Effects of four carboxyl-containing additives on imitation gold electroplating Cu-Zn-Sn alloys in an HEDP system

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Abstract
The requirements for using noncyanide imitation gold plating as decorative electroplating are increasing; thus, continuously improving the quality of the coating of the imitation gold plating and optimizing the coating process have become the current priority. In this experiment, hydroxyethylidene diphosphonic acid (HEDP) was used as the main complexing agent; CuSO4·5H2O, ZnSO4·7H2O, and NaSnO3·3H2O were the main salts; and NaOH and sodium carbonate were used as the buffers to prepare the electroplating solution. Using sodium citrate (SC), sodium potassium tartrate (SS), sodium gluconate (SG), and glycerol (Gl) as four additives, the effects of the number of carboxyl groups on the properties of a Cu-Zn-Sn alloy coating were compared. The electrochemical analysis showed that Cu-Zn-Sn alloy codeposition occurred at -0.50 V vs. Hg|HgO. The scanning electron microscopy (SEM) results showed that the grain size of the coatings obtained with carboxyl-containing additives was more uniform than that obtained with the electroplating solution without additives. The X-ray fluorescence spectrometry (XRF) analysis revealed that the composition of the Cu-Zn-Sn alloy coating obtained by using SC as an additive in the electroplating solution was 89.75 wt% Cu, 9.61 wt% Zn, and 0.64 wt% Sn, and the color of the coating was golden yellow. The X-ray diffraction (XRD) pattern showed that the coating was a mixture of Cu, Cu5Zn8, CuSn, Cu6Sn5, and CuZn phases. The analysis of the electroplating solution by UV, IR, and NMR spectroscopy methods indicates that the additives improve the coating by affecting the complexation reaction of metal ions. These results can provide technical guidance for developing Cu-Zn-Sn ternary alloy electrodeposition technology with the new cyanide-free HEDP alkaline electroplating system.

Keywords Imitation gold plating · Cu-Zn-Sn alloy · Carboxyl-containing additives · HEDP system

Introduction
Electroplating is one of the main methods used to coat industrially obtained metals on electrical conductors. In recent years, research on electroplated copper alloys has continued to develop [1, 2]. Compared with the single metal coating, the ternary Cu-Zn-Sn alloy coating has a better flattening capability, brightness, luster, decorative effect, and gliding property, leading to its widespread use [3]. In the earliest imitation gold plating techniques, cyanide was used as the main complexing agent, and the quality of the coating layer formed during the electroplating process was good. However, the cyanide-containing electroplating solution is toxic, and the waste liquid generated after electroplating is extremely harmful to the environment [4]. Thus, current research has been looking for a green and environmentally friendly cyanide-free electroplating solution.
Cyanide-free electroplating process systems are being developed. The representative electroplating systems include pyrophosphate [5], sorbitol [6–8], EDTA [9, 10], glycine [11], mesylate [12], gluconate [13, 14], HEDP [15, 16], triethanolamine [17], or citrate [18, 19]. HEDP is the main complexing agent in the electroplating solution of the HEDP system. HEDP can form stable water-soluble complexes with various metal ions, such as copper, zinc, and tin, and the resulting coating has fine and uniform crystals. In this system, the cost of the reactant is low, the plating solution is simple and stable, and the corrosion extent of the plating production equipment is relatively small, which is more conducive to production. HEDP was an environmentally friendly complexing agent, because HEDP was nontoxic and HEDP is degraded by sunlight exposure in electroplating wastewater [20].

