were studied as functions of the ion-exchange membrane type and current density.

EXPERIMENTAL

1. Experimental Apparatus

Fig. 1 illustrates the experimental plating equipment and the electrode structure. The DSA was a Ti/IrO₂ electrode on the left and right sides of the electrochemical cell, and a copper plate or PCB board was connected in the center as a cathode to make the copper plating on both sides of the cathode even. An ion-exchange membrane was fixed to the anode surface by an epoxy board to determine the effect of the membrane. A 1-mm-thick poly vinyl chloride net was inserted between the anode and the ion-exchange membrane so that the gas generated during the electrode reaction could be released. The effective area of the electrodes used in this experiment was 5×5 cm². The plexiglass electrochemical cell was 21×7×

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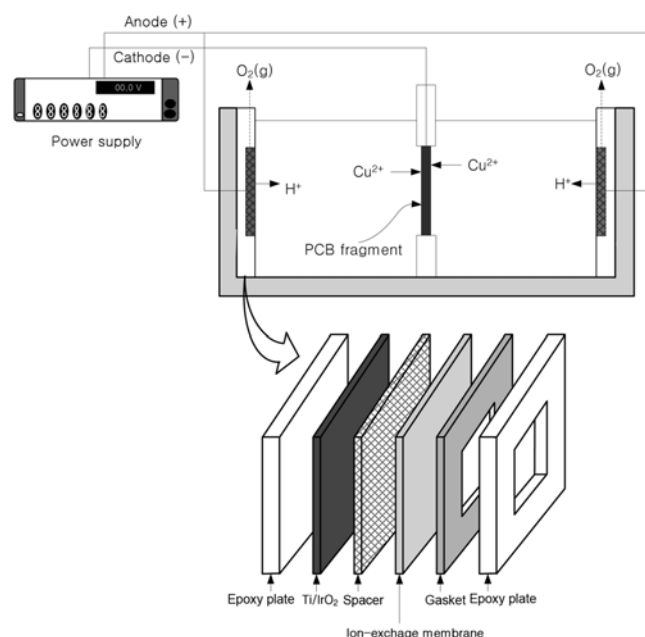


Fig. 1. Schematic diagram of the experimental setup for electroplating of PCBs.

10 cm³. The current level of the DC power supply (Agilent, 6654A) was set in advance.

2. Experimental Method

2-1. Analysis of the Basic Properties of the Organic Brightener

The organic brighteners used for plating in this experiment were BV-111, -112, and -113 (Hojin Platec Co., Inc.). BV brighteners are used for the production of PCB in order to fill blind microvias with copper, pattern plate, and metalize through-holes. Additive BV-111 is responsible for the excellent throwing power, and BV-112 is responsible for the deposition of fine-grained and ductile copper coatings. An optimum degree of brightness is achieved with additive BV-113.

Each organic brightener was diluted in distilled water to a concentration of 10 mL/L. We measured the pH (Orion 230 digital pH meter) and electric conductivity (Con10 basic conductivity meter, Oakton Instruments, Vernon Hills, IL, USA) to analyze the content of the organic compound and ionic substance. Because no chemical information about the brightener was supplied by the manufac-

turer, we measured the total organic carbon (TOC) content (OCT-1, Shimatsu) to analyze the oxidation of the brightener. The presence of organic acid or amine functional group was determined by titrating the diluted organic brightener solution with 0.1 N NaOH.

2-2. Composition of the Plating Solution and Electroplating Experiment

The plating solution used in this experiment was the same as that in general plating processes: 200 g/L of CuSO₄, 50 g/L of H₂SO₄, 10 mL/L of BV-111, 0.5 mL/L of BV-112, and 0.6 mL/L of BV-113. The effects of the different types of ion-exchange membrane and various levels of current density were investigated. First, the oxidation rate of organic brightener was determined by measuring the TOC change in the plating solution for current densities of 10, 20, and 30 mA/cm² in conventional plating without any ion-exchange membrane. Then, using Neosepta AMX, CMX, and CMS (Astom Corp., Japan) ion-exchange membranes in succession, plating was conducted with a current density of 20 mA/cm² to measure the oxidation of organic brightener for each type of ion-exchange membrane. Table 1 shows the properties of the ion-exchange membranes used in this study.

