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A New Approach for Preparing Effective Inhibition Film on Copper Based on Self-assembled Process

Chun Tao WANG[1], Shen Hao CHEN[1,2]*

[1]Department of Chemistry, Shandong University, Jinan 250100
[2]State Key laboratory for Corrosion and Protection, Shenyang 110015

Abstract: A new method for preparing effective inhibition film on copper has been developed. Phenylthiourea (PT) was first absorbed to copper surface to form a monolayer. 1-Dodecanethiol (DT) was then assembled on the surface for modification. Finally, AC voltage was loaded on copper covered the mixed film to improve it further. After these processes, an effective inhibition film was gained because of its high charge transfer resistance and low corrosion current density shown in electrochemical impedance spectra and polarization. The inhibition efficiency was more than 97%.

Keywords: Self-assembly, phenylthiourea (PT), 1-dodecanethiol (DT), AC voltage.

Copper is an important metal in industrial application, in particular, microelectronics. But copper can be oxidized easily in air, and chloride ions in aqueous solution, such as seawater, which is known to significantly promote its corrosion. The protection of copper corrosion has attracted much attention. Self-assembled monolayers (SAMs) can provide a convenient method for the protection of metal corrosion, since the process of self-assembly is simple, and the chemical composition can be designed at molecular level. The SAMs of alkanethiol had been used for candidates of copper corrosion protection[1-4]. For example, the protection efficiencies of 1-dodecanethiol and 1-octadecanethiol monolayer were 65.3% and 80.3%, respectively, after 1 h immersion in 0.5 mol·L^{-1} Na_2SO_4 solution[3]. Investigations showed that the inhibition efficiency was not sufficiently high because of the existence of collapsed sites and pinhole defects. It is therefore essential to explore the collapsed-site-free self-assembled films and to improve their protecting abilities. PT is nitrogen and sulfur-containing organic heterocyclic compound, the delocalized π- electrons in its molecule can enter easily to unfilled orbital of the metal to form a monolayer. DT has a long hydrocarbon chain that is hydrophobe. Coupling the advantage of both of them, we prepared a mixed self-assembled film step by step. For first report, we treated it by AC

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*E-mail: shchen@sdu.edu.cn

voltage to decrease the defects in the self-assembled film, and provide a more effective inhibition film.

Experimental

The electrode was made from 99.9% pure copper rod of 5.8 mm diameter and was polished with $400^{\#}$ and $2000^{\#}$ emery papers *prior* to each experiment. The test was performed in a three-electrode cell. The reference electrode was a saturated calomel electrode (SCE) and the counter electrodes were platinum plates. All potentials were referred to the SCE.

The electrode was polished, washed with tridistilled water, and then etched in a 6 mol•L^{-1} HNO_3 solution for 30 s, rinsed with tridistilled water and absolute ethanol as soon as possible, and immersed in a 0.05 mol·L^{-1} phenylthiourea solution immediately for 30 min. After formation of the film, the electrode was immersed into a 1-dodecanethiol solution with 30 min for modification. Next, at potentials negative to the corrosion potential of the copper, the sinusoidal voltage of 5 mV amplitude was loaded on the copper electrode covered with the mixed film in a 0.5 mol·L^{-1} NaCl solution.

EIS measurements, fitting, potentiostatic polarization measurements were performed by an IM6 impedance and electrochemical measurement system (ZAHNER, Germany). The sinusoidal potential perturbation was 5 mV in amplitude and frequencies ranged from 60 kHz to 0.02 Hz. The EIS of self-assembled films covered copper electrode were obtained in 0.5 mol·L^{-1} NaCl aqueous solution after 30 min immersion at 20±2°C. All the impedance measurements were carried out at corresponding corrosion potential. The polarization curves were recorded from –0.4 to 0.1 V vs.SCE at a scan rate of 1mV/s.

Results and discussion

Electrochemical impedance spectroscopy (EIS)

Figure 1 shows the EIS of copper without self-assembled film. The high-frequency small semicircle is attributed to the time constant of charge transfer resistance (R_t) and doule layer capacitance (C). The straight line is related to diffusion process of soluble copper species ($CuCl_2^-$) from electrode surface to bulk solution[5-6].

Figure 2 represents the EIS of copper electrode covered with PT monolayer, PT modified with DT, and the mixed film loaded AC voltage. The size of impedance plot obtained by pure PT covered copper electrode was larger than that of the bare copper electrode, indicating the self-assembled monolayer were formed on the copper surface. Moreover, modifying the PT monolayer by the subsequent process of DT self-assembly caused the charge transfer resistance (diameter of semicircle) increased significantly. After fitting, the charge transfer resistance (Rt) of bare copper was 0.549 kΩ·cm^2. The value was 6.77 kΩ·cm^2 for PT covered copper after immersing the copper in PT solution for 30 min.