The traditional electroplating process uses additives to improve the quality of the coating. For example, Bonou et al. [21] studied the effect of polyethylene glycol (PEG) and chloride ions on copper electrodeposition. When the additive PEG is used alone in the solution, the deposition efficiency is decreased. Using additive Cl– alone in the solution can promote the reduction reaction of copper. When two additives are used at the same time, a copper reduction blocking reaction occurs. Leon and others [22] established an atomic growth model of Cu electrodeposition under nonequilibrium conditions. In this model, the interface is unstable due to Cu2+ concentration fluctuations and surface diffusion. The interface is stable in the presence of organic additives. The interface evolution in the Cu electrodeposition in the absence and in the presence of organic additives was studied. This model can be used as a powerful tool to predict the interface dynamics of other electrodeposition systems. Dianat et al. [23] studied the molecular dynamics of the additives PEG, bis(3-sulfopropyl)-disulfide (SPS), and chloride in copper metal deposition reactions by density functional theory and found that PEG inhibited the reaction function, while SPS and chloride played a promoting role. Lallemand et al. [24] studied whether organic additives affect the deposition of metals through the current density and concluded that additives do not affect the mechanism of metal deposition but do affect the metal deposition rate. Silva et al. [25] showed that using benzotriazole and cystine as additives can change the composition of the copper-zinc alloy and improve the corrosion resistance of the coating in the citrate electroplating Cu-Zn alloy system. Ding et al. [26] studied the effects of four nitrogen-containing additives on the HEDP electroplating system and finally found that using ammonium fluoride as an additive can make the grains of the coating more uniform and produce coatings with better brightness and gloss.

So far, although many different types of electroplating systems and additives have been reported, they have only been described in terms of their effects, and their mechanisms have not been explained, which has restricted the development of using additives in imitation gold plating. In this study, the HEDP system was used. Four carboxyl-containing additives were added to the system and include sodium citrate (Na3C6H5O7, SC), sodium potassium tartrate (C4H4KNaO6, SS), sodium gluconate (C6H11NaO7, SG), and glycerol (C3H8O3, Gl), where the number of carboxylic acid groups contained in these four molecules is 3, 2, 1, and 0, respectively.

The purpose of this work was to study the effects of four additives on the coating and the reaction mechanism. Therefore, the system used the process parameters in the previous study [26], such as current density, plating time, and pH. Scanning electron microscopy (SEM), X-ray fluorescence spectrometer (XRF), X-ray diffraction (XRD), and other methods were used to characterize the morphology, composition, and crystal morphology of the alloy coatings. The mechanism of complexation in the imitation gold of the electroplating solution was explored by UV, IR, and NMR, which laid a certain theoretical foundation for future research on imitation gold plating mechanisms.

### Experimental

#### Electroplating solution

The sequence in which the electroplating solution is prepared is crucial. First, the main complexing agent HEDP (60%, industrial grade, Shandong Youso Chemical Technology Co.) was measured. Then, CuSO4·5H2O (≥ 99.0%, Tianjin Zhiyuac Chemical Reagent Co.), ZnSO4·7H2O (≥ 99.5%, Tianjin Beichenfangzheng Reagent Factory), Na2SnO3·3H2O (≥ 98.0%, Tianjin Fuchen Chemical Reagent Factory), and Na2CO3 (≥ 99.8%, Tianjin Guangfu Technology Development Co.) were dissolved separately with a small amount of water, and the resulting solutions were then added to HEDP. To dissolve sodium stannate, which is insoluble in water and soluble in an alkaline solution, an appropriate amount of NaOH (≥ 96.0%, Tianjin Beichen Founder Reagent Factory) should be added. When adding a sodium carbonate solution, many bubbles will be generated, so the sodium carbonate solution needs to be slowly added with a plastic dropper. The electroplating solution without additives was used as the blank reference solution (BR). The main components in the BR electroplating solution were 0.18 mol/L CuSO4, 0.06 mol/L ZnSO4, 0.05 mol/L Na2SnO3·3H2O, 100.0 mL/L HEDP, 25.0 g/L Na2CO3, and an appropriate amount of an NaOH solution to achieve a pH of 13.0–13.5. Finally, the different additives were added according to the solution requirements. Four carboxyl-containing additives, namely, SC (≥ 99.0%, Tianjin Beichenfangzheng Reagent Factory), SS (≥ 99.0%, Tianjin Beichenfangzheng Reagent Factory),
had a single-side effective area of 15.0 cm\(^2\). During the elec-
tron transfer process, the voltage continues to increase more than 0.7 V, a large
count of hydrogen bubbles appeared near the electrode, which is mainly oxygen (2H\(_2\)O \(\rightarrow\) O\(_2\) + 4H\(^+\) +4e\(^-\)). The red line was obtained from high to low potentials in the forward scan-
ing, and peaks B (-0.50 V\(_\text{vs. Hg/HgO}\)), C (-1.10 V\(_\text{vs. Hg/HgO}\)), and D (-1.25 V\(_\text{vs. Hg/HgO}\)) represent the deposition of cathode ma-
terial. When the voltage decreased below -1.4 V, a large num-ber of hydrogen bubbles appeared near the electrode. This indicated that the reduction of Cu-Zn-Sn electrodeposition was always accompanied by hydrogen evolution reaction (2H\(^+\) +2e\(^-\) \(\rightarrow\) H\(_2\)). As noted in the literature, the cathodic de-
oposition peak B at -0.50 V\(_\text{vs. Hg/HgO}\) represented the codeposition peak of Cu-Zn-Sn. The deposition peak C at -
1.10 V\(_\text{vs. Hg/HgO}\) mainly represented the deposition of Cu or Cu-containing compounds on the cathode. The deposition peak D at about -1.25 V\(_\text{vs. Hg/HgO}\) represented the codeposition peak of Cu and Sn [27–32].

