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Study of the mechanism of additives on copper dissolution in monoethanolamine-complexed cupric ion solution

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Abstract

The dissolution of copper in monoethanolamine (MEA)-complexed cupric ion solution containing different additives was studied. Bridging ligands, such as F^-, Cl^-, Br^-, I^-, SCN^-, and oxidizers, including $S_2O_8^{2-}$, $Cr_2O_7^{2-}$, MnO_4^- were added to this nonammoniacal etching solution to increase the copper dissolution rate. Potentiodynamic methods were employed to elucidate the dissolution mechanism and the corrosion potential (E_{corr}) was found to shift from 10 to 90 mV as opposed to that of the original solution (0.045 M cupric sulfate and 0.225 M MEA) for bridging ligands. In contrast, some conventional oxidizers were also added in the etchant and the E_{corr} did not shift obviously. Therefore, we proposed that copper dissolution proceeds through an 'inner-sphere' pathway in solution containing bridging ligands. The electron is transferred from the copper surface into the cupric species through the ligands, which greatly influences the copper dissolution rate. The order of effectiveness of these ligands is $SCN^- > I^- > Br^- > Cl^- > F^-$, which is related to their polarizability.

1. Introduction

Alkaline ammoniacal etchant is commonly used in the manufacture of printed circuit boards (PCBs). It is one of the major chemicals for copper etching because of its high etching rate ($40 \sim 70$ μm min^{-1}), high capacity for dissolved copper (>170 g l^{-1}) and acceptable etching factor (about 2). Ammoniacal etchants have been well studied including the formation of passivating layers [1–3] and the influence of the anion on copper corrosion behavior [4–7]. However, ammonia is toxic and offensive, and faces increasingly rigorous regulations. Nonammoniacal etchants were studied to examine their feasibility as possible substitutes.

In 1972, the Shipley Company [8] used nonfuming complexing agents including ethylenediaminotetraacetic (EDTA), monoethanolamine (MEA, $H_2NCH_2CH_2OH$) and their derivatives to replace ammonia in preparing copper etchant. The etchant is less toxic. It can operate at neutral pH and is compatible with many resists, although the etching rate is much lower than with existing ammoniacal etchants. According to the stability constant of these amine-type complexes and our preliminary test on etching factor [9], MEA-type complexes are the most promising for fine-line PCB processing.

In this study, MEA was used as the complexing agent for cupric ions. Flannery et al. [10] studied MEA-complexed cupric ions using the polarographic method. Their results indicate that the coordination number is four per cupric ion so the complex ion is in the form $[Cu^{(II)}(MEA)_4]^{2+}$. Hence, the basic form of MEA-complexed cupric ions has been identified. However, its etching performance can be improved by specific ingredients added to speed up the etching rate. Some bridging ligands like NaCl, NaBr, NaI, and NaSCN have been found effective although the etching rates are still far from satisfactory [9].

How certain metallic materials can be etched in a solution containing specific additives has also been studied extensively. In most cases, the corrosion potential (E_{corr}) or exchange current density (i_0) of the relevant corrosion reaction was measured to understand the reaction mechanisms [1–7, 11–13].

Why a metal dissolution rate can be significantly improved by additives remains largely a mystery. Most of the formulations developed are mainly empirical. The concepts of inner-sphere and outer-sphere mechanisms have been employed to interpret the redox reactions of complexes in homogeneous or heterogeneous systems [14–17]. In the outer-sphere mechanism, an electron is transferred from one activated complex to another through the coordination spheres. In the inner-sphere mechanism, an electron is transferred from one activated complex to another through the bridging ligands.

In this work, the mechanism of copper etching in MEA-complexed etchant with different bridging ligands was investigated. We attempted to explain the corrosion behaviour in terms of the concepts of inner-sphere or outer-sphere electron transfer. Hopefully, the theoretical information obtained could help develop new copper etchants with appropriate additives.

