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CYCLIC VOLTAMMETRIC STUDY OF STAINLESS STEEL SUBSTRATE IN ACIDIC $CuSO_4$ SOLUTION

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ABSTRACT

There is a great interest in understanding the electrochemical process of the stainless steel by studying the current-potential peak appeared from a cyclic voltammogram. In this study, the electrochemical reactions of Cu^{2+} ion on stainless steel surface were investigated by cyclic voltammetry in 0.01 M $CuSO_4$ solution with respect to pH at which Cu^{2+} ion stable (pH 1 – 3). It was found that the decrease of pH has improved the conductivity and throwing power of the solution as shown by current density produced. Chronological events of Cu^{2+}/Cu reactions (reduction of Cu^{2+} - nucleation and growth of Cu and oxidation of Cu to Cu^{2+}) on the stainless steel surface during an entire cyclic voltammetric scan in 0.01 M $CuSO_4$ solution at pH 1 were described by the cyclic voltammogram.

Keywords: Copper; Copper-water System; Cyclic Voltammetry; Electrochemical Process; Redox Reaction

INTRODUCTION

In the case of copper coatings, a very great number of studies have already been undertaken due to huge industrial interest [1]. Indeed, copper coatings have various applications such as contact and the circuitry in the electronic industry, manufacturing printed-circuit boards, undercoating for other metal thin film coatings and the protection and decoration of consumer goods. Electrodeposition of copper is a viable alternative to vacuum-based deposition processes, such as sputtering, plasma deposition or chemical vapor deposition [2]. The electrodeposition method has recently attracted considerable attention in preparing copper coating because by effectively study the parameters involve by cyclic voltammetry, the nature of growth and patterns of the coating can be controlled. The electrodeposition of copper has been studied either on copper substrate [3-5] or numerous foreign substrates like platinum [1,6], glassy carbon [7-9], graphite [10], disposable pencil graphite [11], stainless steel [12-15] and steel [16-17].

The nature of electrode reactions, nucleation mechanisms and growth of the coatings can often be determined based on the cyclic voltammetry behavior [11,18]. There is a

great interest in understanding the electrochemical process of the copper nucleation mechanisms on the stainless steel substrate by studying the current density-potential peak appeared in a cyclic voltammogram. It is important to identify the copper electrodeposition mechanisms from electrochemical information recorded by the cyclic voltammogram in order to produce desired copper coatings.

This paper presents a study of electrochemical process of copper on stainless steel substrate from acidic $CuSO_4$ solution by cyclic voltammetry. Prior to cyclic voltammetric analysis, equilibrium of the copper-water system on pH value was constructed in order to determine the stability and solubility of Cu^{2+} ion concentration in the entire pH range.

EXPERIMENTAL

Stainless steel substrate (20 mm x 20 mm) with 1 mm thickness was mechanically ground on SiC papers from P800 to P2400 grit, in order to remove dirt and oxide layer for better adhesion. After that, the substrate was ultrasonically cleaned in acetone, rinsed with ultrapure water and dried at room temperature. An adhesive tape was used to mask off of the substrates except for a rectangular area of 20 mm^2 in which deposition was desired. Cyclic voltammetry experiment was controlled using an Autolab Potentiostat (Aut302 FRA2), interfaced with a PC running NOVA software by scanning the potential in the cathodic direction at a scan rate of 10 mV/s. The experiment was carried out in a typical three-electrochemical cell with the polished stainless steel as a working electrode, a platinum rod as a counter electrode and Ag/AgCl as a reference electrode. 0.01 M Cu^{2+} bath solution was prepared using reagent grade $CuSO_4$ dissolved with ultrapure water. The pH of the solution was adjusted from pH 1 to 14 by adding reagent grade H_2SO_4 or NaOH. All experiments were performed under room temperature.

RESULTS AND DISCUSSION

Stability of Cu^{2+} ions at various pH Values.

Numerous copper species can be exist in aqueous solution depending on the pH of the solution. It is necessary to determine copper speciation in the entire pH range before chosing the best pH values for further CV studies. Figure 1 shows the copper speciation in the pH 1 – 14 for the system of 0.01 M $CuSO_4$ solution. In acidic condition (i.e: pH 1 – 5), copper is present in the form of stable hexa-aqua cupric ion $[Cu(H_2O)6]^{2+}$, having four equatorial and two axial coordination sites, each occupied by water molecules. Usually, blue solution will produced responsible by the complex $[Cu(H2O)_6]^{2+}$, however, since low concentration of the $CuSO_4$ used under this study, the solution is colorless. When NaOH is added, water molecules are displaced because of the preferred coordination of copper with OH^-. Depending on the NaOH concentration and pH, OH^- can successively replace water molecules in copper's coordination.

