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In situ click-assembling monolayers on copper surface with enhanced corrosion resistance

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ABSTRACT

The self-assembled monolayer (SAMs) of 2-(1-tosyl-1H-1,2,3-triazol-4-*yl*) propan-2-ol (TTP) was in-situ assembled on copper surface via click chemistry reaction between 2, 2-dimethylethynyl carbinol (MBY) and tosyl azide (TA). The electrochemical results indicate that the click-assembled TTP film can strongly suppress the corrosion reaction of copper in 3 wt.% NaCl and its protection efficiency is 93.6%. Polarization curves show that TTP SAMs is an anodic passivation type inhibitor. The adsorption of TTP molecules on Cu_2O (0 0 1) surface is in the flat orientation of the nearby triazole ring and O atoms.

1. Introduction

Copper and its alloys are widely used in desalination industry due to its good thermic conductivity and mechanical properties [1,2]. But copper is apt to corrosion in seawater and cause tremendous economic losses [3–6]. Self-assembling technique is often used to prepare well-ordered organic films on the metal surface, which can highly promise for the protection of metal [7,8]. Because of the hydrophobic effect and intermolecular forces between inhibitor molecules, different kinds of inhibitor molecular aggregation form during the inhibition process. The formation of molecular aggregation influences the assembly of inhibitor molecular on metal surface and inhibition efficiency. Establishing the controllable assembly method is the core of the corrosion inhibition self-assembly research.

Triazole compounds are effective corrosion inhibitors for copper and its alloys [9,10]. Many publications have reported the inhibition effect of benzotriazole (BTA) alone or its synergistic effect with other compounds [11–16]. The derivatives of BTA as copper inhibitors were also investigated by some researchers [17,18]. The click chemistry reaction, which is featured as utilization of easy and selective carbon-heteroatom ligation reaction for the modular construction, has been applied in lots of aspects [19–21]. Cu (I)-catalyzed 1,2,3-triazole formation reaction between azides and alkynes represents the best paradigm of the click chemistry for its properties of high reaction yield, simple reaction and purification conditions [22,23]. Deng et al. [24,25] reported that triazole inhibitors formed via click chemistry on mild steel inhibition. Despite the inhibition effect of triazole compounds strongly depends on the degree of its polymerization, little has been focused on the in-situ click-assembled triazole SAMs on copper surface.

In this paper, the click chemistry reaction was applied to form the self-assembled films in order to inhibit copper corrosion. The click chemistry reaction equation of TA and MBY on the copper surface is shown in Fig. 1. The protection of the click-assembled films against copper corrosion was evaluated by the electrochemical impedance spectroscopy (EIS) and the potentiodynamic polarization curves. Surface microtopography of copper was detected by the scanning electron microscopy (SEM) and the atomic force microscope (AFM). FTIR was applied to test the result of the click-assembling reaction on copper surface. The relation between molecular structure and inhibitive performance was theoretically investigated by quantum chemical calculation and MD simulations.

2. Experimental

2.1. Materials and chemicals

Pure copper (99.99%) was applied in experiments. TA was supplied by Energy Chemical Company and MBY was supplied by

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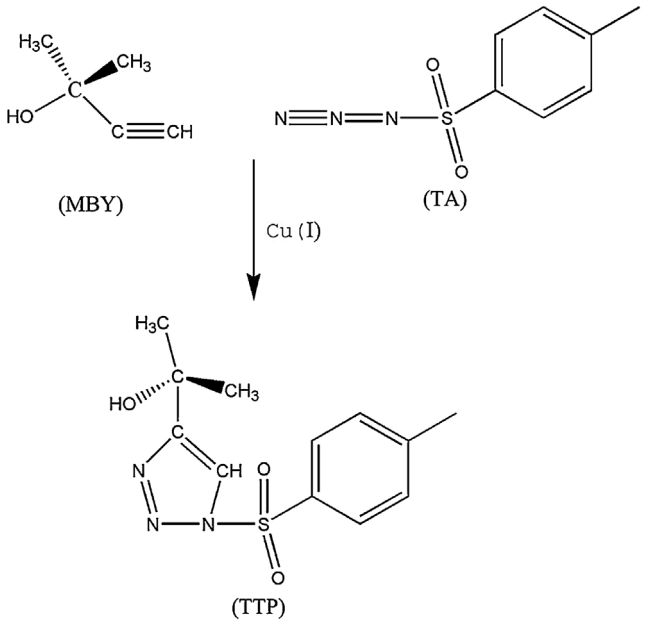

Fig. 1. Click chemistry reaction equation of TA and MBY on copper surface.