2. Experimental details

The copper etchants were prepared with reagent-grade monoethanolamine ($H_2NCH_2CH_2OH$, MEA, Tedia 99.9%), cupric sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, Showa) and distilled water. Cupric sulfate was chosen as the source of cupric ions because the effect of additives could be discriminated clearly. Also it will not be affected by chloride ions if cupric chloride is used. Additives including NaF, NaCl, NaBr, NaI, NaSCN, $K_2Cr_2O_7$, $KMnO_4$ and $K_2S_2O_8$ were added separately to the solution to measure their effect on etching rate. The ratio of the concentration of cupric ions and additives were controlled at $[\mathrm{Cu(II)}]:[\mathrm{additives}] = 1:6 \times 10^{-3}$ for all experiments. The initial pH of all solutions was controlled at 10, through adjustment by sulfuric acid and sodium hydroxide.

Copper weight loss was measured on a rectangular copper specimen (35 mm × 20 mm, 0.5 mm thick), which was first degreased with acetone for 10 min, dried and weighed. It was then immersed in the copper etchant. The etching was performed under 1200 rpm agitation and at various temperatures. After 20 min, the specimen was washed with deionized water, dry, reweighed and the weight loss was determined. The maximum percentage deviation was no more than 5%.

Metal complexes and their bridged complexes are generally charactered by using NMR or u.v.–vis. spectroscopy [18]. In this study, electrochemical measurement was used. Because it is difficult to distinguish the difference between $\mathrm{Cu(MEA)_4^{2+}}$ and $\mathrm{Cu(MEA)_4^{2+}}$ X ($X{=}F^-$, Cl^-, Br^-, I^-, SCN^-) by using spectroscopic methods even at the high concentration (1 M) of additives.

Polarization data (Solartron SI 1286 electrochemical interface potentio/galvanostat) were collected in all the experiments. A software (CorrWare) was used to control the potentio/galvanostat and record the data. The cell contained three electrodes, namely a platinum counter electrode, a reference electrode (SCE) and a working electrode. A pure copper strip (1.1493 cm^2) was used as the working electrode. A luggin capillary was used to minimize the IR drop between the reference and working electrode. The corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were calculated and fitted according to Stern–Geary equation [19].

All the electrochemical experiments were carried out at 25 °C and under nitrogen atmosphere. The scan rate was 1 mV s^{-1}.

3. Results and discussion

3.1. *MEA concentration*

Cupric ion complexed with MEA was previously studied by polarography [10]. The complex was found to contain four MEA ligands as shown in Equation 1,

$$\mathrm{Cu(II)} + 4\mathrm{MEA} \longleftrightarrow \left[\mathrm{Cu^{(II)}(MEA)_4}\right]^{2+} \qquad (1)$$

and the formation constant (K_f) of the complex ion was 3×10^{16}. The effect of MEA concentration on the etching rate is shown in Figure 1. It is found that the rate of copper dissolution increases as the MEA concentration increases up to 2.5 M, which is about five times the concentration of cupric ions. This is probably because without sufficient MEA ligands, the formation of $[\mathrm{Cu^{(II)}(MEA)_4}]^{2+}$ slows down naturally, so the dissolution rate decreases. However, further increase in MEA concentration does not help accelerate the dissolution rate, probably because of the inhibitive effect of MEA ligands [20]. According to Equation 1, the theoretical optimal composition of this nonammonia etchant should be $[\mathrm{Cu(II)}]:[\mathrm{MEA}]=1:4$. The actual optimal Cu(II)/MEA ratio is 5 instead of 4 as Equation 1 might predict. This is reasonable since some MEA molecules should be allocated to complex with the additional Cu(II) ions due to copper dissolution.

Figure 2 shows the copper weight loss versus etching time. Line A represents etching solution prepared in the optimal ratio 5. Line B and line C represent ratio 6 and 4, respectively. Apparently, line A shows the fastest etching effect. From line A, the etching rate was about 0.06 μm min^{-1}, which is much slower than for conventional cupric chloride [22] or alkaline ammoniacal etchant [22–24]. The MEA-type etchant requires effective additives to speed up its etching rate before it can become industrially feasible.

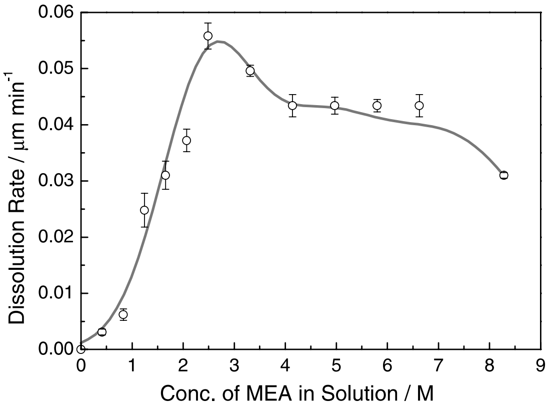

Fig. 1. Copper dissolution rate with different MEA concentration in etching solution at 25 °C under 1200 rpm stirring condition. Cupric ion concentration 0.5 M.