**Results and discussion**

**Effect of the additives on the electrochemical reaction of the electrode**

The effect of additives on the electrode interface was ana-
yzed, as shown by the cyclic voltammetric (CV) curves (Fig. 1). In Fig. 1a, the black line was acquired from low to high potentials in reverse scanning, and peak A (-0.05 V\(_\text{vs. Hg/HgO}\)) means the dissolution of anode materials. When the voltage continues to increase more than 0.7 V, a large number of bubbles appeared near the electrode, which is mainly oxygen (2H\(_2\)O \(\rightarrow\) O\(_2\) + 4H\(^+\) +4e\(^-\)). The red line was obtained from high to low potentials in the forward scan-
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Fig. 1b shows the CV curve obtained when different con-rents of SC were added to the solution. With the increase of SC content, the deposition peaks B, C, and D gradually in-
creased. It shows that the amount of cathode deposited material gradually increased with the increases of SC content. The anodic peak A gradually increased, indicating that the amount of anode dissolved matter gradually increased. It shows that the increase of SC content was beneficial to accelerate the deposition of cathode metals and the dissolution of anode materials.

Fig. 1c shows the CV curve obtained when different con-rents of SS were added to the solution. With the increase of SS content, the cathode deposition peak D gradually disappeared, the peak value of peak C increased initially and then decreased, and the peak value of peak B gradually increased. It shows that the cathodic metal deposition reached the maxi-
mum when the content of SS was 20 g/L. With the increase of SS content, the potential at anode dissolution peak A was
basically unchanged, and the peak value gradually increased, indicating that the increase of SS additive content promoted anode dissolution.

Fig. 1d shows the CV curve obtained when adding different contents of SG to the solution. When the SG content increased from 17.5 g/L to 30 g/L, the peaks of deposition peaks C and D disappeared, and the peak B gradually increased. The change in the deposition peak indicated that the amount of deposited copper, zinc, and tin metal has changed. There was no significant change in the potential and peak value of the dissolution peak A, and a new dissolution peak E appeared at 0.45 V vs. Hg/HgO. It shows that the SG affected the dissolution of the anode. When the content of SG increased, the codeposition peak of Cu-Zn-Sn shifted from -0.05 V vs. Hg/HgO to -0.02 V vs. Hg/HgO, indicating that cathodic polarization occurred at this time. The electrode reaction changed. The potential of the dissolution peak A shifted to -0.25 V vs. Hg/HgO, and the peak value decreased slightly, indicating that the excessive SG concentration was not conducive to anode dissolution.

