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Reaction mechanisms of copper electrodeposition from 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) solution on glassy carbon

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ABSTRACT

The specific forms of the coordination compounds were calculated and the specific process of copper reduction was investigated in non-cyanide alkaline baths with 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP, or H_4L) complexing agent. The results indicate that Cu^{2+} coordinated with HEDP molecules to form CuL_2^{6-} coordination compound, and OH^- would coordinate with CuL_2^{6-} to form more stable $Cu(OH)_2L_2^{8-}$ complex as pH increased. The electrochemical reduction of Cu^{2+} on glassy carbon electrode is composed of individual reduction processes of the above-mentioned two coordination complexes. The reduction processes are irreversible and controlled by diffusion. As the overpotential increased, the low-coordinate compound CuL_2^{6-} was reduced to copper first, following by the reduction of high-coordinate compound $Cu(OH)_2L_2^{8-}$. The copper electrodeposition involves nucleation process, and the electrocrystallization is consistent with progressive nucleation in three dimensions.

1. Introduction

Cyanide copper plating possesses outstanding bonding force and is widely applied as an undercoat for steel die casting parts, zinc die casting parts and bulk aluminum materials. Due to the highly toxicity of cyanide, the research on alternative cyanide-free copper-plating techniques has been developed very rapidly in recent decades. The representative cyanide-free copper-plating systems include pyrophosphate [1] and sulphate solutions containing diphosphonic acid [2], polyethylene glycol [3], gluconate [4], sucrose [5], ammonia [6], Tartrate [7], or glycine [8]. Diphosphonic acid refers to one type of organic phosphonic acids which contain a P—C—P bond. Compared to pyrophosphates containing a P—O—P bond, diphosphonic acid retains a similar surface activity. Moreover, the small polarity of C—P bond overcomes the disadvantage that pyrophosphates are susceptible to the attack of OH^- and yield orthophosphates by hydrolysis at high pH [9–10]. Thereby, diphosphonic acid is able to coordinate with a variety of metal ions, including Cu^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+}, to generate stable coordination compounds [10–13]. In particular, one of such diphosphonic acids, HEDP, possesses outstanding coordination ability for metal ions and has been applied in electroplating, environmental water treatment and bio-medicine. In electroplating applications, HEDP is used as coordination agent in plating bath to obtain Cu [2] and Zn-Ni alloy coatings [14]. Noticeably, the cyanide-free alkaline copper-plating system with HEDP as coordination agent provides many advantages, including simple components, high stability, easy operation and maintenance, high current efficiency as well as superior throwing power to the cyanide system [15]. It has been proved that copper coating on steel substrate with excellent performance could be achieved in alkaline copper sulfate plating solution using HEDP as main coordination agent [16]. However, most of the reported studies on HEDP copper plating system are focused on the technical portion while the theories of the reduction process and the nucleation mechanism are not well understood [2,17,18]. The specific forms of the coordination compounds and the specific process of reduction are not clear on HEDP electrodeposition bath [19].

In this paper, combining with the coordination ionic form distribution maps of Cu^{2+}-HEDP-OH^- system under different pH values, the copper electroplating mechanism and initial behavior of copper electrocrystallization on a glassy carbon electrode were studied by electrochemical methods.

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2. Experimental

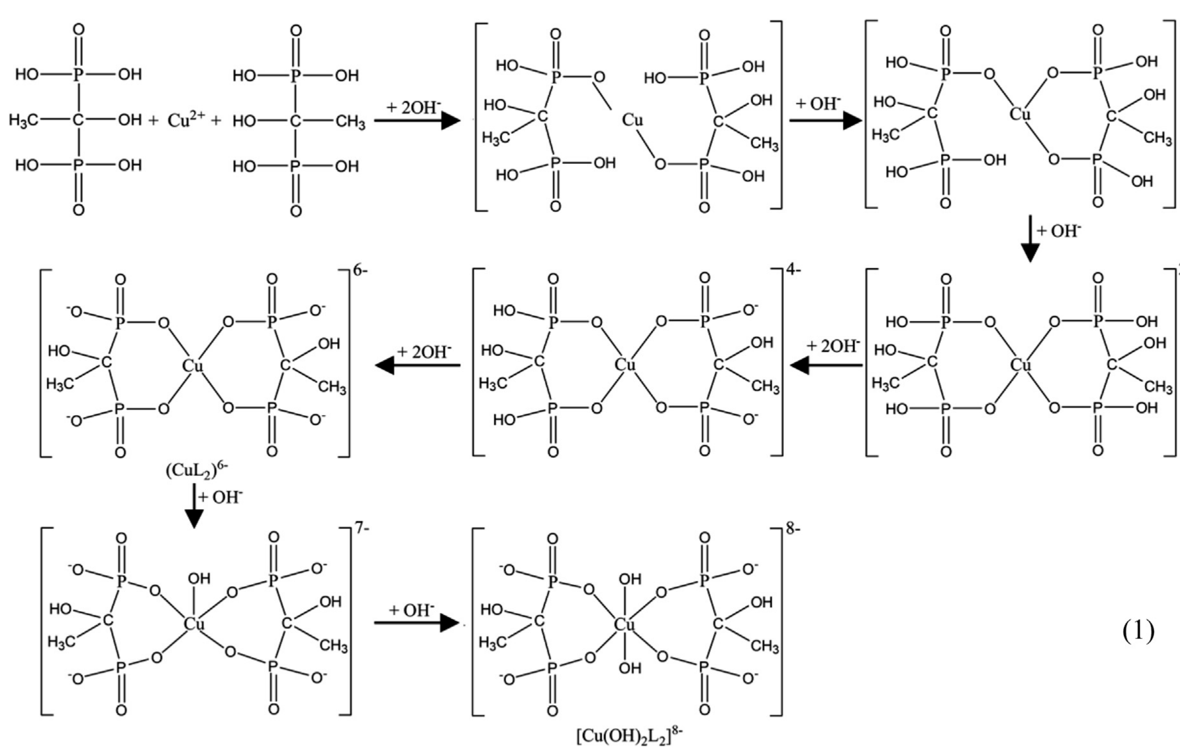
0.0192 M HEDP solution and 0.0192 M HEDP + 0.0064 M $CuSO_4$ solution were prepared for determination of pH titration curve. 0.1 M of supporting electrolyte, K_2SO_4, was added to the titration solution to maintain a constant ionic strength. After standing for 24 h, the solutions were titrated with 1 M KOH and the pH value was measured with a pHS-25 pH meter (Shanghai precision & Scientific Instrument Co., Ltd.). The experiments were carried out at 25 °C and all reagents were of analytical grade. All of the solutions were prepared with double-distilled water.

