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Study on Triazinethiol Electropolymerized Films Prepared by Cyclic Voltammetry and Galvanostatic on Copper Alloy Surface

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Poly (6-N,N-dibutylamino-1,3,5-triazine-2,4-dithiol) nanofilm (PDB) were prepared by cyclic voltammetry and galvanostatic electropolymerization of 6-N,N-dibutylamino-1,3,5-triazine-2,4-dithiol monosodium (DBN) on copper alloy surface. The polymeric nanofilms were characterized by means of FT-IR spectra, contact angle, potentiodynamic polarization and cyclic voltammetry test. FT-IR spectra showed that PDB film was fabricated on copper alloy surface by CV and G electropolymerization. The results of contact angle and cyclic voltammetry test indicated that PDB film prepared by galvanostatic was more hydrophobic and had higher compact extent. The potentiodynamic polarization also suggested that the PDB film prepared by galvanostatic had higher protection efficiency.

Keywords: Polymeric Nanofilm; Copper Alloy; Cyclic Voltammetry; Galvanostatic; Compactness

1. INTRODUCTION

Copper and its alloy have been widely used for production of wires, sheets and tubes, due to its excellent thermal conductivity and good mechanical workability. However, their expanding application has been seriously limited because of susceptibility to corrosion in aggressive media. Therefore, the use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. Lots of researches have been carried out to protect copper from corrosion, so until now numerous possible inhibitors have been investigated. In recent years, organic compounds and their derivatives have been mostly used as inhibitors, such as azoles [1-3], amines [4-7], amino acids [8-10] and many others. Since the publication of Mori K's researches on preparation of polymeric nanofilm on iron plate by electrochemical methods [11], adsorption and polymerization of triazinedithiol (TDT) film on different metal surface have attracted many researchers [12-16]. In the previous study, TDT polymeric nanofilm had been successfully obtained on different metal by means of electropolymerization of the TDTs [15, 17-19]. There were direct joining of metals to rubbers, inhibiting metallic corrosion and preparation of high dielectric film [20-22]. However, the comparison of the electropolymerization methods has not been reported so far. It is necessary to study the properties of polymeric nanofilm prepared by different electropolymerization method on metal surface to determine the optimal electropolymerization method.

In this paper, we demonstrate the fabrication of PDB nanofilms by cyclic voltammetry and galvanostatic electropolymerization methods on copper alloy surface. The properties of PDB nanofilm were characterized by contact angle, polarization test and cyclic voltammetry test.

2. EXPERIMENTAL SECTION

2.1. Materials

Test specimens (50 × 30 × 0.1mm) of copper alloy (Cu: 88.0 ~ 91.0%; Zn: 9 ~ 12%) were prepared by cutting a large plate into pieces. All test plates were polished with a series of polishing agent, followed by ultrasonic degreasing in acetone for 15min and dried in nitrogen air. 6-N,N-dibutylamino-1,3,5-triazine-2,4-dithiol monosodium (DBN) was synthesized by the reaction of 1,3,5-triazine-2,4,6-trichloride with dibutyl amine and NaSH, according to the method described in the previous paper [18]. All of the chemicals were employed as analytical reagent (AR) without any further treatment. Distilled water was used as solvent, and Na_2CO_3 aqueous solution was used as the supporting electrolyte for electropolymerization. The concentrations of DBN and Na_2CO_3 were kept constant at 3mM and 0.15M, respectively.

2.2. Electropolymerization of DBN on copper alloy suface

The electropolymerization of DBN was performed using an electrochemical workstation (CHI 660C). The electrolytic cell was equipped with a working electrode (copper plate, WE), two counter electrodes (stainless steel plates, CE) and a reference electrode (saturated calomel electrode, SCE). All potentials given were referenced to the SCE. Cyclic voltammetry electropolymerization (CV) was conducted from -0.1~1.1V at 20mV/s in 0.1M Na_2CO_3 aqueous solution with DBN for three circles. Galvanostatic electropolymerization (G) was conducted at current density of 0.02mA/cm^2 in 0.1M Na_2CO_3 aqueous solution with DBN (3mM) without stirring for 6min. After the electropolymerization, the working electrode was removed from the electrolytic cell and immediately rinsed by distilled water and ethanol, then dried in air.

