Study of the inhibitive effect of mixed self-assembled monolayers on copper with SECM

Caixia Li\textsuperscript{a,b}, Liang Li\textsuperscript{a,b}, Chao Wang\textsuperscript{a,b,}\textsuperscript{*}

\textsuperscript{a} Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P.R.China
\textsuperscript{b} School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, P.R.China

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Mixed self-assembled monolayers (SAM\textsubscript{mix}) were formed by 2-(Pyridin-2-yliminomethyl)-phenol (HL) and 1-dodecanethiol (DT) molecules on copper surface. The inhibitive ability of SAM\textsubscript{mix} in sodium chloride solution was characterized in situ by the scanning electrochemical microscope (SECM). The results show that the compactness and the stability of SAM\textsubscript{mix}, formed by the two organic materials in an appropriate sequence, are improved and the inhibition efficiency (η\% ) increases markedly. They also verify that SAM\textsubscript{mix} are formed due to the existence of collapsed sites and pinhole defects on SAMs of single materials on the surface of copper. The re-arrangement and the competitive adsorption of HL and DT molecules may have impact on the quality of SAM\textsubscript{mix}. Possible structures of SAM\textsubscript{mix} are suggested based on the experimental results.

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1. Introduction

The self-assembled monolayer (SAM), as one of the inhibition methods for copper corrosion, has been extensively investigated over the past few decades owing to its relative density and stable structure [1–4]. The compactness [4], the stability [5] and the thickness [6] have great impact on the inhibitive ability of the films. However, due to the existence of collapsed sites and pinhole defects in the monolayer [7], the compactness of SAM on the surface of copper needs to be improved.


Growing interest has been devoted to improving the inhibition efficiency with defect-free SAM\textsubscript{mix} [10,11]. Chen \textit{et al.} [10] prepared SAM\textsubscript{mix} with alkanethiol and phenylthiourea on copper surface, and the EIS and polarization results showed that the resulting surface presented satisfactory resistance in aggressive medium. However, the classical electrochemistry characterization can only provide global information about the inhibitive behavior of SAM\textsubscript{mix}. New experimental methods are needed to observe these processes at the electrode/electrolyte interface \textit{in situ} during the anodic dissolution of copper with SAM\textsubscript{mix}.

SECM has been successfully used to observe organic inhibitors for copper added directly to the solution before the test [5,12–14]. In the present work, it is employed to study the local compactness and stability of SAM\textsubscript{mix} formed by 2-(Pyridin-2-yliminomethyl)-phenol (HL) and 1-dodecanethiol (DT) molecules on copper. The inhibitive processes of SAM\textsubscript{mix} were observed \textit{in situ}. Its inhibition efficiency (η\% ) was calculated according to the impedance test and the potentiodynamic polarization respectively. The elemental composition of SAM\textsubscript{mix} was obtained based on XPS results. At the same time, the electrochemical behavior of pure SAMs of HL or DT was also recorded for comparison.

2. Experimental

2.1. Experiment measurements

A stationary copper sheet (1 mm thickness and 99.99\% purity), to be used as the substrate, was cut into square specimens of 0.36 cm² soldered with Cu-wire and masked with epoxy resin. A saturated calomel electrode (SCE) was used as the reference electrode, along with a platinum sheet as the counter electrode. The reference electrode was inserted in a Luggin capillary probe located at 2 mm from the substrate. All potentials in this work are referred to the SCE scale.

The classic electrochemical experiments were accomplished by Solartron 1287/1260 (Ametek Solartron Analytical, Hampshire,
UK). Impedance spectra, collected at the open circuit potential ($E_{ocp}$), were obtained in the frequency range from 100 kHz to 10 mHz and a 10 mV amplitude of the excitation signal. The potential of the polarization was scanned positively from -0.15 to +0.15 V (vs. $E_{ocp}$) with a sweep rate of 1.0 mV s$^{-1}$.

The SECM measurements were carried out by the CHI 910B electrochemical station. A four-electrode system was used. The SECM tip was a 25 μm platinum microelectrode. The distance between the ultra-microelectrode tip and the substrate was set at 20 μm with the help of a CCD (Charge Coupled Device). The tip potential was set at 0.40 V, which was based on the oxidation of ferrocene-methanol to ferrocenium ion. The substrates, facing upwards, were immersed in 0.10 mol dm$^{-3}$ NaCl solution containing 1.0 mmol dm$^{-3}$ ferrocene-methanol. All the substrates were held at the potential of -0.08 V (0.05 V higher than the open circuit potential), optimal for the observation of the pit formation on the surface of the copper electrode [15–17].

The sample surface was analyzed using XPS (ESCALAB 250, Thermo-VG Scientific) with the spot size of 900 μm, the energy step size of 0.050 eV and Al Ka radiation. The surface morphology of the electrode was observed by SEM (HITACHI S-3400N) before and after the electrochemical test respectively.