The cathode was replaced by a PCB with via holes and the plating experiment was repeated under similar conditions (10, 20, and 30 mA/cm², with and without the CMS ion-exchange membrane) to investigate the effect of the membrane on the plating performance of PCB via holes. A scanning electron microscope (SEM) image (JSM-6335F, JEOL) of the plated PCB was examined to determine the effect of the ion-exchange membrane on the plating.

RESULTS AND DISCUSSION

1. Analysis of Organic Brightener Properties

After the organic brightener was diluted in distilled water to a concentration of 10 mL/L, the pH, conductivity, and TOC content of each solution was measured. Table 2 shows that BV-111 and 112 exhibited strong acidity with pHs of 2.94 and 2.97, respectively, while BV-113 exhibited mild acidity with a pH of 4.44. The TOC content of BV-111 was 1128 mg/L, the highest of all the organic brighteners.

The presence of an ionic substance like organic acid in the organic brightener is significant in determining the possibility of organic compound transfer through the ion-exchange membrane. To determine the presence and content of ionic substances included in the

Table 1. Properties of ion exchange membranes used in this study [21]

Trade name	Type	Resistance (Ωcm^2)	Transport number	Water content (wt%)	Thickness (mm)
Neosepta AMX	Strongly basic	2.0-3.5	0.98	25-35	0.16-0.18
Neosepta CMX	Strongly acidic	2.5-3.5	0.98	25-35	0.17-0.2
Neosepta CMS	Strongly acidic	1.5-1.8	0.98	35-40	0.15-0.17

Table 2. Characteristic properties of organic brightener (10 mL/L) used in this study

Organic brightener	Function	pH	Conductivity ($\mu\text{S/cm}$)	TOC (mg/L)
BV-111	Excellent throwing power	2.94	461	1128
BV-112	Deposition of fine-grained and ductile copper coating	2.97	484	49.0
BV-113	Optimum degree of brightness	4.44	60.1	36.6

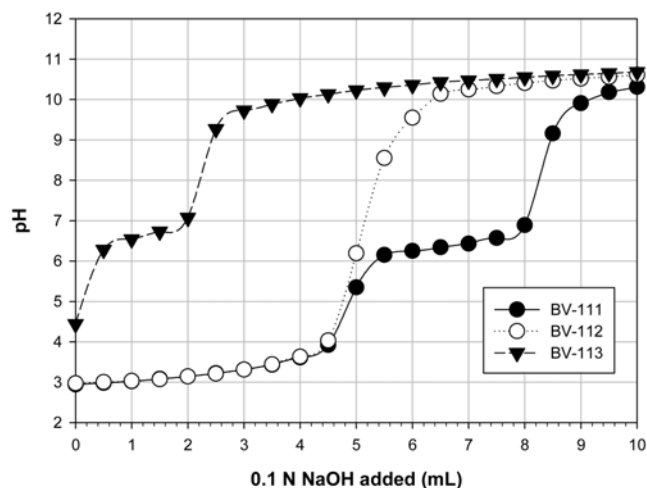


Fig. 2. Titration curves of diluted brighteners (10 mL/L) with 0.10 N NaOH solution.

organic brightener, 100 mL of brightener at a concentration of 10 mL/L was titrated with 0.1 N NaOH. Fig. 2 shows the resulting titration curve. It was clear that there was a strong acid content to BV-112 because its titration curve corresponded to a strong acid titrated with a strong base [19]. On the other hand, the pH increased slowly in the range of 5.5–7.0 for BV-111 and BV-113, corresponding to an organic compound with a carboxyl group included in the organic brightener. These organic acids can be partially dissociated corresponding to the pH of a solution with anionic characteristics [19]. Therefore, when the anion-exchange membrane is combined with the anode, these organic acids pass through the membrane and oxidize on the anode. An analysis of the chemical property of the brightener determined that the cation-exchange membrane was more effective than the anion-exchange membrane.