2.3. Characterization

FT-IR was carried out by attenuated total reflection spectroscopy (Bruker Tensor 37). The contact angle was measured by optical contact angle measuring instrument (SL100) at room temperature with 2μL distilled water. The anticorrosion property was evaluated by potentiodynamic polarization test in 0.5M NaCl solution with Pt counter electrode at room temperature. The scan rate was 1mV/s and the exposed area was 1cm^2. The compactness test of CV and G electropolymerized films were studied by cyclic voltammetry from -1.0~0.4V at 20mV/s in 0.1M NaOH solution with two stainless steel plates as counter electrodes.

3. RESULTS AND DISSUSION

3.1. FT-IR spectra analysis of PDB film

FT-IR spectra of PDB nanofilms on copper surface are shown in Figure 1. It was noted that the presence of triazine ring was confirmed by the absorption peaks at 1567 cm^{-1}, 1538 cm^{-1} and 1467 cm^{-1} due to >C=N– bonds. Dibutyl amino groups were confirmed by the absorption peaks at 2959cm^{-1}and 2918cm^{-1} due to C–H asymmetric stretching vibrations of $–CH_2$ and $–CH_3$ and the absorption peak at 2853cm^{-1} due to C–H symmetric stretching vibrations of $–CH_2$ and $–CH_3$, as well as the absorption peaks at 1476cm^{-1} due to bending vibration and 723cm^{-1} due to rocking vibration of $–CH_2$. The above results indicated that PDB nanofilms were formed on copper alloy surface by electropolymerization of DBN.

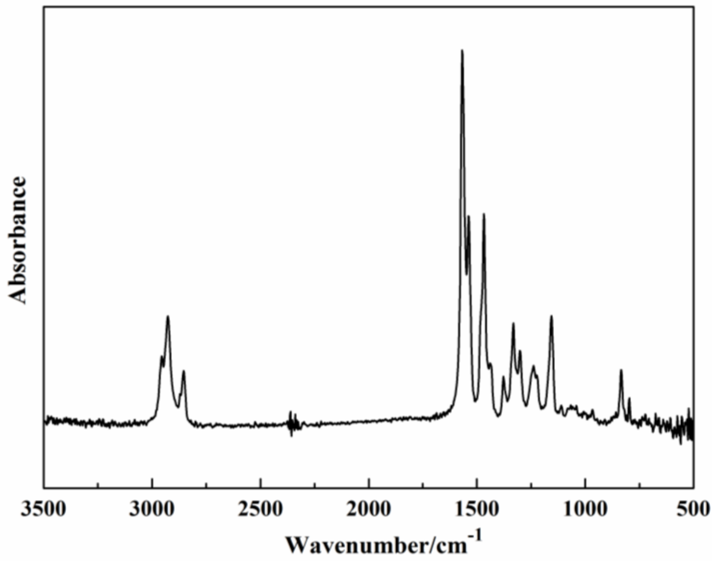

Figure 1. FT-IR spectra of PDB film on copper alloy surface

3.2. Contact angle

Figure 2 shows the contact angles of blank, PDB nanofilm covered copper alloy surface by CV and G methods. The contact angle of the blank copper alloy surface is 78.99°, suggesting that the substrate has the weak hydrophobicity due to the natural copper oxide film. As for the PDB film covered surface by CV method, the contact angle increases to 94.24°. However, as for the PDB nanofilm covered surface by G method, the contact angle is up to 103.33°. These results indicate that DBN monomers are electropolymerized on copper alloy surface to form the PDB nanofilm. The hydrophobicity of the surface was improved after electropolymerization due to the triazine ring and dibutyl amino groups in the PDB film, and the PDB covered surface by G method had better hydrophobicity. Humid environment is one reason of copper alloy corrosion, and the hydrophobic surface of substrate is benefit for the protection of copper alloy. Therefore, the anticorrosion property of PDB nanofilm covered copper alloy surface will be enhanced as the hydrophobicity has been improved.