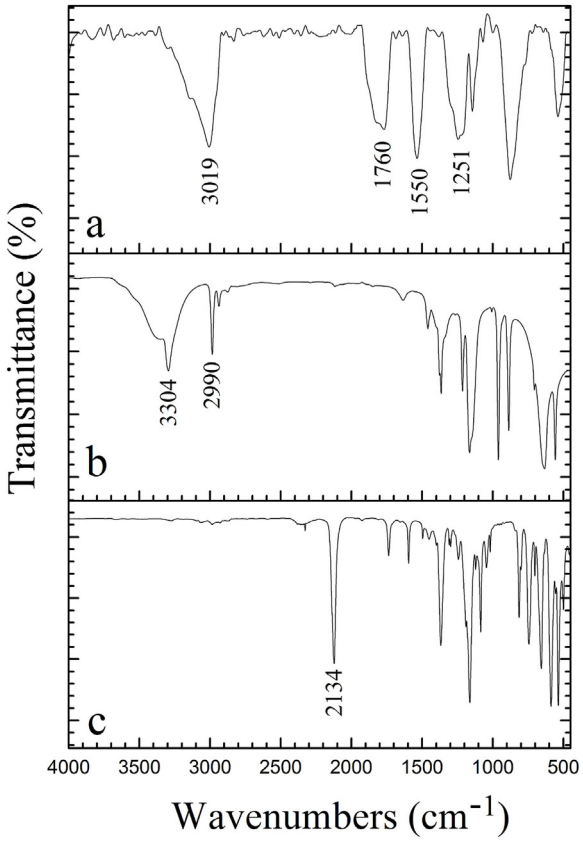

Fig. 2. FTIR spectra of (a) reflection mode of copper with the click-assembled (TA+MBY) SAMs; (b) pure MBY; (c) pure TA.

Aladdin Chemistry Co. Ltd. The aggressive medium was 3 wt.% NaCl solution prepared by AR chemicals and deionized water.

2.2. Click-assembling experiment methods

The copper electrodes were gradually abraded with different grades of emery paper and polished by polishing slurry finally.

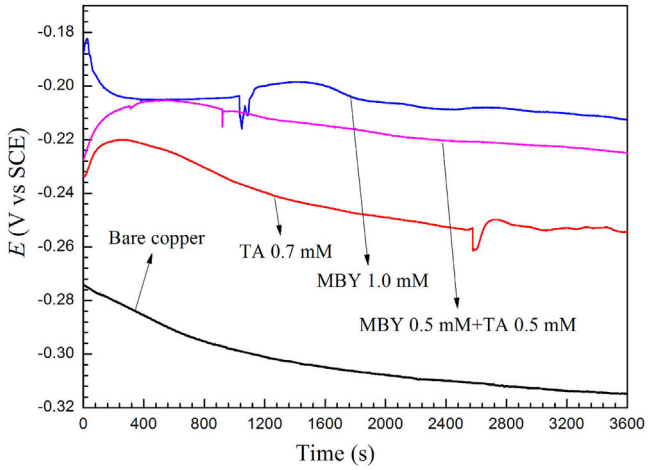

Fig. 3. Variation of OCP vs time for copper electrode in 3 wt.% NaCl (temperature 25 °C).

Then electrodes were degreased with AR grade ethanol and cleaned with deionized water. The assembling solutions were ethanol with different concentrations of TA, MBY, and mixture of TA/MBY, respectively. Then copper electrodes were thoroughly immersed in assembling solutions for 1 h at room temperature. After assembled, the electrodes were rinsed with enough deionized water in order to get rid of the physical adsorption molecules. Then the assembled electrodes were dried with a steam of nitrogen. Finally copper electrodes were immersed in 3 wt.% NaCl solutions for 1 h and its electrochemical performance was tested.

2.3. Electrochemical measurements

Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE, exposure area greatly larger than WE's) and a saturated calomel electrode (SCE, Cl^- concentration 0.357 g/mL) as the reference electrode. A bare copper electrode or a SAMs-covered copper electrode was used as the working electrode (WE). The WE was sealed in an epoxy resin so that the exposure area is 0.5 cm^2. The electrochemical analysis was conducted on Solartron 1287. Electrochemical Interface coupled with a Solartron 1260 Impedance/Gain-Phase Analyzer. During test, the cell was open to the air without stirred or deaerated. EIS was measured at OCP in the frequency range from 0.02 Hz to 100 kHz with a 5 mV AC drive signal. The potential range of potentiodynamic polarization curves was −250 to +250 mV (vs. E_{corr}) at a scan rate of 1 mV/s. All potential values in the paper were referred to SCE. All the experiments were included three-parallel samples. For potentiodynamic polarization analysis, Tafel extrapolation was done by Corroware soft with the data from 150 mV to 100 mV deviating from the open circuit potential. Electrochemical analysis was used Zsimpwin and CorrWare software and the fitted error values are below 10% and chi-square is below 10^{-4}.

2.4. SEM imaging and EDS characterization

Copper specimens were grinded by different grades of emery paper (#800, #1200 and #2000) and rinsed with AR grade ethanol and distilled water. After 24 h dipping in 3 wt.% NaCl solutions without and with SAMs at room temperature, copper samples were rinsed with deionized water, and then allowed to air dry. Scanning electron microscope (SU-1500, Hitachi Company) images under an accelerating voltage of 20 kV were taken to observe the surface microstructure of the samples. The composition of the surface film on specimens was recorded by an energy dispersive spectroscopy.

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