

# The Effect of Additives and Current Density on Mechanical Properties of Cathode Metal for Secondary Battery

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Electrolyte copper foils used as a cathode material in secondary cells require the mechanical characteristic of high elongation ratios. In this study the effects of additives, current densities, and concentrations of sulfuric acid used in electrolyte plating on the mechanical characteristics of copper foils are analyzed. In the case of additive A, no significant changes in tensile strength and crystal structure were observed, but the elongation ratio is reduced by 43% when 100 ppm of additive is added. For additive B, the elongation ratio is rapidly decreased even though the growing orientation of crystals becomes parallel to the faces of (111) and (220) from the face of (200). In the case of decreasing current densities or increasing concentrations of sulfuric acid, the elongation ratio is respectively increased by 74% and 54%, and the growing orientation of crystals is directed from (200) to (111). Also, for additive A at low current densities, the increase in crystal sizes differed from that of high current densities. This approach represents a possible method for additionally improving elongation ratios by properly controlling the amount of the additive A.

**Keywords:** elongation, crystal growth, electrodeposition, copper foil, additive

## 1. INTRODUCTION

The development and growth of secondary power cells creates an opportunity for the expansion of mobile phones, notebooks, PCs, PDPs, and other mobile devices. Also, the continuing development of most advanced industrial fields, such as hybrid electric vehicles (HEV), mobile IT, the intelligent robot industry, and environment friendly energy industry, seriously requires the technical and industrial development of such secondary cells, which are core elements in these fields.<sup>[1]</sup> Copper foils, which have advantages of excellent thermal conductivity, low electric resistance, relatively low cost, and mass production, have been largely used in various industrial fields.<sup>[2-4]</sup> Also, they are attractive for use as a cathode material in secondary cells due to their favorable economic value, compared to roll annealed foils.

Among plating baths that can be used for copper electrolyte plating, a sulfuric acid-copper sulfate electrolyte method provides relatively fast plating rates, low costs, low toxicities, and evenness in the strength and flexibility of plated foils.

The plating bath using this electrolyte has been largely used in producing electronic parts. Also, many studies on this issue have been conducted.<sup>[3-7]</sup> However, there have been few studies on the change in mechanical characteristics that result from adding additives. Regarding studies on additives which have been performed under general electrolyte copper foil conditions, Shin *et al.*<sup>[8]</sup> reported that the additive Ultra increased the residual stress of electrodeposited layers by an average of 76% and showed a fining of crystal sizes. Also, according to Kim *et al.*<sup>[2]</sup> producing electrolyte copper foils at room temperature by adding gelatins revealed that crystal sizes are reduced and elongation ratios are significantly decreased. However, they showed that there are no significant changes in yield and tensile strengths. In addition, according to the results of the experiment implemented by Stantke,<sup>[9]</sup> although gelatins in an electrolyte play a role of polarizer in the initial stage, such an effect is significantly decreased after 10 - 50 minutes. In this study, the mechanical characteristics of electrolyte copper foils were investigated based on the additives A and B and varying current densities. Also, the effects of varying the concentration of sulfuric acid, and its relationship to the mechanical characteristics and crystal structure were examined.

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## 2. EXPERIMENTAL PROCEDURE

### 2.1 Plating system

A 2L electrolyte plating bath was used to produce copper foils using an electrolyte plating process, and bubbles were generated in this process by supplying air at a rate of 2 L/min, in order to allow easy movements of additives and  $\text{Cu}^{2+}$  ions. During the plating process the processing temperature was constantly maintained at  $50^\circ\text{C}$  ( $\pm 0.5^\circ\text{C}$ ). Regarding the electrode in this process, an insoluble anode and a titanium plate, which was sequentially abraded using abrasives #600 -

#1200, were used. The electrolyte was composed of 50 g/L of Cu and 100 g/L of  $\text{H}_2\text{SO}_4$  and the distance between the electrodes was constantly determined to be 10 cm. High and low molecular organic were used as the additives A and B respectively. Also, the additives were applied in either a single or complex manner. Table 1 shows the experimental conditions.