2. Oxidation of Organic Brightener According to the Current Density without an Ion-exchange Membrane

Plating experiments were performed for DSA electrodes with-

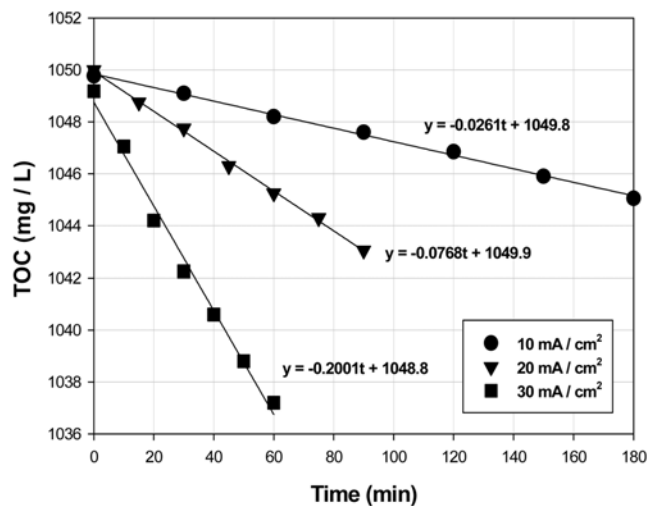


Fig. 3. Changes in the TOC concentration of the plating solution during electroplating without an ion-exchange membrane for different current densities.

out ion-exchange membranes at current densities of 10, 20, and 30 mA/cm² to measure the oxidation rate of organic brightener in the electroplating process.

Fig. 3 shows the TOC content of the plating solution as a function of time for different current densities. The organic brightener in the plating solution was considered to be oxidized on the anode and consumed. The reduction of organic brightener was 1.5, 4.7, and 12.0 mg/L for current densities of 10, 20, and 30 mA/cm², respectively, for a plating time of 60 min. Thus, the amount of oxidized organic brightener increased as the current density increased.

The oxidation rate of organic compounds can be calculated from the slope of the graph of the TOC content as a function of time. Fig. 3 shows that as the current density increased, the oxidation rate of organic compounds also increased from 0.026 to 0.077 to 0.20 mg/L/min. This was caused by the increased oxidation rate of the organic compounds due to the increased electrode potentials on the anode as the current density increased [20]. An increase in the current density during the plating process can increase the plating speed. However, our experiment showed that an increased current density caused problems by significantly increasing the oxidation rate of the organic brightener in the plating solution.

3. Effect of the Ion-exchange Membrane on Brightener Oxidation

Fig. 4 shows the TOC concentration in the plating solution as a function of time for a plating current density of 20 mA/cm². AMX was used for the anion-exchange membrane, and CMX and CMS were used for cation-exchange membranes. Fig. 4 shows that for 120 min of electroplating, the TOC amount decreased linearly, and the decrease was most pronounced for CMS followed by CMX and AMX in that order. The cation-exchange membrane more effectively inhibited the oxidation of organic brightener than the anion-exchange membrane. As mentioned earlier, this is caused by the organic substance in the organic brightener that can be transferred toward the anode through the anion-exchange membrane. The CMS was significantly more effective as a cation-exchange membrane than the CMX membrane at inhibiting oxidation of the organic compounds. Because the CMS membrane is designed to transfer only the monovalent cations, it can inhibit the diffusion of organic com-