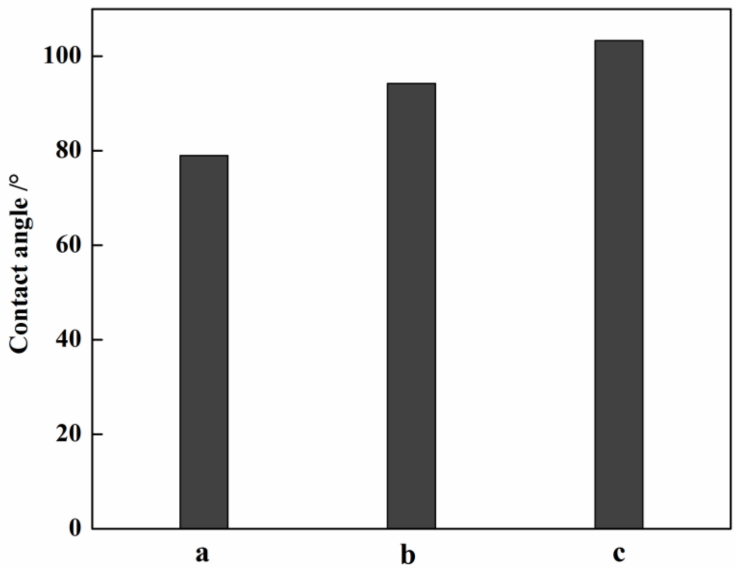

Figure 2. Contact angle of copper alloy surface

(a) blank surface, (b) PDB film covered surface by CV electropolymerization,
(c) PDB film covered surface by G electropolymerization

3.3. Compactness test by cyclic voltammetry

The cyclic voltammetry curves of the blank and PDB nanofilm covered copper alloy surface by CV and G methods from -1.0~0.4V at 20mV/s in 0.1M NaOH solution are shown in Figure 4. The two obvious activated anodic peaks A and B could be attributed to continuous formation of Cu_2O and CuO as a result of electrooxidation of the basal copper alloy. And it is clear that the copper oxidized species are reduced at more negative potentials according to the cathodic peaks A1 and B1. Moreover, it is shown that the reduction charges are more than the oxidation charges especially for peak A1, which is due to the fact that this cathodic peaks are complementary to the anodic peak A and B/C, respectively. It is probable that copper by virtue of its reducing properties interferes with the formation of copper oxide films, indicating simultaneous dissolution of copper under the critical potential. It was proposed that the chemically formed CuO reduced to copper through the copper cathodic peaks and this is contributed in an increase in their reduction charges [23, 24].

It is noted that the surface covered with or without PDB film has no significant influence on the general shape of the voltammograms. Compared with the blank surface, the reaction currents largely reduce for the PDB covered surfaces and their peak potentials shift to more positive direction. The current of the PDB covered surface by G method was the lowest, suggesting the better performance in the protection of the copper alloy from oxidation and corrosion. Therefore, the film prepared by G method is more compact than that by CV method.

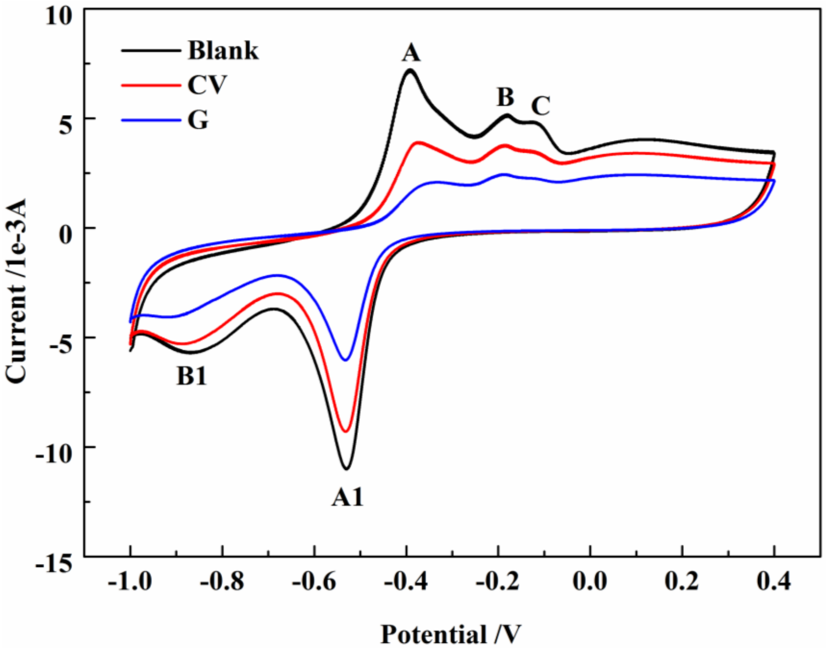

Figure 3. Cyclic voltammetry curves of the blank and PDB nanofilm covered surface by CV and G methods in 0.1M NaOH solution