Fig. 1e shows the CV curve obtained when different contents of Gl were added to the solution. As the content of Gl increased, the peak value of peak D decreased initially and then disappeared, the peak value of peak C disappeared, and the peak value of peak B gradually increased. The change in the deposition peak indicated that the amount of deposited copper, zinc, and tin metal has changed. In addition, a miscellaneous peak F appeared at the potential of -0.8 V vs. Hg/HgO, and the peak value gradually increased with the increase of Gl content. The peak value of peak F reached the maximum when the Gl content was 30 mL/L. Combined with electroplating experiments, it was found that the increase of Gl resulted in a coating with a black surface. Therefore, peak F might be the black oxide formed by the deposition, which was not conducive to the codeposition of the Cu-Zn-Sn alloy. Combined with XRD analysis, it was found that the oxide
was CuO. During the increase of Gl content, the potential and peak value of peak A remained basically unchanged, indicating that the increase of Gl content did not affect the dissolution of the anode.

In summary, it can be concluded that the content of each additive affected the electrodeposition. Combined with the stability analysis of the plating solution, it is concluded that the optimal content of the four additives SC, SS, SG, and Gl, respectively, was 22 g/L, 20 g/L, 30 g/L, and 20 mL/L. Fig. 1f shows the BR and the CV curves of the four additives SC, SS, SG, and Gl at the optimal content. When the additive was SC, the peaks of the deposition peak and the dissolution peak both reached the maximum. It shows that SC promoted the dissolution of anode materials, thereby accelerating the compensation of the lost ions at the cathode, which was beneficial to promote the deposition of components of the deposit. When the additive was SS, the potentials of the deposition peak and the dissolution peak remain unchanged, and only the peak height changes. This shows that the amount of deposited copper, zinc, and tin metal has changed. Cathodic polarization occurred when the additive was SG, and the peaks of the deposition peaks B, C, and D were lower, and the deposition amount of the cathode was less. At the same time, the anodic deposition peak value was also reduced, indicating that the additive was not conducive to the dissolution of the anode material. When the additive was 20 mL/L Gl, the peaks of deposition C and D decreased, and the impurity peak F appeared at the same time, which was not conducive to the codeposition of Cu-Zn-Sn alloy. This shows that the four carboxyl-containing additives also have an effect on electrodeposition. Among them, the SC additive contained the most carboxyl group, which has the most favorable effect on Cu-Zn-Sn alloy electrodeposition.

Effect of the additives on the surface micromorphology of the coatings

It can be seen from Fig. 2 that the BR coating surface was composed of spherical grains of varying sizes of 0.3-0.8 μm (Fig. 2a). After adding 22 g/L SC to the BR, the coating obtained contains approximately 0.1-0.5 μm spherical grains (Fig. 2b), and the grain size was relatively uniform. After adding 20 g/L SS to the BR, the grain size was approximately 0.1-0.5 μm, the grains were uniform, and there were more fine grains (Fig. 2c). When 30 g/L SG was added, the grain sizes on the surface of the coating were approximately 0.1-0.3 μm, but there were obvious cracks in the coating. (Fig. 2d). When 20 mL/L Gl was added to the BR, the size of the spherical grains on the surface of the coating was approximately 0.2-0.5 μm, but local cracks appeared obviously (Fig. 2e). Compared with that of the BR, the size of the grains in the coating was reduced after adding the four additives, so additives with different numbers of carboxyl groups all have the effect of grain refinement.

Effect of the additives on the copper, zinc, and tin content in the coatings

XRF was used to analyze the composition of the coating obtained in the presence of the four additives (Table 1). The coatings contained mainly copper, the zinc content was less than the copper content, and the tin content was trace. In the BR solution, the content of the copper, zinc, and tin components in the coating was 90.12 wt%, 9.46 wt%, and 0.42 wt%, respectively. At this time, the copper content in the coating was relatively high, which can explain why the coating color was dark yellow but locally reddish in Fig. S1 of the supporting literature. With the addition of the additives, the copper content in the coatings has been reduced. When the content ratio of copper, zinc, and tin in the coating changed, the color of the obtained coating was different. The comparison showed that when 22 g/L SC was added to the BR, the Cu content was reduced to 89.75 wt%, the Zn content was 9.61 wt%, and the Sn content was 0.64 wt%. At this time, the copper, zinc, and tin in the coating reach the optimal content ratio. The plating tablet appeared to be uniform golden yellow. When 20 g/L SS was added to the BR, the copper, zinc, and tin contents were adjusted slightly, but the plating tablet has a uniform light yellow color. These results better explained the changes in the color of the coatings, as described in the supporting literature.