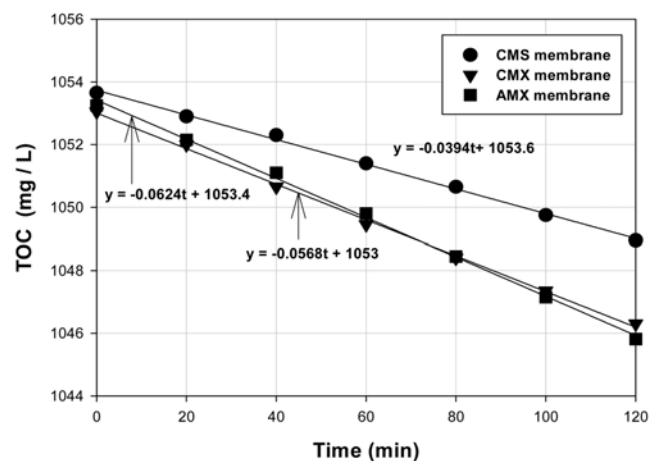


Fig. 4. Changes in the TOC concentration of the plating solution during electroplating with an ion-exchange membranes.

pounds [21-24].

The oxidation rates of TOC were found to be 0.062, 0.057, and 0.039 mg/L/min for the AMX, CMX, and CMS ion-exchange membranes, respectively. This represents a significant reduction compared to the oxidation rate of 0.077 mg/L/min for no ion-exchange membrane. The experiments showed that using electrodes combined with ion-exchange membranes can effectively inhibit the consumption of organic brightener, and the CMS membrane was the best of those tested.

4. Effect of Current Density on the CMS-covered Electrode

CMS, a cation-exchange membrane, most effectively inhibited the consumption of organic brightener. A plating experiment was performed with a CMS membrane on a DSA electrode with current densities of 10, 20, and 30 mA/cm² to measure the effect of current density when using an ion-exchange membrane. Fig. 5 shows the TOC content as a function of time for each current density. When the current density increased from 10 to 30 mA/cm², the TOC oxidation rate increased from 0.041 to 0.055 mg/L/min; this difference

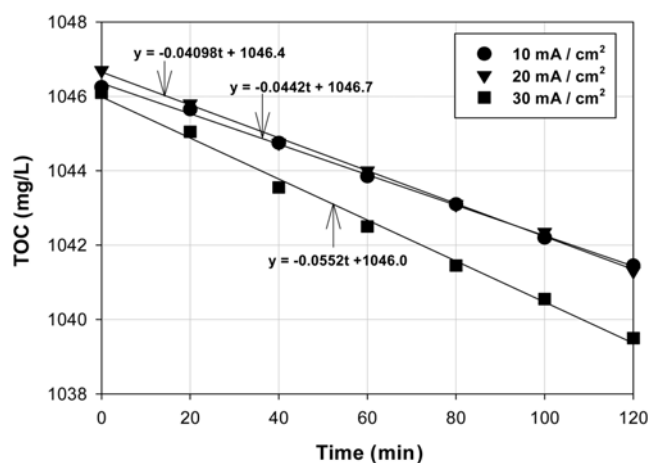


Fig. 5. Changes in the TOC concentration of the plating solution during electroplating with a CMS membrane for different current densities.

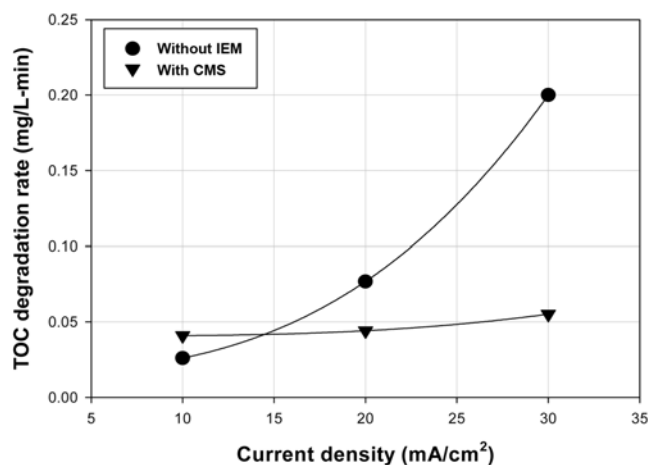


Fig. 6. Comparison of the TOC degradation rate during electroplating with and without an ion-exchange membrane (IEM) for different current densities.

was not significantly large.