3.4. Polarization test

Figure 3 displays the potentiodynamic polarization curves of blank and PDB nanofilm covered copper alloy surface by CV and G methods in 0.5M NaCl solution. It can be seen that the corrosion potentials (E_{corr}) of blank, PDB film covered surfaces by CV and G are -0.184V, -0.176V and -0.166V, respectively. The corrosion current density (I_{corr}) decreases from 5.206×10^{-3}A/cm^2 for blank copper alloy to 5.288×10^{-4}A/cm^2 for PDB covered surface by CV method. As for PDB covered surface by G method, the I_{corr} reduces to 2.549×10^{-4}A/cm^2, exhibiting favorable inhibitive performance. The protection efficiency (PE) of PDB film covered surface by CV and G methods can be calculated by the equation below [14]:

$$\text{PE}(\%) = 100 \times [1- (i / i_0)]$$

where i and i_0 are the I_{corr} of the treated and the blank copper alloy, respectively. The protection efficiency is 89.8% for PDB film covered surface by CV method, while 95.1% for PDB film covered surface by G method. The right shift of E_{corr} and decrease of I_{corr} indicated that the corrosion of copper alloy was considerably suppressed by the PDB film, and the PDB film covered surface by G method was denser than that by CV method. It can be concluded that the PDB covered copper alloy demonstrates excellent anticorrosion property.

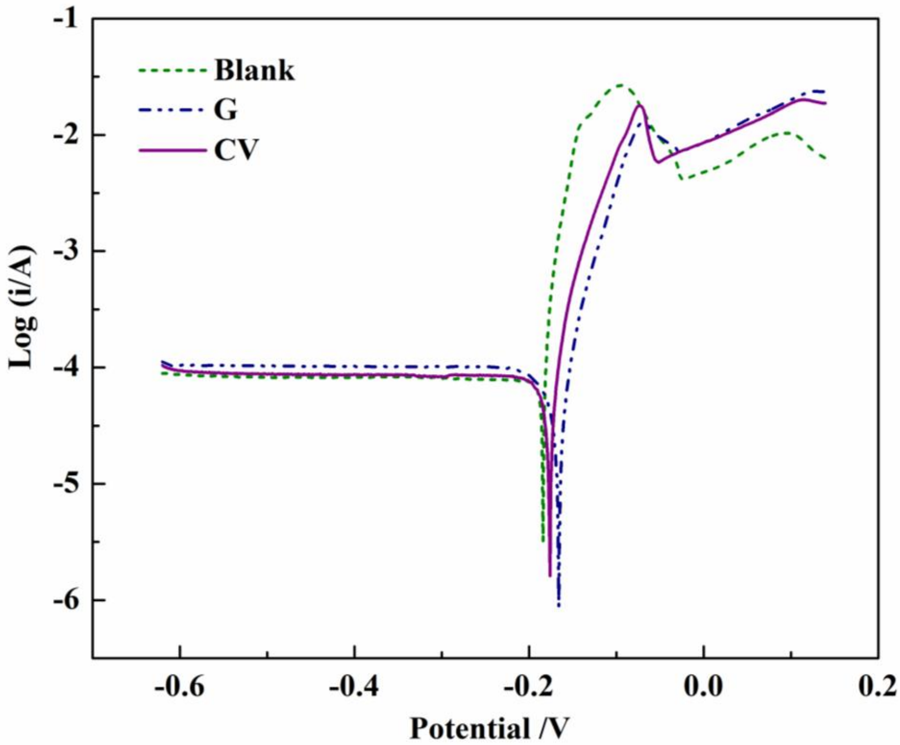

Figure 4. Polarization curves of the blank and PDB nanofilm covered copper alloy surface by CV and G methods measured in 0.5M NaCl solution after 1h exposure

4. CONCLUSIONS

PDB nanofilms were successfully fabricated on copper alloy surface by CV and G electropolymerization methods. The PDB nanofilms proved to be hydrophobic, compact and had excellent protection efficiency. The contact angle, polarization test and compactness test all indicated that the PDB nanofilm by G electropolymerization method is the most compact, also has the best hydrophobicity and protection efficiency of 95.1%.

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