Effects of the additives on the phase structure of the coatings

It can be seen from Fig. 3 that XRD patterns of the coatings were obtained in the presence of the different additives in the plating solution. The results were compared to the expected patterns provided by the Committee on Powder Diffraction Standards (JCPDS), Cu (JCPDS 04-0836), Cu5Zn8 (JCPDS 71-0397), CuSn (JCPDS 44-1477), Cu6Sn5 (JCPDS 45-1488), CuZn (JCPDS 08-0349), and other crystals were observed [33–37]. The coating consisted of Cu, and the 2θ positions of the diffraction peaks were 42.124°, 50.888°, 64.456°, and 90.888°. The 2θ positions of the diffraction peaks corresponding to the Cu5Zn8 phase were 42.124°, 44.504°, 64.456°, 82.348°, and 90.988°. The 2θ positions of the diffraction peaks corresponding to Cu6Sn5 were 42.124°, 44.504°, 50.888°, and 75.172°. The 2θ positions of the diffraction peaks that correspond to CuSn were 42.124°, 43.608°, 75.172°, and 90.988°. The 2θ positions of the diffraction peaks corresponding to CuZn were 42.124°, 75.172°, and 82.348°.

Comparing the BR and SC curves, it was found that the 2θ position of the diffraction peak was almost unchanged when
22 g/L additive SC was added to the BR plating solution, but the height of the diffraction peak changed slightly. This shows that using SC as an additive did not affect the material composition of the coating alloy. When 20 g/L SS was added to the BR solution, the 2θ position of the diffraction peak did not change. When the additive was SG, the height of the diffraction peak at the 2θ position at 42.124° significantly increased, and those diffraction peaks were corresponding to CuSn, Cu5Sn5, CuZn, Cu5Zn8, and Cu. The diffraction peak at the 2θ position of 50.888° decreased, and this peak represented CuSn and Cu. The analysis shows that the Zn content in the coating alloy was relatively high at this time, which was
consistent with the conclusion obtained from the electrochemical analysis and XRF results. When 20 mL/L Gl was added, CuO (JCPDS 44-0706) diffraction peaks appeared at 41.492°, 93.576°, and 95.028°. This shows that the additives will affect the composition content of the coating, and using Gl as an additive will also affect the phase composition of the coating alloy. The XRD results were consistent with the conclusion obtained from electrochemical analysis.

Since XRF cannot directly test the oxygen content, the oxygen content in the coating was not discussed in Table 1. Therefore, energy dispersive spectroscopy (EDS) was used to analyze the oxygen content in different coatings. The analysis showed that no oxygen could be detected in the coatings obtained from BR and additives containing SC, SS, and SG. However, 0.57% oxygen was detected in the coating containing Gl additives. This conclusion was consistent with XRD analysis results.

**Effect of the additives on the UV-Vis spectra of the electroplating solutions**

Fig. 4a is the UV-Vis spectra of the plating solution containing different additives, and Fig. 4b shows the maximum absorption wavelength of the five plating solutions. The maximum absorption peak of the BR was at 221 nm. After adding SC, SS, SG, and Gl to the electroplating solution, maximum absorption peaks were observed at 223 nm, 224 nm, 231 nm, and 226 nm, and it can be seen that the maximum absorption peaks have redshifted to different extents.

The reason for the redshift was not only the difference in the number of carboxyl groups in the four additives but also the number of hydroxyl groups in the four additives. Both carboxyl and hydroxyl groups are auxochromes, which cause the wavelength of the maximum absorption peak to shift in the long-wave direction, causing a redshift. Among the additives, the total number of the two groups was the largest in the SG molecule, so the redshift was most obvious. However, comparing the UV spectra of the four additives, the position of the maximum absorption peak changes, and it is concluded that the UV absorption peak was mainly affected by the different additives. It is concluded that the maximum absorption peaks will be redshifted when additives were added to the plating solution. A proper redshift was beneficial to the formation of metal complex ions and the deposition of Cu-Zn-Sn ternary alloys.