### 2.2 Analysis

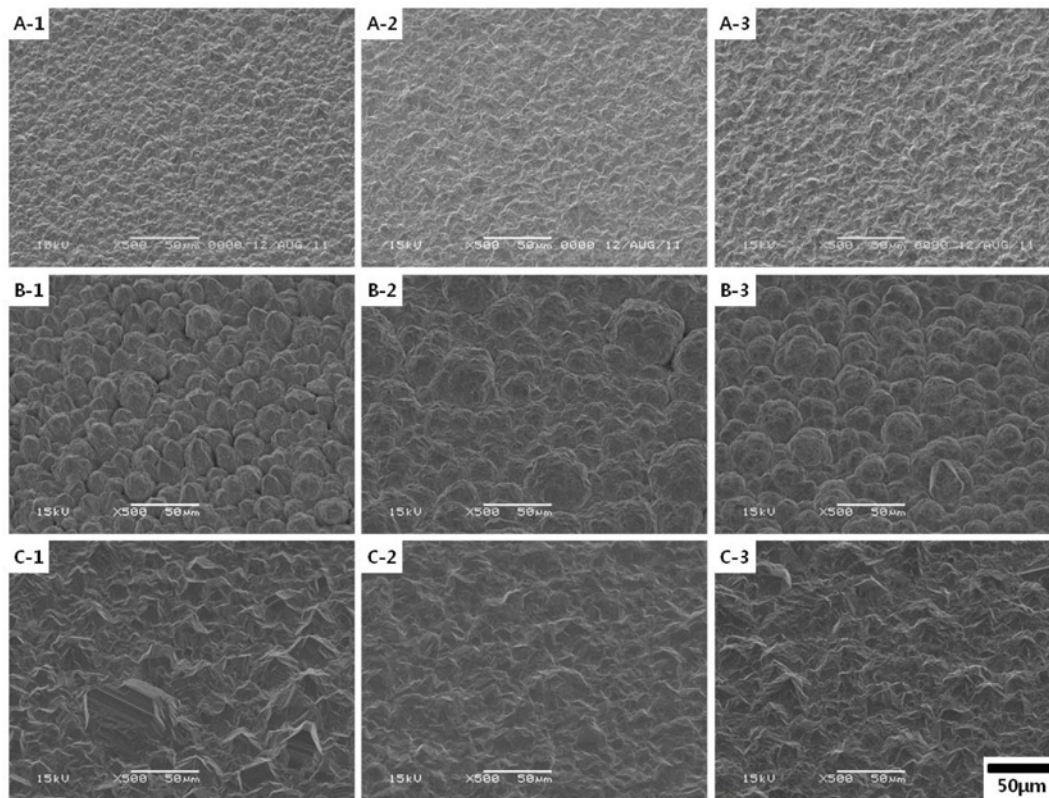
For observing the surface structure, crystal size, and crystal structure of electrodeposited layers, a scanning electron microscope (SEM, JSM-5900, JEOL, Japan) and XRD (Dmax III-A type, Rigaku Co., Japan) were used. Also, a surface roughness tester (SV-3000M4, Mitutoyo, Japan) and a four-point probe (CMT-SR1000N, AIT, Korea) were used to measure surface roughness and specific resistance respectively. A tensile test (AG-X, Shimadzu, Japan) was used to measure the tensile strength and elongation ratio of copper foils. For analyzing the size of crystals in the cross-section of the electrodeposited layers, EBSD (EDAX-TSL; S-4300se, Hitachi, Japan) was used.

**Table 1.** Copper electrodeposition condition.

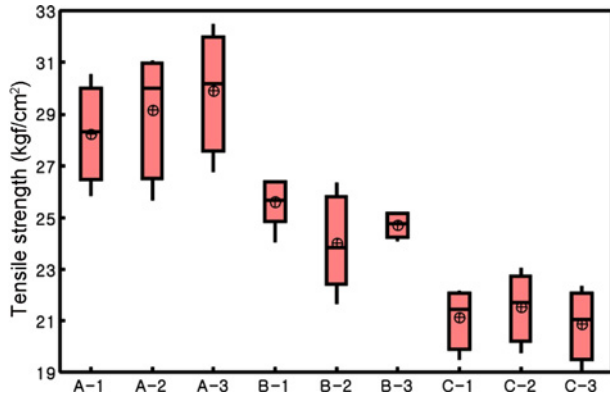
	Current density ( $\text{mA}/\text{cm}^2$ )	Additive A (ppm)	Additive B (ppm)	$\text{H}_2\text{SO}_4$ (g/L)
A-1	300	0	0	100
A-2	300	30	0	100
A-3	300	100	0	100
B-1	300	0	0	200
B-2	300	0	10	200
B-3	300	0	60	200
C-1	100	0	0	100
C-2	100	100	0	100
C-3	100	30	10	100

