



Study of the protection performance of self-assembled monolayers on copper with the scanning electrochemical microscope



Caixia Li, Liang Li, Chao Wang*, Yongyan Zhu, Weichao Zhang

Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, PR China
School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, PR China

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ABSTRACT

The protection performance of self-assembled monolayers (SAMs) formed by 2-(Pyridin-2-yliminomethyl)-phenol (HL) on the surface of copper has been studied *in situ* with the scanning electrochemical microscope (SECM). The pitting dynamic processes were observed in sodium chloride solution without the presence of SAMs, but they tended to be inhibited by SAMs if the assembly time was long enough. During the scanning process, the self-assembled method decreases the interaction between the HL molecules and the SECM tip greatly.

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1. Introduction

A great deal of attention has been paid to the corrosion of copper for its high electrical and thermal conductivities. Inhibition methods are important means for the protection of metals against corrosion, especially through the organic inhibitors, such as, azoles [1–8], quinolines [9], and Schiff bases [10].

Many approaches have been used to characterize the corrosion behavior of copper. The potentiodynamic polarization [11], the electrochemical impedance spectroscopy (EIS) [12] and the scanning electron microscope (SEM) [8] are the frequently used methods. The scanning electrochemical microscope (SECM) has been successfully used to investigate the localized dissolution behavior of metallic materials, such as stainless steel [13–19] and Al alloys [20]. It has also been used to study organic inhibitors for copper added to the solution directly before the test [21–24]. However, the current obtained at the SECM tip may be affected because the organic inhibitors can not only interact with the copper surface, but may also exert chemical activities on the SECM tip [21,23]. As such, the current measured at the tip may not have arisen solely from the variations in the activity of the investigated surface, but from the surface blockage of the tip as well. So the tip current is not a precise indicator of the corrosion of the substrate.

The self-assembled monolayers (SAMs) formed on the surface of the metal substrate are promising in the protection of metal

substrate from corrosion [25–28]. Since the changes of the tip current can reveal various degrees of copper corrosion and degradation of the films, SECM can be used to characterize the inhibitive behavior of SAMs [21]. The influence brought about by the interaction between the inhibitors and the tip can be ignored on the condition that the organic substance interacts solely with the surface of the copper electrode.

In the present work, 2-(Pyridin-2-yliminomethyl)-phenol (HL) was assembled on copper surface before the protection performance of the SAMs in 0.1 M NaCl solution was analyzed with the application of SECM coupled with the electrochemical methods. The assembly method decreased the interaction between the HL molecules and the tip of SECM. The effect of the proportion of Cu(I) on the quality of SAMs was studied by potentiodynamic polarization and theoretical calculation.

2. Experimental

2.1. Experiment measurements

The SECM measurements were carried out by CHI 910B electrochemical station at room temperature. A four-electrode system was used. A stationary copper sheet of 1 mm thickness and 99.99% purity was used as the substrate. It was cut into square specimens of 0.36 cm², soldered with Cu-wire and masked with epoxy resin. The SECM tip was a 25 μm platinum microelectrode. A saturated calomel electrode (SCE) was used as the reference electrode, with a Luggin capillary probe located at 2 mm from the substrate, and the counter electrode was the platinum sheet. All

* Corresponding author at: School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, PR China. Tel.: +86 516 83403003; fax: +86 516 83403320.

E-mail address: wangc@jsnu.edu.cn (C. Wang).

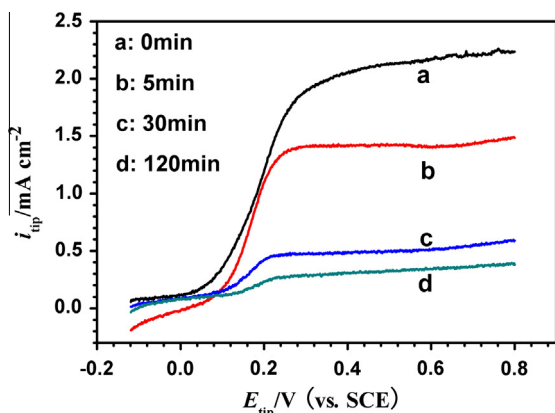


Fig. 1. The $i_{\text{tip}}-E_{\text{tip}}$ curves of the SECM tip towards the Cu electrodes at -0.1 V (vs. SCE) in 0.1 M NaCl + 1 mM FcMeOH solution at the scan rate of 10 mV s^{-1} with different assembly times.

potential values reported here are referred to SCE. The distance between the ultramicroelectrode tip and the substrate was set at 20 μm with the help of a CCD (Charge Coupled Device). The substrates, facing upwards, were immersed in 0.1 M NaCl solution containing 1 mM ferrocene-methanol (FcMeOH). The tip potential was set at 0.4 V (vs. SCE), which is based on the oxidation of ferrocene-methanol to ferrocinium ion. All the substrates are held at the potential of -0.1 V (vs. SCE), 0.03 V higher than the open circuit potential, optimal for the observation of the pit formation on

the surface of the copper electrode [29–31]. The surface morphology of the electrode was observed by SEM (HITACHI S-3400N) after 180 min polarization at -0.1 V (vs. SCE).