**Effect of the additives on the FTIR spectra of the electroplating solutions**

The analysis in Fig. 5 shows that there was an absorption peak at 3370 cm⁻¹ in the spectrum, and it is inferred that this peak was a stretching vibration absorption peak attributed to the free and associated hydroxyl groups. The absorption peak at 3370 cm⁻¹ appeared because HEDP, NaOH, and the four additive molecules in the electroplating solution all contain hydroxyl groups. The absorption peak at 2450 cm⁻¹ was the stretching vibration peak attributed to the C-H bond in the methyl (-CH₃) group in HEDP. When the additive was SG, the peak value of infrared absorption peak was the largest. When the additive was SS, the peak value is second. The absorption peaks at 1600 cm⁻¹ and 1450 cm⁻¹ were attributed to the asymmetric and symmetric stretching vibrations of the C=O bond in the carboxylate group in the solution. The absorption peak at 1100 cm⁻¹ was attributed to the main complexing agent HEDP and the stretching vibration of the C-O bond in each additive molecule. When the additive was SS, the absorption peak value reached the maximum at 1600 cm⁻¹ and 1100 cm⁻¹. The weak peak at 980 cm⁻¹ was attributed to the symmetric stretching vibration of the P-O bond in HEDP. Therefore, with the addition of carboxyl additives, the position of the infrared absorption peak of the plating solution is basically unchanged, but the height of the absorption peak changed. That is, a certain content of carboxyl additives does not have an effect on the infrared absorption peak of the electroplating solution but has an effect on the complexation of metal ions.
Effect of the additives on the NMR spectra of the electroplating solutions

To investigate the reaction mechanism of the additives used in this experiment, a deuterated reagent was used in place of deionized water to prepare the electroplating solution, and the $^1$H nuclear magnetic resonance spectrum was obtained in Fig. 6. The chemical shifts of the test absorption peaks were summarized in Table 2. It can be seen from the data that the peak 1$^\#$ with a chemical shift of 4.74 ppm was the absorption peak corresponding to H in the deuterated reagent [38]. HEDP has three kinds of H atoms with different chemical environments: H in HO-P-, H in the HO-C- group, and H in the -CH$_3$ group. The chemical shifts of 3.70 ppm and 3.68 ppm of peak 2$^\#$ were formed by H in the HO-C- group. The absorption peak 4$^\#$ at a chemical shift of 1.40 ppm was generated by H in HO-P-. The absorption peak 3$^\#$ at chemical shifts of 1.28, 1.24, and 1.20 ppm was a triplet formed by H in the -CH$_3$ group, and the splitting was caused by the two P on the same carbon. It can be known from Table 2 that when the additives of 22 g/L SC, 20 g/L SS, and 30 g/L SG were added, the peak chemical shift and peak shape did not change, and only the peak height changed. This is because the additives will affect the complexation reaction of the metal ions, meaning that the peak-producing groups cannot rotate freely, and the height of the absorption peak changed. The peak height can reflect the reaction intensity of the metal ions and complexing agent to a certain extent. When the additive was 20 mL/L Gl, the chemical shift is 2.47 ppm, and peak 3$^\#$ appeared at 2.34 ppm. Peak 3$^\#$ was a peak attributed to the two symmetric -CH$_2$- groups in the molecular structure. The analysis shows that the four additives with different numbers of carboxyl groups will all react with metal ions.

Reaction mechanism of electroplating

The molecular formula of the main complexing agent HEDP was C(CH$_3$)(OH)(PO$_3$H$_2$)$_2$. The molecular structure was characterized to contain two phosphonic acid groups and five hydroxyl groups, known as H$_4$L, which can form a six-membered ring chelated with metal ions. When the pH of the solution was 13.0-13.5, HEDP mainly existed in the form of L$^{4-}$ ions [39–41].