## 3. RESULTS AND DISCUSSION

Figure 1 shows the results of the analysis of the surface of the electrodeposited layers. Group A shows the results



**Fig. 1.** Surface morphologies of copper foil with various conditions.

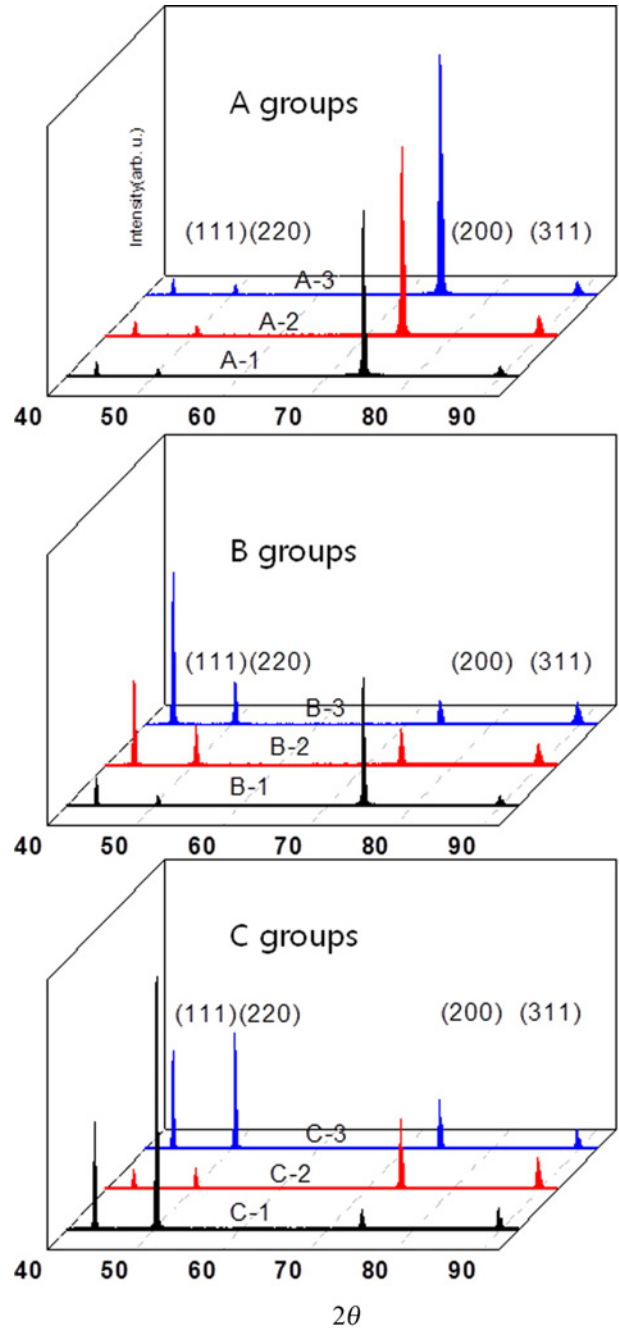


**Fig. 2.** Tensile strength of electrodeposited copper foil with various conditions.

obtained by varying the amount of additive A, and there are no specific changes in the surface according to the amount. In the case of group B, adding additive B, some changes in crystal shapes on the surface are shown. This differed from group A with additive A. The groups B-2 and B-3 show a change in crystal shapes, from angular horn shapes to spherical shapes; this is compared to group B-1 without additives. It is considered that additive B has the effect of suppressing the growth of crystals to a vertical direction. Comparing the effects of the concentration of sulfuric acid between group A-1 and group B-1, the surface evenness is decreased due to the increase in crystal sizes on the surface as the concentration is increased to a high level. Also, it tends to induce crystals in the vertical direction against the matrix. In the case of decreasing current densities, although crystal sizes are increased on the surface, some large crystals, more than  $50 \mu\text{m}$ , exist on the surface in some sections. However, the effect on increasing crystal sizes is less than that of group B-1, which shows a high concentration level of sulfuric acid. However, since large crystals on the surface are decreased by adding additive A, additive A plays a role as a leveler.