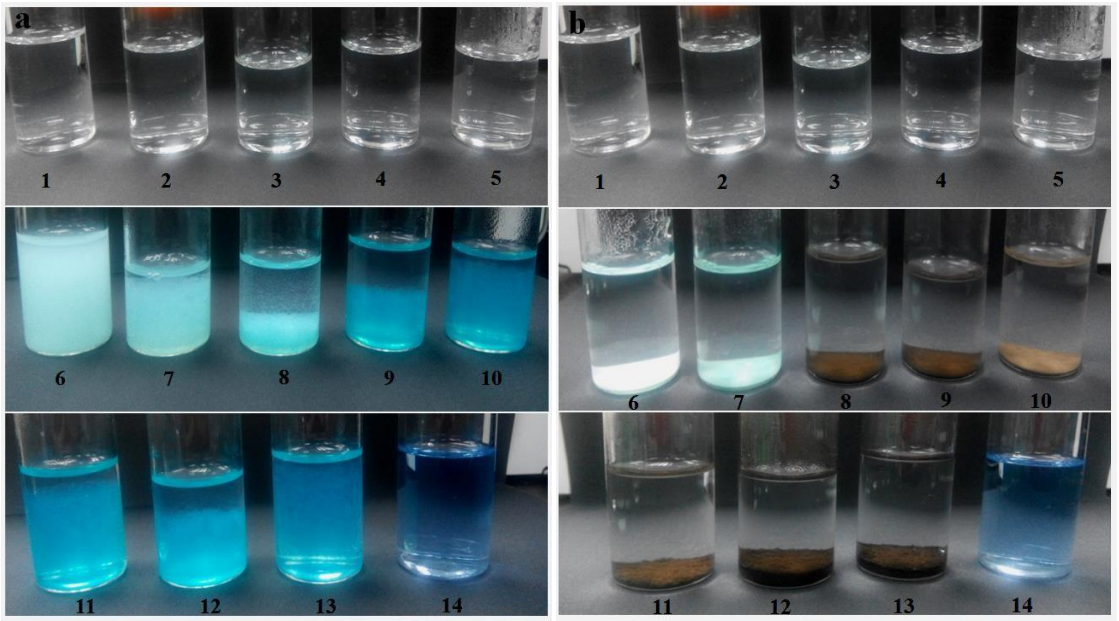

Figure 1: Equilibrium of 0.01 M $CuSO_4$-Water System (a) Freshly-prepared and (b) After Few Hours at pH 1 – 14 at 25 ^oC

The addition of NaOH in the solution makes the OH^- hitting a hexa-aqua copper ion, than formed new complex ion. The pH 6 – 7, slightly soluble of new complex ion, $[Cu(H_2O)_5OH]^+$ is formed. At this moment, the soluble Cu^{2+} ion concentration in the solution decrease yielding to the turbid turquoise mixed precipitate, as can be seen in Figure 1a, 6 – 7. After a few hours, the turquoise precipitate was settled down in light blue solution (Figure 1b, 6 – 7). Continue adding of the NaOH in solution makes copper hydroxide ($Cu(OH)_2$), the new complex formed no longer charge or called neutral complex, as the predominant species at pH 8 – 13. At this time, slightly soluble deep blue solution (Figure 1a, 8 – 13) turned to black precipitate in colorless solution (Figure 1b, 8 – 13). Further adding of the NaOH up to ph 14, anionic complex, $[Cu(H_2O)_3(OH)_3]^-$, is produced with clear deep blue solution. This solution, both at Figure 1a, 14 and Figure 1b, 14, is stable since precipitate has redissolved.

Based on the copper speciation in the entire ph range, pH 1 – 3 were selected for the CV studies. The motivation of the value pH 1 – 3 were selected because of the solubility and stability of the Cu^{2+} in the solution. At pH 4 and 5, even Cu^{2+} stable, however, were not considered for CV study because at higher applied potentials, Cu^{2+} is no longer stable and $Cu(OH)_2$ will be formed.

Cyclic Voltammetry (CV)
The chemisty of the copper-water system was further studied using CV, in order to determine the characteristic and the nature of electrode reactions. The resulting plot of current density vs potential is termed by cyclic voltammogram. All CV experiments were scanned starting from 0.5 V to – 0.5 V and back to 0.5 V at 10 mV/s. The value

of vertex potential was limited to – 0.5 V in order to avoid hydrogen evolution reaction (HER) occurs dominantly during scanning.