Fig. 6 shows the TOC reduction rate as a function of current density to provide a more detailed comparison of plating using only a DSA electrode without an ion-exchange membrane and using a CMS membrane. The oxidation rate of organic compounds in the plating solution increased rapidly as the current density increased in the absence of an ion-exchange membrane. However, there was very little difference in the oxidation rate for different current densities with a CMS membrane. This was because the CMS blocked physical contact between the DSA anode and the plating solution to inhibit oxidation of the brightener. When the current density was 10 mA/cm², the oxidation rate with the ion-exchange membrane was higher than that without the membrane. This was because the organic compound in the plating solution was adsorbed on the ion-exchange membrane rather than being oxidized by the electrode reaction. These tests show that combining CMS with the anode effectively inhibited oxidation of the organic brightener, even when plating with increased current density.

5. Via Hole Plating of a PCB Using an Electrode Combined with an Ion-exchange Membrane

Even if plating using an ion-exchange membrane effectively inhibits the oxidation of organic brightener, it will not be usable if it reduces the overall plating performance. We therefore performed an experiment to test the plating performance of PCB via holes with and without an ion-exchange membrane. In an electrochemical set, a PCB with via holes was connected to the cathode and the same plating experiment was performed under the same conditions as before. The via holes were 350 μm in diameter and 100 μm deep.

The structure of the electrodeposits is known to mainly depend on applied current densities [25,26]. Fig. 7 shows an SEM image of a PCB via hole plated without using an ion-exchange membrane. The hole was rough and unevenly plated for a current density of 10 mA/cm². However, the roughness decreased and the PCB surface and hole interior were plated more smoothly and uniformly as the current density increased. The plating on the PCB surface was 25 μm thick while that inside the hole was 15 μm thick, because the electric field was weaker inside the hole than on the surface.

Fig. 8 shows an SEM image of a PCB plated using a CMS-covered anode. Unlike the case without the ion-exchange membrane, the PCB surface and the via hole interior were plated precisely and evenly regardless of the current density. This even plating quality was caused by the enhanced throwing power due to the evenly formed distribution of the electrode's potential due to its combination with the ion-exchange membrane [27-29]. This result shows that plating using an ion-exchange membrane effectively inhibits oxidation of the organic brightener, which has been a problem in conventional plating, and has the advantage of increasing the throwing power to improve the plating performance.

CONCLUSIONS

The oxidation rate of organic brightener and the effect of ion-exchange membranes on the plating performance were studied by performing electroplating in a process where an ion-exchange membrane was combined with a DSA. Experiments using a Ti/IrO₂ DSA and a copper plate cathode with varying current densities showed that the oxidation rate of the organic brightener increased rapidly