In BR solution with copper sulfate, zinc sulfate, and sodium stannate as main salts, the copper ions in the electroplating solution might exist in the form of a large amount of CuL$_2$$_8^{-}$ and a small amount of CuL$_2$$_6^{-}$. The reduction processes were as follows:

$$\text{CuL}_2^{6-} + 2e^- \rightarrow \text{Cu} + 2L^{4-} \quad (1)$$

$$\text{Cu(OH)}_2L_2^{8-} + 2e^- \rightarrow \text{Cu} + 2L^{4-} + 2OH^- \quad (2)$$

In the BR solution, the zinc ions in the electroplating solution existed as a large amount of Zn(OH)$_4^{2-}$ and a small amount of ZnL$_2$$_6^{-}$, which were expressed as follows:

$$\text{ZnL}_2^{6-} \rightarrow \text{ZnL}_2^{2-} + L^{4-} \quad (3)$$


\[
\begin{align*}
\text{ZnL}_2^{2-} + 2e^- & \rightarrow \text{Zn} + \text{L}_4^{4-} \quad (4) \\
\text{Zn(OH)}_4^{2-} + 2e^- & \rightarrow \text{Zn} + 4\text{OH}^- \quad (5) \\
\text{While Sn existed in the form of Sn(OH)}_3^{-}, \\
\text{Sn(OH)}_3^{-} + 2e^- & \rightarrow \text{Sn} + 3\text{OH}^- \quad (6)
\end{align*}
\]

It can be seen from the CV curve that when the additive was SC with the highest carboxyl content, it can promote the dissolution of the anode material. It shows that the carboxyl group acted as a buffer in the plating solution and prevents the pH in the plating solution from dropping too fast. Through the analysis of UV and FTIR spectroscopy and NMR results, it was found that the metal ion complexes appeared in the electroplating bath after adding the carboxyl-containing additives. This shows that the additives can be used as an auxiliary complexing agent to complex with metal ions, thereby promoting the codeposition of Cu-Zn-Sn.

**Conclusion**

In this work, the effect of the number of carboxyl groups on the coatings codeposited with different phases was investigated. It was concluded by an SEM analysis that with the addition of carboxyl-containing additives, the grain size of the alloy grains was reduced, and the more carboxyl-containing additives added, the better the effect. The XRF results show that when the electroplating solution contains the SC additive with the highest carboxyl number content, the obtained coating contains 89.75 wt% Cu, 9.61 wt% Zn, and 0.64 wt% Sn. At this time, the content ratio of Cu/Zn/Sn in the coating was optimized, and its appearance was golden yellow. The XRD analysis showed that the coating was a mixture of Cu, Cu$_5$Zn$_8$, CuSn, Cu$_6$Sn$_5$, and CuZn phases. The electrochemical analysis showed that metal codeposition occurs at -0.50 V vs. Hg/HgO, and using a certain amount of carboxyl groups as additives can promote metal codeposition. UV, IR, and NMR spectroscopy methods were used to study the solution and showed that

| Sample composition | Chemical shift (ppm) |
|--------------------|----------------------|
|                    | Peak 1$^a$ | Peak 2$^b$ | Peak 3$^a$ | Peak 4$^a$ | Peak 5$^a$ |
| BR                 | 4.74       | 3.70, 3.68 | 1.40       | 1.20, 1.21, 1.23 |
| BR+22 g/L SC       | 4.74       | 3.37, 3.46 | 1.31       | 1.02, 1.00, 0.98 |
| BR+20 g/L SS       | 4.74       | 3.48       | 1.35       | 1.00         |
| BR+30 g/L SG       | 4.74       | 3.42, 3.32 | 1.32       | 1.22, 1.18, 1.15 |
| BR+20 mL/L Gl      | 4.74       | 3.48, 3.46 | 2.47, 2.34 | 1.33         | 1.02, 1.00, 0.98 |
additives with different carboxyl numbers can improve the coating because the carboxyl groups affect the complexation of the metal ions in the solution.

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