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Structures of Copper(II) Complexes Which Deposit Copper in Chemical Copper-plating Bath

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Synopsis. The deposition of copper from alkaline solutions containing various copper(II) complexes and formaldehyde was studied. It was found that one-to-one copper(II) complexes of hepta-, hexa-, and quadridentate ligands deposit copper on reduced platinum by means of autocatalytic reduction, and that, under particular conditions, copper(I) oxide is deposited on oxidized platinum from the solutions containing quadridentate ligands.

It is well known that copper metal is catalytically deposited on the surfaces of noble metals from solutions which contain some kinds of copper(II) complexes and reducing agents. As the deposited copper also has a good catalytic activity, the reduction proceeds autocatalytically. This reduction method has been widely utilized as "chemical copper plating" in industry, especially in the manufacture of printed circuit boards.

For this reduction, several reaction mechanisms have been proposed. Saubestre¹⁾ reported the following half-reactions for reductions in alkaline solutions containing the tartrate ion as the complexing agent and formaldehyde as the reducing agent:

$$HCHO + 3OH^- \longrightarrow HCOO^- + 2H_2O + 2e^- \qquad (1\text{-a})$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad (1\text{-b})$$

Although hydrogen gas is evidently generated on the plating surface, he discussed no details of the evolution of hydrogen. Tilley²⁾ and Lukes³⁾ proposed the following half-reactions:

$$2HCHO + 4OH^- \longrightarrow 2HCOO^- + H_2 + 2H_2O + 2e^- \qquad (2\text{-a})$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad (1\text{-b})$$

Konishi⁴⁾ and Saito⁵⁾ reported that not the hydrated copper(II) ion, but the copper(II) complex, participates in this reduction. It seems, however, that there is no direct evidence for what kind of copper(II) species deposits copper. A study has, therefore, been made to deepen our understanding of this reduction.

Experimental

Preparation of Plating Solutions. The following reagents were used as the complexing agents for the copper(II) ion: D-mannitol, D-sorbitol, dulcitol, ethylenediaminetetraacetic acid (H_4edta), 1,2-cyclohexanediaminetetraacetic acid (H_4cdta), *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (H_3hedta), diethylenetriaminepentaacetic acid (H_5dtpa), L-, D-, and *meso*-tartaric acids, *meso*-erythritol, ethylenediamine (en), diethylenetriamine (dien), and triethylenetetramine (trien). Known amounts of copper(II) sulfate, one of the above complexing agents, and sodium hydroxide were dissolved in deionized water in the above order. These mixtures were then kept at 29 °C for 24 h. Known amounts of a formaldehyde solution kept at 29 °C were added to the above mixtures before use. All the reagents used were of an A. R. grade.

Apparatus and Procedure. A cleaned platinum substrate (0.2 mm × 14 mm × 20 mm) was oxidized electrolytically in nitric acid (1 : 1) (oxidized substrate). In some runs, the substrate was reduced by immersing it in a 0.2 mol/dm³ formaldehyde and 0.4 mol/dm³ sodium hydroxide solution (reduced substrate) in order to differentiate the reactivities of the copper(II) complexes studied. Copper or copper(I) oxide was deposited on the substrates by immersing them in the plating solutions (250 cm³) at 29 °C for 60 min. The amounts of deposits were determined by chelatometric titration. The amounts of hydrogen evolved during the deposition were measured by the use of the apparatus shown in Fig. 1 in the following manner. The apparatus, filled with a plating solution, was kept at 29.0 °C, and then the air in the apparatus and dissolved in the plating solution was replaced with hydrogen by bubbling. The substrate, S, was placed over the plating solution by means of a hanger, H, and a magnet, M, and then the plug, P, and the stopcock, S, were closed. The substrate was immersed in the plating solution by moving the magnet. After an appropriate time, the substrate was raised and the pressure increase was measured by means of a water manometer, WM.

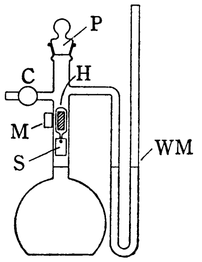

Fig. 1. Apparatus for measuring hydrogen evolution.

Results and Discussion

The deposition rate of copper on the oxidized substrate is shown in Fig. 2, with H_4edta used as the complexing agent. The rate was virtually independent of the concentration of H_4edta added. The rate on the reduced substrate was the same as that on the oxidized substrate within the limits of experimental errors.

It is well known that H_4edta forms a stable one-to-one complex with the copper(II) ion.⁶⁾ Therefore, the concentration of this complex must be almost constant under the present conditions, whereas the concentration of the hydrated copper(II) ion decreases steeply with an increase in the concentration of H_4edta as follows:

$$[Cu^{2+}] \approx c_c/K(c_l - c_c), \qquad (3)$$

where K is the stability constant of the complex and where c_c and c_l represent the concentrations of copper(II) sulfate and the complexing agent respectively.