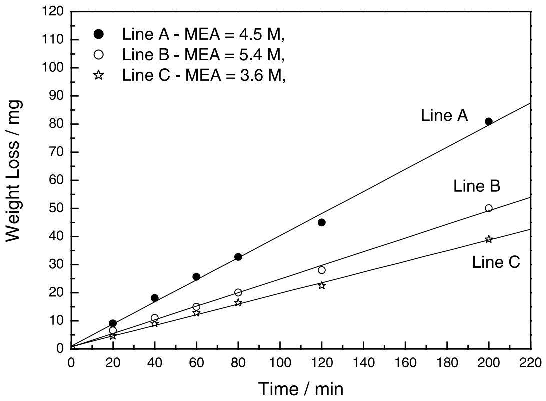

Fig. 2. Copper weight loss (WL) in 0.9 M cupric sulfate + 3.6 M MEA (line A), 0.9 M cupric sulfate + 4.5 M MEA (line B) and 0.9 M cupric sulfate + 5.4 M MEA (line C) at 25 °C under 1200 rpm stirring condition. WL (mg): line A (●) 0.39 × time (min); line B (○) 0.24 × time (min); line C (☆) 0.19 × time (min).

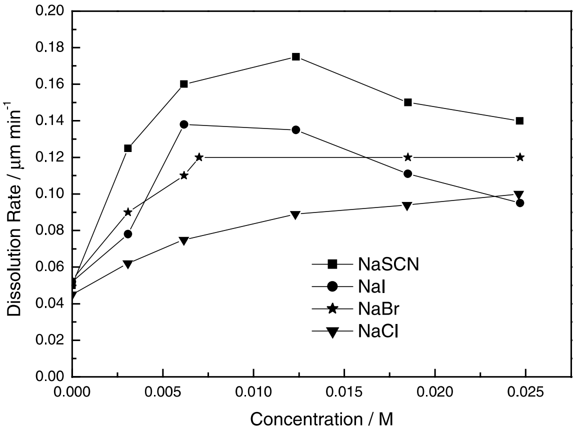

Fig. 4. Effect of bridging ligands concentration on dissolution rate in $[Cu^{(II)}(MEA)_4]^{2+}$ solution at 25 °C under 1200 rpm stirring.

3.2. *Effect of additives*

It is a common practice to use additives to adjust the corrosion rate of copper [22, 24–26]. In this study, bridging ligands including halides (NaF, NaCl, NaBr, NaI) and NaSCN and oxidizers like $K_2Cr_2O_7$, $KMnO_4$, $K_2S_2O_8$ were used. Figure 3(a) and (b) show the copper weight loss in different additives (conc. 6 mM) at 25 °C and under 1200 rpm stirring. As seen in Figure 3(a), bridging ligands, especially NaSCN and NaI, were useful in speeding up the copper dissolution. Oxidizers did not seem to accelerate the dissolution rate significantly according to Figure 3(b). The result implies that the dissolution reaction pathways in solutions containing oxidizers and nonadditives are different. The slow reaction process was accelerated. So the effect of bridging ligands on copper dissolution was studied in greater detail. Figure 4 shows the relation between the concentration of bridging ligands and the copper dissolution rate. At high concentration of bridging ligands, especially NaI and NaSCN, the copper dissolution rate decreased. Many studies report the specific adsorption of halide ions on the electrode surface and their poisoning effect on chemical reactions [27–33]. Marques et al. [27] reported the poisoning effect of SCN^- on the reduction of O_2 and H_2O_2 on graphite electrodes. Wu et al. [31] and Schweinsberg et al. [30] studied the effect of I^- on copper dissolution. They found that the copper dissolution rate increased in the presence of I^-. However, overdosage of I^- leads to an inhibitive effect. In this case, the addition of I^-(~5 mM) and SCN^-(10 ~ 15 mM) promote copper dissolution, but excess additive inhibits dissolution. This may be attributed to the specific adsorption of I^- and SCN^-, which reduces the number of active sites available for $[Cu^{(II)}(MEA)_4]^{2+}$ to react on the copper surface [32, 33]. Therefore, overdosing of bridging ligands inhibits copper dissolution.