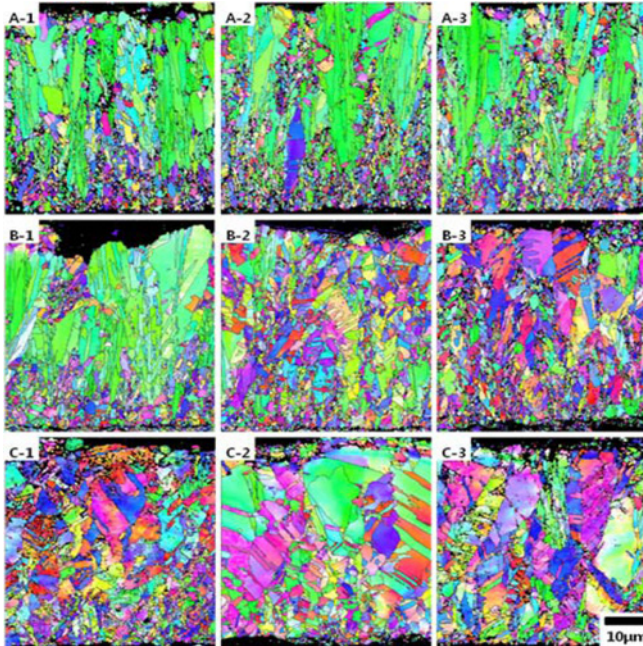
Figure 2 represents the results of the analysis of the tensile strength of electrodeposited layers. There are no significant differences in each group according to the given conditions, and the  $p$ -values in group A, B and C are 0.604, 0.186, and 0.765, respectively. Here, as the  $p$ -values are larger than 0.05, a null hypothesis is established. Although there are no significant differences in the amount of additives, the effects of the concentration of sulfuric acid and current densities are clearly seen. In the case with a high concentration level of sulfuric acid, the tensile strength is decreased by 9%. Also, in the case with a low current density level, the tensile strength is decreased by 25%. Thus, decreasing tensile strength is more strongly affected by current density than the concentration of sulfuric acid.

Figure 3 shows the results of an analysis of the crystal



**Fig. 3.** XRD patterns of copper foil with various conditions.

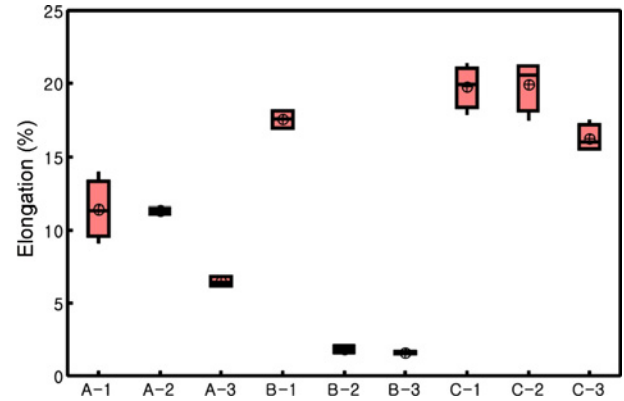
structure in electrodeposited layers, performed to verify the cause of the changing tensile strength. In the case of adding additive A, the change in the crystal structure is very small. However, for group B with additive B, it shows an increasing peak of (111) while the peak of (200) is decreased, according to the increase in the amount of additives. Also, decreasing current densities decrease the peak of (200), while the peaks of (111) and (220) are increased. In particular, the peak of (220) is significantly increased. Regarding group C,



**Fig. 4.** Orientation maps of electrodeposited copper foil with various additives concentrations and current density.

although the peak of (200) is increased by adding additive A in a single manner, it shows a lower strength level than the case with a high current density level. In addition, when additive B is added in a complex manner, the increase of the (220) peak is larger than the peak of (111). Regarding group B, the strength of the peak of (111) is larger than the peak of (220) and that is considered due to the decrease in current densities and its correlation. In the changes in these crystal structures, it is noted that the orientation of crystal growth varies somewhat according to the crystal sizes and thicknesses in the electrodeposited layers.