When the PT covered copper electrode was immersed in DT solution for 30 min, the charge transfer resistance was up to 12.14 kΩ·cm^2, showing that the density of self-assembled film was improved after modifying the pure PT film with DT.

The coverage on substrate surface is a key factor for the self-assembled films, and the charge transfer resistance is associated with it. Coverage (θ) could be obtained by [7]

$$(1-\theta) = Rt^\circ / Rt$$

Where Rt° and Rt are the charge transfer resistance of bare copper electrode and film covered electrode at the same condition. The coverage for pure PT was 91.9% and 95.6% for mixed film. It was considered that a little collapse and pinholes existed still in the mixed film. It is difficult to solve this problem by self-assembly process itself.

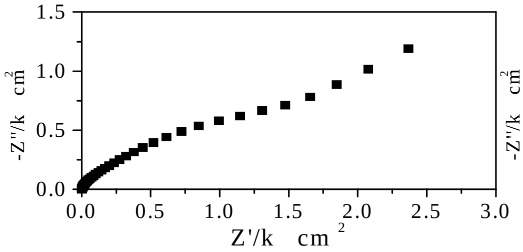


Figure 1 Nyquist impedance diagram measured in a 0.5 mol·L^{-1} NaCl solution for bare copper electrode

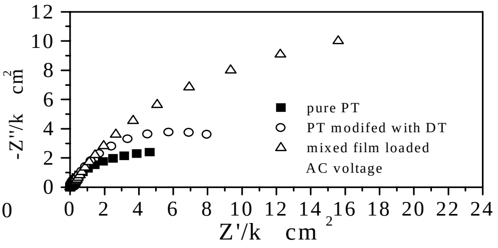


Figure 2 Nyquist impedance diagrams measured in 0.5 mol·L^{-1} NaCl solutions for Cu electrode covered with various films.

AC voltage was expected to reduce the collapse sites and pinholes for improving the quality of the mixed film. At potential negative to the corrosion potential (-0.236 V) of the copper, the sinusoidal voltage of 5 mV amplitude was loaded on the copper electrode covered with the mixed film in a 0.5 mol·L^{-1} NaCl solution. No potential positive than the corrosion potential of the copper was used to avoid desorption of the film associated with anodic dissolution of copper substrate. After treating with the AC voltage, the charge transfer resistance and coverage was measured and calculated as before. The result revealed that charge transfer resistance increased enormously to 31.71 kΩ·cm^2, and the coverage was 98.1%.

Polarization

Polarization curves for copper electrodes bare, PT monolayer covered, DT-modified PT film and AC treated mixed film in an aerated 0.5 mol·L^{-1} NaCl solution are shown in **Figure 3**. Suppression of both cathodic and anodic processes of copper corrosion was observed, after covering with various films. After loading AC voltage on the mixed film, the suppression of current density in the polarization curve was much more.

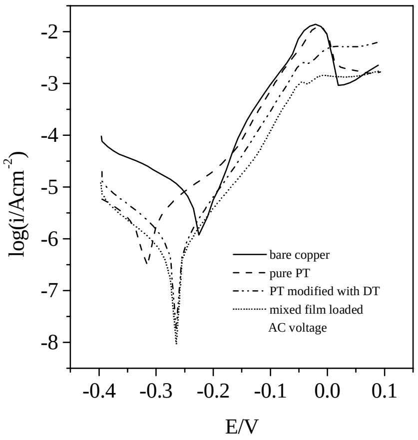
The corrosion current densities of electrode bare and film-covered were obtained by

Tafel extrapolation of polarization curves to the corrosion potential (E_{corr}). The inhibition efficiency (P%) can be calculated using the following formula:

$$P\% = 100\times(1-i/i°)$$

Where i and $i°$ denote the corrosion current densities of copper electrodes covered with and without self-assembled films in 0.5 mol•L^{-1} NaCl solutions. The inhibition efficiency of film covered electrodes, PT and subsequently modified with DT, were 91.2 and 95.1%, respectively. After treating the mixed film with AC voltage, the inhibition efficiency was up to 97.3%. The improving effect maybe associated with the reorientation of the adsorbed molecules as well as the complexation of chlorid negative ion in solution with PT and Cu (I) on the copper surface in the case of applied AC voltage.

Figure 3 Polarization curves obtained in 0.5 mol•L^{-1} NaCl solution for Cu electrodes witl without various films.



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