3.3. *Temperature effect*

Figures 5(a) and 5(b) show the Arrhenius plots in solutions containing various bridging ligands and oxidizers, respectively. The activation energies calculated are listed in Table 1. All solutions contained 0.9 M cupric, 4.5 M MEA, 6 mM additives and were under

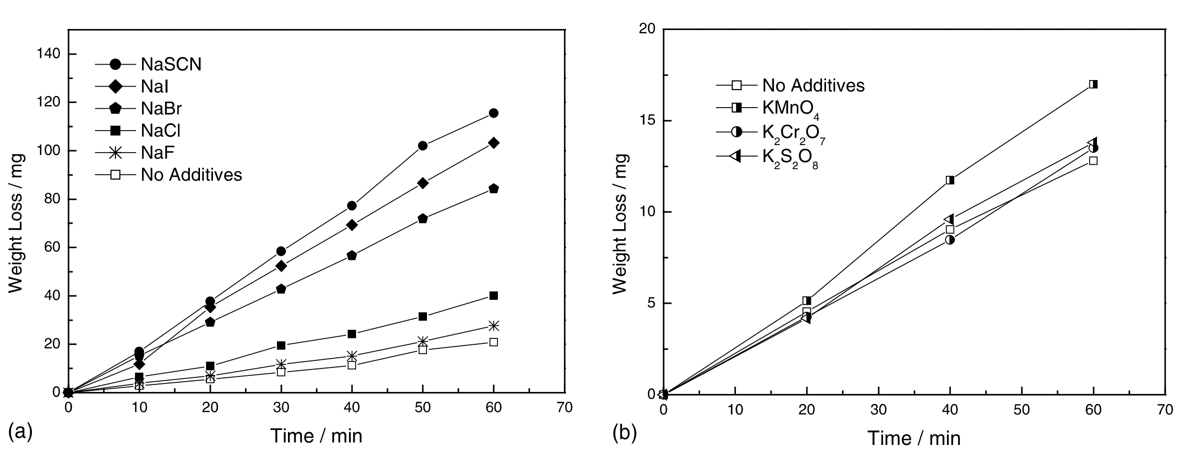

Fig. 3. Copper weight loss in different additives containing solutions at 25 °C under 1200 rpm stirring, (a) ligand-type additives NaF, NaCl, NaBr, NaI, NaSCN, (b) oxidizer-type additives $K_2Cr_2O_7$, $KMnO_4$, $K_2S_2O_8$. Additive concentration 6 mM.

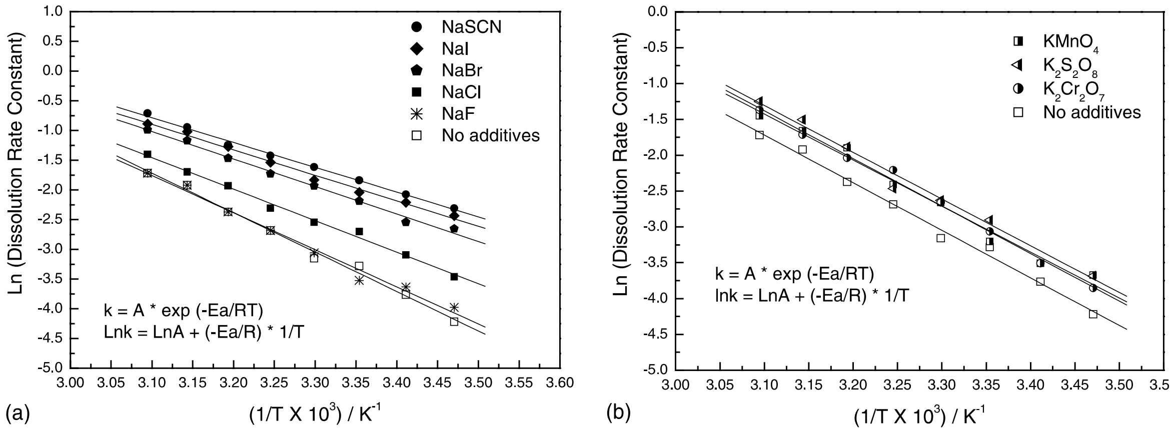

Fig. 5. Arrhenius plots of copper dissolution in $[Cu^{(II)}(MEA)_4]^{2+}$ solutions (0.9 M cupric sulfate and 4.5 M MEA) containing different additives (a) bridging ligands (b) oxidizers; concentration of additives were controlled at 6 mM.