The above findings, therefore, suggest that not the hydrated copper(II) ion, but the copper(II) complex deposits copper. The slight decrease in the rate shown

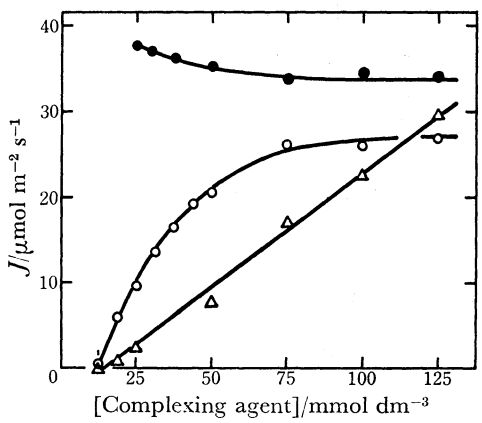

Fig. 2. Relations between the deposition rate of copper and the concentration of the compexing agent in Cu(II)-H_4edta (●), Cu(II)-D-mannitol (○), and Cu(II)-D-sorbitol (△) plating solutions. $CuSO_4$: 25, HCHO: 100 mmol/dm^3, pH: 12.8, Temp: 29 °C.

in Fig. 2 may be explained in terms of retardation due to the adsorption of edta^{4-}, Hedta^{3-}, *etc.*

Hexitols such as D-mannitol and D-sorbitol have six OH groups. These reagents may be expected to form two-to-one and/or one-to-one complexes with the copper(II) ion. Hence, the reactivity of their complexes was studied. As is shown in Fig. 2, the deposition of copper began just at $c_l/c_c=0.50$ in both plating solutions, and the rate increased with the increase in the c_l. In the range of $2c_l<c_c$, copper(II) hydroxide was precipitated. These findings indicate that D-mannitol and D-sorbitol react with the copper(II) ion as follows:

$$2Cu^{2+} + H_nL + 4OH^- \rightleftharpoons [Cu_2H_{(n-4)}L] + 4H_2O, \quad (4)$$

$$Cu^{2+} + H_nL + 2OH^- \rightleftharpoons [CuH_{(n-2)}L] + 2H_2O, \quad (5)$$

where H_nL represents a ligand, and that the one-to-one complex ($[CuH_{(n-2)}L]$) deposits copper.

In order to obtain further proof, the reactivities of various copper(II) complexes were studied. These complexes can be classified into three categories. The first-group complexes consist of the copper(II) ions and either hepta- or hexadentate ligands such as H_4edta, H_4cdta, H_3hedta, H_5dtpa, D-mannitol, D-sorbitol, and dulcitol and deposit copper by forming hydrogen, regardless of the surface state of the substrate. The second-group complexes are composed of the copper(II) ions and quadridentate ligands such as L-, D- and *meso*-tartaric acids, and *meso*-erythritol and deposit copper accompanied by the formation of hydrogen on the reduced substrate and copper(I) oxide, but not accompanied by the formation of hydrogen on the oxidized substrate under particular conditions ($c_l/c_c\approx 2$). In this group, the species which give copper are probably one-to-one complexes, in view of the findings described in the preceding paragraphs. The formation of a one-to-one copper(II)-tartrate complex was previously verified by EPR under conditions similar to the present case.[7] The third-group complexes are those with the copper(II) ions surrounded by nitrogen atoms only (en, dien, and trien); they are completely inactive.

In all the cases of copper deposition, each plating solution gave almost the same rates for both oxidized and reduced substrates under the same conditions. It can, therefore, be suggested that the platinum oxide (PtO_x) formed on the oxidized substrate is quickly reduced when it is immersed in the plating solutions and that the reduced platinum catalyzes the deposition of copper.

The amounts of hydrogen formed during the deposition were measured in the plating solutions containing H_4edta. The H_2/Cu ratios ranged from 0.94 (pH=11.3) to 0.96 (pH=12.8), in agreement with Lukes' results.[3] It is well known that the formate ion, a product of Reaction 1-a or 2-a, is also a reducing agent. However, no deposits were obtained from the present solutions when sodium formate was used as the reducing agent. Accordingly, Reaction 2-a must be operative, at least in more than 94% of the total deposits.

From these results, it may be concluded that the one-to-one copper(II) complexes, whose general structures are shown in Fig. 3, are autocatalytically reduced by formaldehyde in an alkaline solution as follows:

$$PtO_x \xrightarrow{HCHO,\ OH^-} Pt \quad (6)$$

$$[CuH_{(n-2)}L] + 2HCHO + 4OH^- \xrightarrow{Pt,\ Cu} Cu + 2HCOO^- + H_2 + 2H_2O + H_{(n-2)}L^{2-}. \quad (7)$$

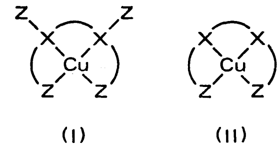

Fig. 3. General structures of copper(II) complexes which deposit copper.
X's are N or O atoms. Z's are polar groups such as $-COO^-$, $-CH_2COO^-$, $-CH_2OH$ or $-CH(OH)CH_2OH$.

As has been described above, the second-group complexes gave copper(I) oxide on the oxidized substrate at $c_l/c_c\approx 2$. This finding suggests that, under these conditions, PtO_x is not reduced, but catalyzes the partial reduction of some copper(II) species to deposit Cu_2O as:

$$\text{Cu(II)-species} \xrightarrow{HCHO,\ OH^-/PtO_x} Cu_2O. \quad (8)$$

A study of this deposition is now in progress.

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