All the potentiodynamic polarization and the EIS experiments were accomplished by Solartron 1287/1260 (Ametek Solartron Analytical, Hampshire, UK). Impedance measurements were carried out at the open-circuit potential (E_{ocp}) in the frequency range from 100 kHz to 10 mHz at an AC amplitude of 10 mV (peak to zero, or 20 mV peak to peak). The potential range of the polarization curves was ± 0.5 V (vs. E_{ocp}) with a sweep rate of 1 mV s^{-1} . Before each experiment of the potentiodynamic polarization and EIS, the copper electrode was immersed in 0.1 M NaCl solution for 10 min to attain a quasi-steady state. All electrolytes were prepared from reagents of the analytical grade and distilled water.

2.2. Assembly method

Before each experiment, the sample was first abraded with emery paper (400 , 600 and 1200 grit) followed by fine polishing with alumina paste (0.05 μm particle size) to achieve a mirror finish, then washed with alcohol and distilled water in an ultrasonic bath. The samples with HL SAMs were prepared [26,28] as follows: Firstly, the polished copper specimen was etched in 7 M HNO_3 solution for 15 s to provide a fresh surface. Then, it was rinsed with distilled water and absolute ethanol quickly and immersed in 1 mM HL ethanol solution immediately for different durations (5 min, 30 min, 120 min). Finally, the sample was dried with a nitrogen stream and stored in a desiccator until characterization.

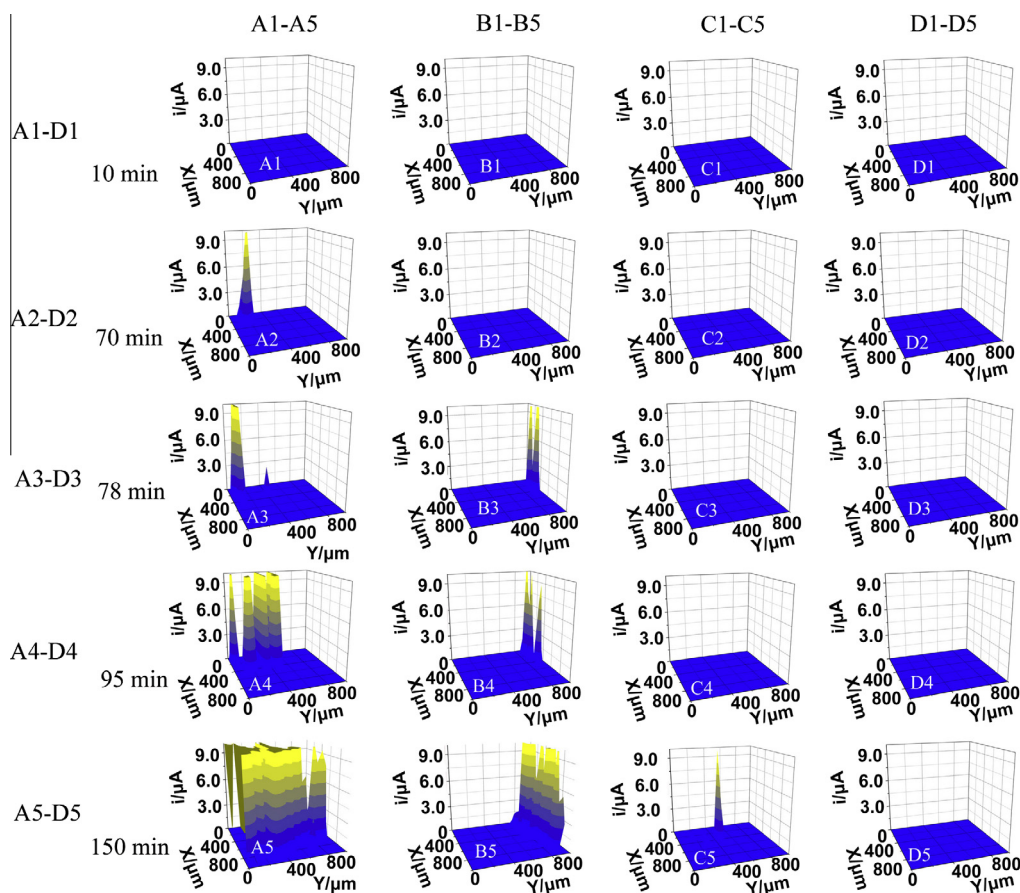


Fig. 2. The SECM images of the Cu electrodes at -0.1 V (vs. SCE) in 0.1 M NaCl + 1 mM FcMeOH solution. The tip potential being controlled at 0.4 V (vs. SCE) and the scanning time for each image (1000 $\mu\text{m} \times 1000$ μm) 2.5 min. The assembly times for the samples: 0 min for A1–A5, 5 min for B1–B5, 30 min for C1–C5, 120 min for D1–D5; the SECM recording times: 10 min for A1–D1, 70 min for A2–D2, 78 min for A3–D3, 95 min for A4–D4, 150 min for A5–D5.

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