The electrolytic solution for measurement consisted of 0.16 M $CuSO_4$ and 0.48 M HEDP with pH adjusted by NaOH or H_2SO_4 solution. The electrochemical experiments were carried out by an AutoLab PGSTAT 30 electrochemical workstation, using a three-electrode system with glassy carbon electrode (area S = 0.071 cm^2) as the working electrode, saturated calomel electrode as the reference electrode and a platinum electrode as the auxiliary electrode. The glassy carbon electrode was polished to mirror by a piece of 0.05 μm α-Al_2O_3 powder-covered wetting fine cloth and then rinsed with double-distilled water for several times before each experiment. The tests included cyclic voltammetry (CV), chronoamperometry (CA) and linear sweep polarization (LSP). The solution was purged with N_2 for 3 min prior to assay and kept static during testing.

3. Results and discussion

3.1. Analysis of the coordination ionic form of Cu^{2+}-HEDP-OH^- system

The pH-metric titration curves shown in Fig. 1 are obtained by adding 1 M KOH into different solutions with volume of 250 ml, including free $CuSO_4$ solution, free HEDP solution and solution containing a 1:3 M ratio mixture of Cu^{2+} and HEDP. After dropping ~4 ml of KOH into free $CuSO_4$ solution, the pH value changes from 6 to 11, leading to the formation of copper hydroxide precipitate. When the solution contains only free HEDP, two equivalence points are observed between pH 3.8 to 5.6 and 7.7 to 9.7, suggesting the stepwise dissociation of protons from hydroxyl groups in HEDP. Interestingly, when the solution is a mixture of Cu^{2+} and HEDP, the titration curve is not a simple linear summation of the curves from free $CuSO_4$ and HEDP solutions and shows only a single region of pH elevation. It seems that the pH upheaval in the region 5–10 covers the two equivalence points of free HEDP, which can be explained by the rapid generation of coordination compound from Cu^{2+} and fully deprotonated HEDP. Additionally, pH value lifts a little around 11 as pointed by the arrow in Fig. 1. When pH > 2, the titration curve of Cu^{2+}-HEDP mixture significantly shifts to the right. That is to say, after the addition of Cu^{2+} in HEDP solution, more KOH is needed to achieve the same pH because it requires more KOH to neutralize the additional protons in solution released from the new coordination compound formed by HEDP and Cu^{2+}. When the amount of added KOH is between 21 ml and 24 ml, the color turns from light blue to dark blue obviously, indicating that Cu^{2+} and HEDP form a more stable coordination compound after mixing. When the pH is higher than 10.8, the color of the solution changes from dark blue to dark green, which is probably due to the reason that the newly added OH^- coordinates with Cu^{2+}-HEDP complex and forms new coordination complex after the fully deprotonation of HEDP. The precipitate appears as the pH value rises to about 13. A likely explanation is that the excess hydroxyl ions in the solution would compete with HEDP to bind with Cu^{2+}, which generated the insoluble copper hydroxide precipitation. According to the work by H. Wada and Q. Fernando [20], when the employed metal: ligand ratio was 1:10, no insoluble complexes of copper were formed. The predominant metal complex species in solution was $CuHL^-$ from pH 4.6 to 5.8 and CuL^{2-} from pH 6.9 to 8.8. It is worthwhile to note that CuL^{2-} possessed a more stable six-membered ring structure as compared to $CuHL^-$. According to changes of the molar ratio of Cu^{2+}: HEDP: OH^- during titration process, we propose that the reaction process shown in reaction (1) occurs with rising pH.



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