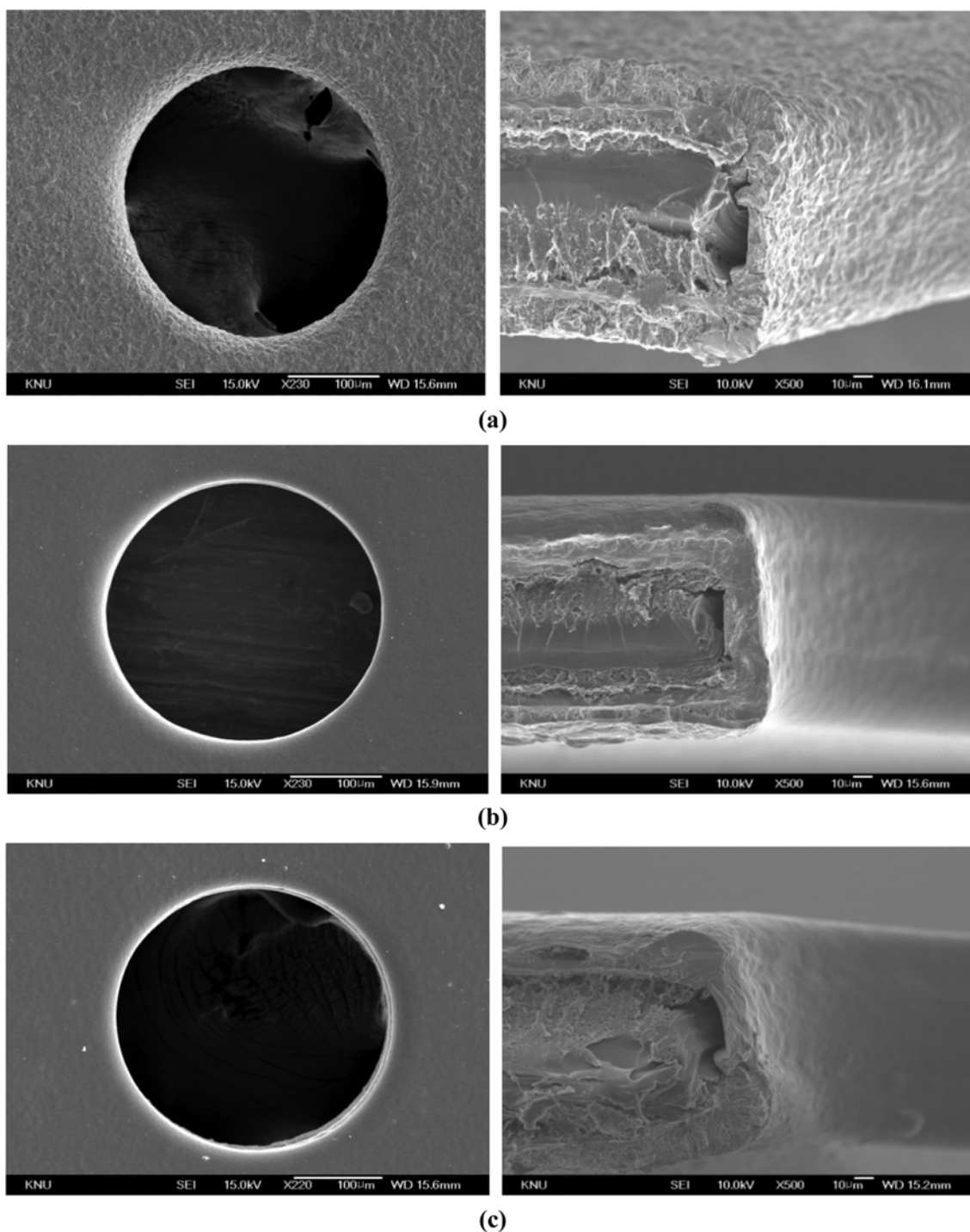


Fig. 7. SEM images of a PCB via hole after electroplating without an ion-exchange membrane for various current densities. (a) 10 mA/cm², (b) 20 mA/cm², and (c) 30 mA/cm².

as the current density increased. Adding an ion-exchange membrane to the surface of the anode under the same conditions significantly decreased the oxidation rate of the organic brightener. In addition, a cation-exchange membrane more effectively inhibited oxidation than an anion-exchange membrane. This was likely due to the organic substances in the brightener that have anionic functional groups. Using a CMS cation-exchange membrane decreased the oxidation rate the most, independent of the current density. This quality makes

the CMS membrane effective at inhibiting organic brightener oxidation.