Table 1. Activation energies (E_a) of different additives containing $[Cu^{(II)}(MEA)_4]^{2+}$ solutions*

Additives (6 mM)	E_a/kJ mol^{-1}
No ligands	55.24
NaSCN	34.68
NaI	35.66
NaBr	38.54
NaCl	44.16
NaF	51.92
$KMnO_4$	54.25
$K_2S_2O_8$	53.38
$K_2Cr_2O_7$	55.19

*Activation energy of copper dissolution in ammonia containing media is about 5–7 kJ mol^{-1}.

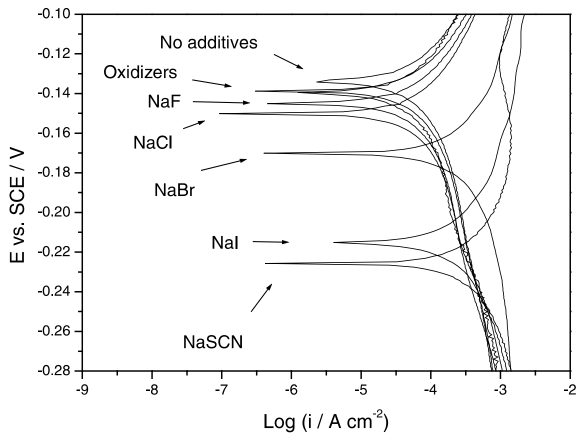

Fig. 6. Shift of E_{corr} (vs SCE/V) with different bridging ligands under 1200 rpm stirring at 25 °C. Current density in A cm^{-2}. Each solution contained 0.045 M $CuSO_4$, 0.225 M MEA and the concentration of additives was 0.3 mM; the oxidizers were $K_2Cr_2O_7$, $KMnO_4$ and $K_2S_2O_8$. Scan rate 1 mV s^{-1}.

1200 rpm stirring. The concentration of $[Cu^{(II)}(MEA)_4]^{2+}$ was kept constant so that the rate change was a direct measure of the rate constant. Table 1 shows that the activation energy (E_a) for copper dissolution decreased significantly when bridging ligands were added but remained constant at about 54 kJ mol^{-1} if oxidizers were added. The activation energy of copper dissolution in ammonia containing media is about 5–7 kJ mol^{-1} [13, 34]. So the activation energies of copper dissolution in solution with additives are much higher than those in aqueous ammonia or ammoniacal etchants (Table 1). The high E_a values in our case are due to the inhibitive property of MEA. This is similar to other corrosion systems that contain inhibitors [35]. In general, a significant change of activation energy represents a change in the reaction pathway. So the addition of bridging ligand to copper etching solution must involve a change in the dissolution pathway.

3.4. *Corrosion potential*

Another measure of the effect of additives can be obtained from the determination of corrosion potential (E_{corr}). Figure 6 shows the anodic polarization curves of copper dissolution; the E_{corr} and i_{corr} can be obtained, as is shown in Table 2. Yang et al. [36, 37] found a shift in rest potential when bridging ligands were added in a copper deposition bath. Similarly, there should be a shift in E_{corr} in the copper dissolution when bridging ligand is added.

The shift of E_{corr} can be defined according to Equation 2:

$$\Delta E_{corr,\,shift} = E_x - E_0 \tag{2}$$

where $\Delta E_{corr,\,shift}$ is the shift in corrosion potential, E_0 is the E_{corr} value without additives, and E_x is E_{corr} with additives. If bridging ligand is added, E_{corr} shifts in the negative direction.