Effect of Solution pH

The effect of pH of the solution (pH 1 – 3) on CV of stainless steel in Cu^{2+} ions (0.01 M) is given in Figure 2. It is found that when the pH is decreased (concentration of H_2SO_4 increased) some significant differences were observed on the plotted voltammograms. The presence of zero current density from the beginning of the scan to about + 0.1 V, – 0.1 V and – 0.2 V for pH 3, pH 2 and pH 1, respectively, indicated no reaction occured in this potential range. After that, the cathodic current began to increase, resulting the formation of the cathodic peak, E_{pc}, which corresponds to copper reduction according to the reaction (1):

$$Cu^{2+} + 2e \rightarrow Cu. \quad (1)$$

The intensity of current at the E_{pc} is influenced by the pH of the solution. Evidently, when the pH of the solution decreases, the E_{pc} is more sharp and the current is more significant. The reduction potential of Cu^{2+}/Cu is pH independent based on Nernst Equation as in Eq. (2). However, the effect of the voltammograms corresponding to pH 2 and pH 3 were compensated for the solution resistance, and the E_{pc} is affected by solution pH on the stainless steel electrode [8].

$$E_{cell} = E^0_{Cu^{2+}/Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}. \quad (2)$$

When the potential reaches a predetermined switching potential (i.e.: - 0.5 V), the scan was reversed the direction towards more positive potentials. As the current decayed but remained cathodic, it is indicating further reduction of copper species. As the potential became more positive, at about 0 V, the current become anodic, increased and formed anodic peak, E_{pa} (the exact peak potential depends on the pH). Since the copper reduced during the forward scan, during the reverse scan it is oxidized back to Cu^{2+}, according to reaction (3). After E_{pa}, the current decayed slightly anodic until the end of the scan.

$$Cu \rightarrow Cu^{2+} + 2e. \quad (3)$$

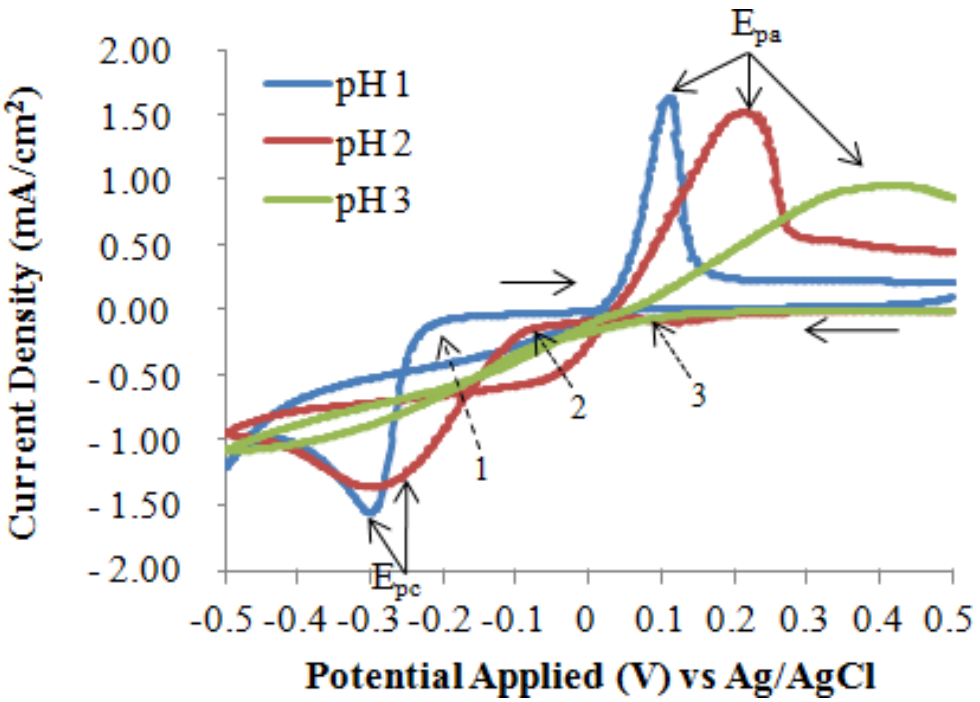

Figure 2: Cyclic Voltammogram of Stainless Steel Substrate in 0.01 M $CuSO_4$ (pH 1) solution at 25° C. Scan Rate: 10 mV/s. The Arrows Indicate the Direction of the Cycle Scan.