Plating was conducted using a PCB with via holes as the cathode under the same conditions to determine the effect of ion-exchange membranes on the plating performance. The surface of the PCB and the hole interiors were plated precisely and evenly under these conditions. This result shows that plating using an ion-exchange membrane effectively inhibits the oxidation of organic brightener,

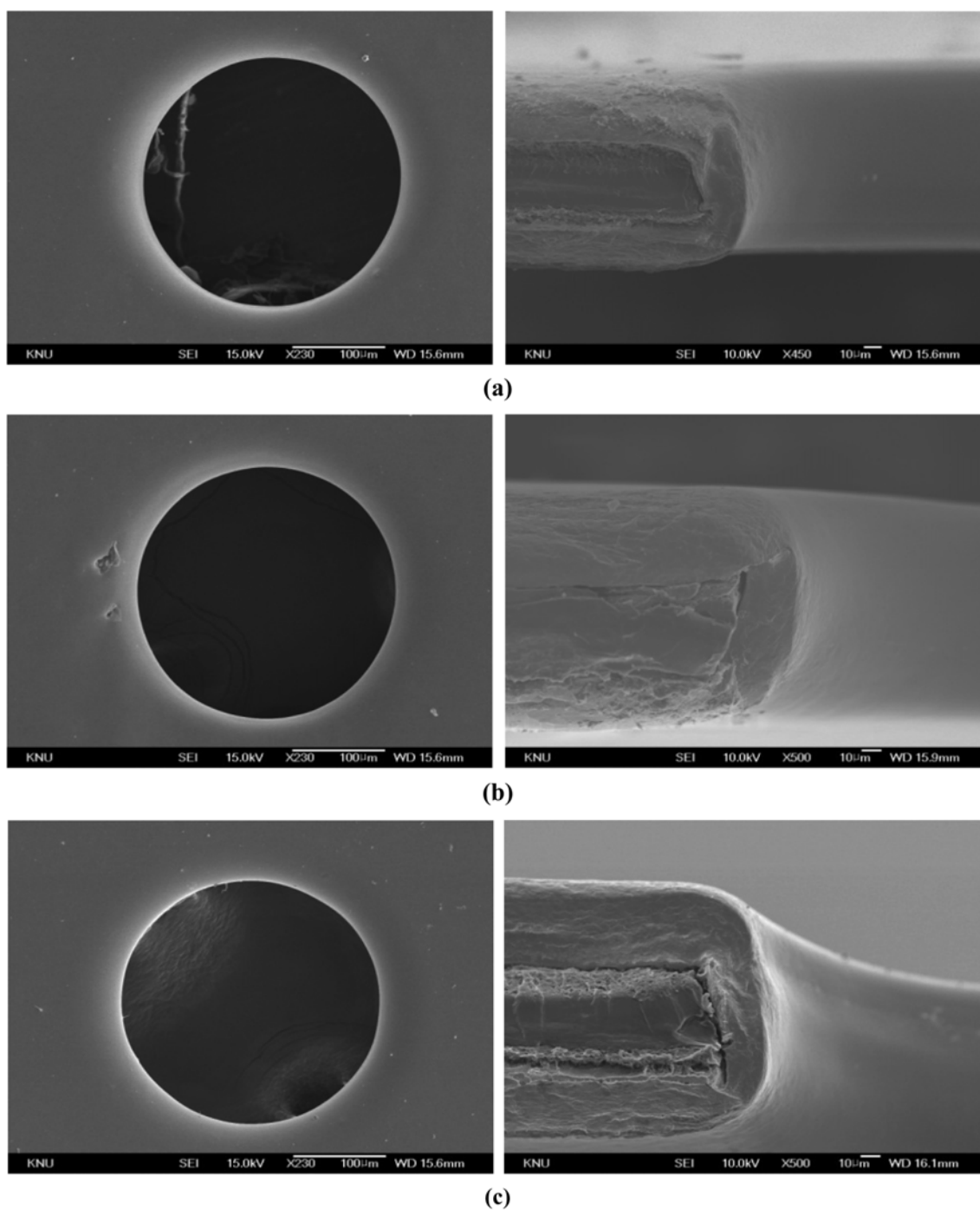


Fig. 8. SEM images of a PCB via hole after electroplating with a CMS membrane for various current densities. (a) 10 mA/cm², (b) 20 mA/cm², and (c) 30 mA/cm².

which has been problem in conventional plating process, and also assists in achieving an even plating performance.

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