$\Delta E_{corr,\,shift}$ values are shown in Table 2 and are in the following order: oxidizers, NaF < NaCl < NaBr < NaI < NaSCN. Similarly, i_{corr} changes in the following pattern: oxidizers, NaF < NaCl < NaBr < NaI < NaSCN. Thus, the values of $\Delta E_{corr,\,shift}$ or i_{corr} are directly related to the effectiveness of additive in accelerating copper dissolution.

Table 2. E_{corr}, $\Delta E_{\mathrm{corr,\ shift}}$ and i_{corr} values of different bridging ligands containing solutions

Bridging ligands (6 mM)	No ligands	F^-	Cl^-	Br^-	I^-	SCN^-
E_{corr} vs SCE/V	−0.134	−0.146	−0.151	−0.169	−0.215	−0.226
i_{corr}/mA cm^{-2}	0.1211	0.1418	0.1524	0.5160	0.6267	0.7848
$\Delta E_{\mathrm{corr,\ shift}}$ vs SCE/V	–	−0.012	−0.017	−0.035	−0.081	−0.092

These additives can be classified as hard and soft acids and bases [38] as shown in Table 3. Generally, soft acids and bases are more polarizable than hard acids and bases. Polarizability is related to the facility of electron transfer, which in the present case lies in the following order: $F^- < Cl^-, Br^- < I^-, SCN^-$. This is consistent with our previous finding that I^- and SCN^- are most capable of electron transfer for copper dissolution. The effect of bridging ligands in speeding up copper dissolution is also of the same order, meaning that electron transfer is governed by the polarizability of the bridging ligands added.

4. Mechanism study

Taube [14] first identified two electron transfer mechanisms, namely an inner-sphere or an outer-sphere mechanism for homogeneous reactions. In an outer-sphere reaction, an electron is transferred from one activated complex to another in which the original coordination spheres of the activated complex are maintained. In contrast, an electron is transferred through the ligand from one activated complex to another in an inner-sphere reaction.

In a heterogeneous redox reaction, such as reaction on the electrode, an electron is transferred between an electronic conductor and an ionic conductor. In an outer-sphere reaction, the reactant does not interact strongly with the electrode surface. Otherwise, in an inner-sphere reaction, a ligand absorbs on an electrode and bridges to the electrode surface directly. There is a strong interaction of the reactant, intermediates or products with the electrode. Many studies [16, 17, 39, 40] have described the intermolecular electron transfer at metal surfaces including platinum, gold, silver and mercury electrodes. The results indicate that the inner-sphere reaction occurs with bridging ligands.

In this study, these two mechanisms seem to fit the dissolution of copper in MEA-complexed solutions with bridging ligands when the copper reacts with the etchant. When copper dissolves in $[Cu^{(II)}(MEA)_4]^{2+}$ solution without bridging ligands, $[Cu^{(II)}(MEA)_4]^{2+}$ accepts an electron from the copper metal surface and is converted to $[Cu^{(I)}(MEA)_2]^+$. Then it transfers the electron to the bulk solution, which contains dissolved oxygen or other oxidizing agents for the regenerative reaction. The electron transfer is accomplished with the primary coordination spheres remaining intact. This process matches with the outer-sphere reaction mechanism, which is described as follows:

Step 1: $[Cu^{(II)}(MEA)_4]^{2+}$ diffuses to the copper surface,

$$Cu^{(0)} + \left[Cu^{(II)}(MEA)_4\right]^{2+} \longleftrightarrow \left[Cu^{(0)} - Cu^{(II)}(MEA)_4\right]^{2+} \tag{3}$$

Step 2: Copper dissolves and $[Cu^{(II)}(MEA)_4]^{2+}$ accepts an electron from the copper surface,

$$\left[Cu^{(0)} - Cu^{(II)}(MEA)_4\right]^{2+} \xrightarrow{\text{electron transfer}} \left[Cu^{(I)} - Cu^{(I)}(MEA)_4\right]^{2+} \tag{4}$$

Step 3: The successor complex decomposes and $[Cu^{(I)}(MEA)_4]^+$ converts to $[Cu^{(I)}(MEA)_2]^+$,

$$\left[Cu^{(I)} - Cu^{(I)}(MEA)_4\right]^{2+} \longrightarrow Cu^{(I)} + \left[Cu^{(I)}(MEA)_2\right]^{+} + 2MEA \tag{5}$$

Hence, the total reaction is

$$Cu^{(0)} + \left[Cu^{(II)}(MEA)_4\right]^{2+} \longrightarrow Cu^{(I)} + \left[Cu^{(I)}(MEA)_2\right]^{+} + 2MEA \tag{6}$$

This is an autocatalytic reaction consisting of depolarization of the copper surface by $[Cu^{(II)}(MEA)_4]^{2+}$ ions.