Chronology Events during CV Scan

Chronology of events on the stainless steel surface during an entire CV scan in 0.01 M $CuSO_4$ (pH 1) is presented in Figure 3. It can be described that at the beginning process which at OCP, no reduction or deposition of copper occurred on the stainless steel substrate. The reduction reaction of the electroactive species (copper ions) in the bath started to occur at about – 0.2 V (on the forward scan). At this potential, a stable nucleus of copper is starting to nuclei on the stainless steel surface.

The cathodic current density slowly increased between – 0.2 V until – 0.3 V indicating the nucleation of stable nuclei of copper on the stainless steel surface and the process occurred was controlled by electron transfer. After that, the cathodic current density slowly decreased until the vertex potential (– 0.5 V), which corresponds to the further nucleation and growth of the stable copper nucleus and the process was controlled by mass transport or diffusion control. On the reverse scan, copper nucleus that already exists on the stainless steel surface still undergoing growth phase as long as the current still in cathodic direction.

When the scan was reversed in the switching potential (E = – 0.5 V), two crossovers formed at – 0.25 V (E_N) and 0 V (E_{co}). The E_N potential is a crossover potential at which nucleation and growth take place with a measurable rate is known as the nucleation overpotential, which can be employed to estimate the experimental value of

nucleation overpotential. While, the E_{co} potential is defined as the crossover potential at which copper undergone reduction (being deposited) or oxidation (dissolved). The difference between the E_N and E_{co} was due to the nucleation overpotential on stainless steel substrate resulting from the crystallographic misfit between copper and stainless steel.

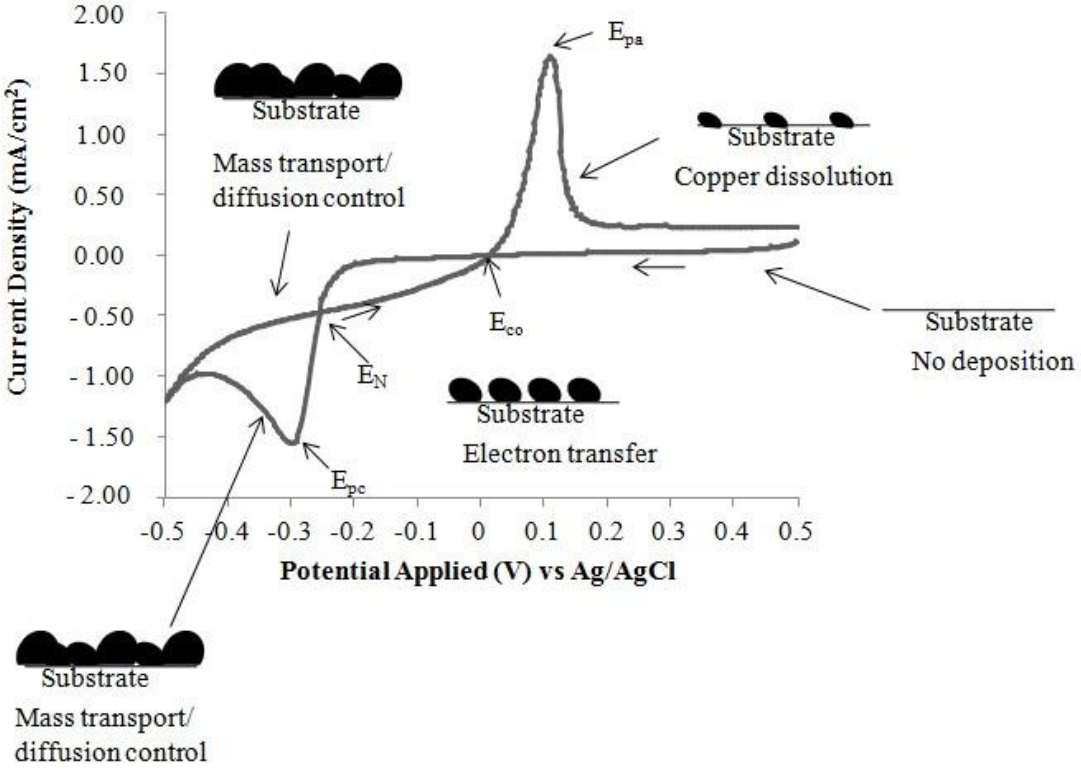

Figure 3: Schematic Presentation of Redox Reaction of Cu^{2+}/Cu on Stainless Steel CV using in 0.01 M $CuSO_4$ (pH 1) solution at 25 ^oC. Scan Rate: 10 mV/s. The Arrows Indicate the Direction of the Cycle Scan

At potentials more positive than E_{co}, the anodic peak, E_{pa}, is observed, which could be associated to the copper dissolution and/or oxidation from the stainless steel electrode. After peak, E_{pa}, the current is drastically reduced slightly anodic, until the end of the scan. Going further in the positive direction, the current density will be decayed to zero and remained zero means all copper oxidized and removed by dissolution.