Figure 4 shows the results of the analysis of the cross-section of electrodeposited layers using EBSD. In general, there are fine crystals on the initial electrodeposited layers with a thickness of about 10  $\mu\text{m}$ , and the crystals are grown to a specific orientation and show increases in sizes. In the case of the additive A, there are no significant differences in crystal sizes or orientations, as well as the previous analysis. In the case of additive B, however, a clear tendency is exhibited, in which the crystals show a disorder in orientations with the increasing amount of additives. Group C, with a low current density level, shows a disorder in crystal growing orientations compared to the other groups and an increase in crystal sizes due to the addition of additive A. However, in the case of high current density, although longish crystal shapes are grown in a direction vertical to the matrix, the shapes appear as polygonal shapes when the current density is at a low level. Thus, it is considered that there are some differences in the role of additives according



**Fig. 5.** Elongation of electrodeposited copper foil.

**Table 2.** Grain size of electrodeposited copper foil.

	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3
Grain size (avg. nm)	77	67	65	85	75	69	96	107	101

to current densities.

Figure 5 represents the results of the measurement of the elongation ratio of copper foils according to given conditions. Although there are no specific changes in tensile strengths and crystal structures according to the amount of additive A, the elongation ratio is largely decreased by increasing the additive from 30 ppm to 100 ppm. Based on Kim *et al.*,<sup>[2]</sup> in the case of the high current density, the additive suppressed a local growth in crystals, and cannot be fallen out during a electrodeposition process, and forms some fine pores inside the electrodeposited layers and that leads to decrease tensile strengths and elongation ratios. Adding additive B, however, produces sudden decreases in tensile strengths and elongation ratios. Also, as shown in Fig. 1, weaknesses in mechanical characteristics appear, even though crystal shapes and structures are changed. Group C with a low current density level, shows a decrease in the effects of additives. In the comparison of the group A-3 with adding 100 ppm of the additive A and the group C-2, although the group A-3 represents a decrease in the elongation ratio by 43% compared to that of the case without adding additives, the group C-2 shows no significant differences in the elongation ratio compared to the group C-1. Also, in the results of the analysis of crystal sizes as noted in Table 2, although the additive A decreases the crystal sizes in the group A-3 with a high current level, it conversely increases crystal sizes when the current density is low level. When the concentration of sulfuric acid is increased, and current densities are decreased, crystal sizes are increased, and that leads to an increase in elongation ratios. Based on Ibanez *et al.*,<sup>[10]</sup> a large amount of nuclei preferentially form for a high current density level. however, crystal sizes are increased due to a high tendency

in growing crystals from the previously generated nuclei for a low current density and that leads to increase elongation ratios.

#### 4. CONCLUSIONS

Electrolyte copper foils were produced by adding the additives A, B, C into an electrolyte through a single or complex manner using a galvanostatic method. The results of the analysis of the mechanical and chemical characteristics of the foils for each given condition by controlling the concentration of sulfuric acid and current densities are as follows.

Additive A showed no significant changes in crystal shapes on the surface of the electrodeposited layers, the tensile strengths, or the crystal shapes, but did show a 43% decrease in elongation ratio after adding 100 ppm of the additive. It is estimated that the additive that remained inside the layers plays a role in defects.

Additive B produced a tendency that strongly affected the growth of crystals parallel to the faces of (111) and (220) from the face of (200), but the changes in crystal sizes were small. However, there was an effect on crystal shapes, changing them from angular to circular shapes, and a decrease in the elongation ratio in electrodeposited layers.

The increase in the concentration of sulfuric acid produced a decrease in crystals growing to the face of (200) and an increase in the tendency to grow to the faces of (111) and (220). Also, at the concentration of 200 g/L it increased the elongation ratio by 54% compared to that of 100 g/L.

Current density of 100 mA/cm<sup>2</sup> improved the elongation ratio by 73.7%, compared to that of 300 mA/cm<sup>2</sup>, and the crystal structure grew from the orientation of (200) to the orientations of (111) and (220). In addition, adding additive A with a low current density level produced a decrease of crystals growing in the vertical direction against the matrix and increased crystals growing parallel to the matrix.

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