According to Haim's theory [41], the role of the bridging ligand in inner-sphere electron-transfer reactions is applicable to our case. According to the shift in E_{corr} with different bridging ligands added, the electron transfer through the bridging ligands may proceed via the inner-sphere reaction mechanism. The basic steps are as follows:

Step 1: $[Cu^{(II)}(MEA)_4]^{2+}$ diffuses to the copper surface and attaches itself to bridging ligands ($X = F^-$, Cl^-, Br^-, I^-, SCN^-). Then a binuclear ligand-bridged complex structure is formed with X being the bridging ligand,

Table 3. Classification of Lewis acids and bases*

	Hard	Borderline	Soft
Acids	H^+, Li^+, Na^+, K^+	Cu^{2+}, Ni^{2+}, Fe^{2+}	Cu^+, Ag^+, Au^+, Pd^{2+}
Bases	F^-, NH_3, SO_4^{2-}	Cl^-, Br^-, $SC\underline{N}^-$	$\underline{C}N^-$, I^-, $\underline{S}CN^-$, R_2S

*Underlined element is the site of attachment to which the classification refers.

$$\mathrm{Cu}^{(0)} + \left[\mathrm{Cu}^{(\mathrm{II})}(\mathrm{MEA})_4\mathrm{X}\right]^+ \xleftrightarrow{\text{adsorption}} \left[\mathrm{Cu}^{(0)} - \mathrm{X} - \mathrm{Cu}^{(\mathrm{II})}(\mathrm{MEA})_4\right]^+ \qquad (7)$$

Step 2: Copper atom ($\mathrm{Cu}^{(0)}$) in $[\mathrm{Cu}^{(0)}—\mathrm{X}—\mathrm{Cu}^{(\mathrm{II})}(\mathrm{MEA})_4]^+$ releases an electron through the bridging ligand to $[\mathrm{Cu}^{(\mathrm{II})}(\mathrm{MEA})_4]^{2+}$ and forms monovalent cuprous.

$$\left[\mathrm{Cu}^{(0)} - \mathrm{X} - \mathrm{Cu}^{(\mathrm{II})}(\mathrm{MEA})_4\right]^+ \xrightarrow{\text{electrontransfer}} \left[\mathrm{Cu}^{(\mathrm{I})} - \mathrm{X} - \mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_4\right]^+ \qquad (8)$$

Step 3: The binuclear ligand-bridged complex $[\mathrm{Cu}^{(\mathrm{I})}—\mathrm{X}—\mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_4]^+$ decomposes and $[\mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_4]^+$ converts to $[\mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_2]^+$,

$$\left[\mathrm{Cu}^{(\mathrm{I})} - \mathrm{X} - \mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_4\right]^+ \longrightarrow \mathrm{Cu}^{(\mathrm{I})}\mathrm{X} + \left[\mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_2\right]^+ + 2\mathrm{MEA} \qquad (9)$$

and the total reaction is,

$$\mathrm{Cu}^{(0)} + \left[\mathrm{Cu}^{(\mathrm{II})}(\mathrm{MEA})_4\mathrm{X}\right]^+ \longrightarrow \mathrm{Cu}^{(\mathrm{I})}\mathrm{X} + \left[\mathrm{Cu}^{(\mathrm{I})}(\mathrm{MEA})_2\right]^+ + 2\mathrm{MEA} \qquad (10)$$

5. Conclusion

Adding bridging ligands like NaCl, NaBr, NaI or NaSCN can accelerate copper dissolution in MEA-complexed solution, but NaF does not have an obvious effect. The accelerating effect can be explained in terms of electron transfer via the inner-sphere mechanism. Soft acids or bases like I^- or SCN^- are the preferred accelerators, because they possess better electron transfer ability. Thus, the choice of bridging ligand-type additives for speeding up copper dissolution can be determined by its electron transfer ability through the inner-sphere mechanism.

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