Effect of Number of Cycles

In order to investigate the reversibility of reactions in the system under study, 50 cycles of CV in 0.01 M $CuSO_4$ solution at pH 1 was run (Figure 4). It can be seen that the current at the end of the first cycle was slightly anodic, indicating that an oxidation reaction (Cu/Cu^{2+}) was still present. At the beginning of the second cycle, the current remained anodic. E_{pc} peak (at about – 0.2 V) in the second cycle was lesser and more positive potential than E_{pc} peak (at – 0.3 V) in the first cycle, indicating a reduced

concentration of reacting Cu^{2+} species in the bulk solution since some amount of copper that has been reduced at first cycle did not completely dissolved . The anodic peak, E_a was also smaller that the corresponding peak in the first cycle. Increase the number of cycles make E_{pc} and E_{pa} peaks less significant and the E_N and E_{co} more closer means that the electrodeposition of copper is more likely to deposit on the newly formed copper coating.

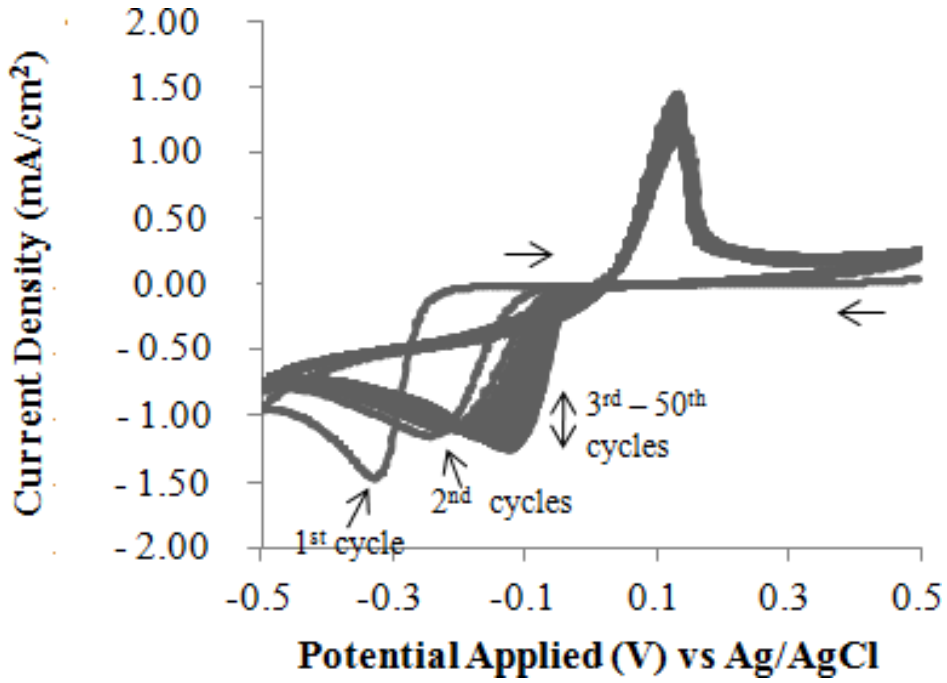

Figure 4: Cyclic Voltammograms (50 cycles) of Stainless Steel Substrate in 0.01 M $CuSO_4$ (pH 1) at 25 ^oC. Scan rate: 10 mV/s

CONCLUSIONS

The copper reduction-oxidation mechanisms of stainless steel in acidic $CuSO_4$ was investigated by cyclic voltammetry technique. It was found that reduction of Cu^{2+}/Cu was affected by the pH of the 0.01 M $CuSO_4$ solution. The voltammogram of stainless steel in 0.01 M $CuSO_4$ at pH 1 shows the reduction reaction of the Cu^{2+}/Cu started to occur at – 0.2 V. Then, current density continuously increased on the forward scan indicates nucleation and growth of stable nuclei of the copper on stainless steel surface. Reversed scanning in the anodic direction indicates dissolution of copper Cu/Cu^{2+}.

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