Before each experiment, the copper electrode was immersed in 0.10 mol dm$^{-3}$ NaCl solution for 10 minutes, and the experiments were conducted at room temperature. All electrolytes were prepared from reagents of the analytical grade and doubly distilled water.

2.2. Preparation of SAMs and SAM$_{mix}$

The sample was polished with emery paper (400, 600 and 1200 grit) followed by fine polishing with alumina paste (0.050 mm particle size) to achieve a mirror-like brightness before being washed with water and etched in 7 mol dm$^{-3}$ HNO$_3$ solution for 20 s. After that, it was rinsed with doubly distilled water and absolute ethanol as quickly as possible, and then bathed immediately in:

1. absolute ethanol solution containing 1.0 mmol dm$^{-3}$ HL for 60 min to obtain SAM$_{HL}$;
2. absolute ethanol solution containing 1.0 mmol dm$^{-3}$ DT for 60 min to obtain SAM$_{DT}$;
3. absolute ethanol solution containing 1.0 mmol dm$^{-3}$ DT for 30 min, and then absolute ethanol solution containing 1.0 mmol dm$^{-3}$ HL for 30 min to form SAM$_{DT/HL}$;
4. absolute ethanol solution containing 1.0 mmol dm$^{-3}$ HL for 30 min, and then absolute ethanol solution containing 1.0 mmol dm$^{-3}$ DT for 30 min (SAM$_{HL/DT}$) [11].

Each of the assembly solution was aerated by a stream of N$_2$ for 10 min before and through the self-assembly process. The organic inhibitor HL was synthesized and its composition and purity was checked. DT was purchased from Alfa Aesar. The structures of HL and DT molecules are shown in Fig. 1.

3. Results and discussion

3.1. Electrochemical measurements

3.1.1. EIS measurements

As shown in Fig. 2, the Nyquist plot for bare copper displays an obvious capacitive loop at high frequency and Warburg impedance at low frequency. The former is attributed to a time constant related to both the charge transfer resistance and the double-layer capacitance; the latter indicates the diffusion of the soluble corrosion products (CuCl$_2^-$) from the surface of the electrode to the bulk solution and O$_2$ from the bulk solution to the surface of the electrode [18].

With the films on their surfaces, the plots of the specimens exhibit obvious difference both in shape and size from that of the bare one. The diameter of the capacitive loop and the Warburg coefficient ($\sigma_w$) increase in various degrees under different assembly conditions, indicating different degrees of coverage on the samples. The inhibition efficiency ($\eta$) can be calculated by employing Eq. (1) [19,20].

$$\eta = \frac{R_p - R_p^0}{R_p^0} \times 100 \quad (1)$$

where $R_p$ and $R_p^0$ are the polarization resistance of Cu with and without SAMs respectively, whose values are approximately equal to the radius of the semicircle. The $\eta$ is listed in Table 1. Due to the poor compactness of SAM$_{HL}$, the $\eta$ is only 60%, which arises from the steric hindrance of the aromatic nucleus in HL molecules. Thanks to the S-H head group of DT, which is readily linked to a copper atom, the hydrophobic long hydrocarbon chain can provide a thick film on the surface of copper [10]. Thus the $\eta$ for SAM$_{DT}$ reaches 89%, obviously higher than that of HL.

Although the thickness of the film may also influence $\eta$ [6], it is difficult to measure on the surface of polycrystalline copper, which is different from the case of aluminium [21,22]. However, the films formed on the surface of the polycrystalline copper after the immersion in organic solutions can be defined as multilayers [23,24]. The first is the self-assembled monolayer (SAM) formed by the stable chemical adsorption, while others are formed by the
physical adsorption due to the Van der Waals force. The latter ones are metastable, thus the inhibitive behavior mainly depends on the first layer, namely SAM. In other words, the self-assembled monolayer (SAM) in our work mainly refers to the first layer formed by the chemical adsorption [9,25]. So, the discussions about the difference of $\eta$% in this paper will be mainly based on the compactness and the stability of the covering films.

$\text{SAM}_{\text{mix}}$ were prepared by making use of the special structures of HL and DT molecules. When SAM$_{\text{HL}}$ were modified by DT molecules, the $\eta$% for SAM$_{\text{HL/DT}}$ is up to the maximum value of 95%, indicating a marked improvement in the density of $\text{SAM}_{\text{mix}}$, in which DT molecules fill the defects of SAM$_{\text{HL}}$. For comparison, the mixed self-assembled monolayers of SAM$_{\text{DT/HL}}$ were prepared. The $\eta$% for SAM$_{\text{DT/HL}}$ is 87%, which is much lower than that of SAM$_{\text{HL/DT}}$. Due to the relative density and the long hydrocarbon chain of SAM$_{\text{DT}}$ and the redundant structure of the HL molecules, it is difficult for HL to modify the defects on SAM$_{\text{DT}}$, resulting in similar $\eta$% for SAM$_{\text{DT/HL}}$ as SAM$_{\text{DT}}$. Furthermore, the Warburg impedance disappears after the electrodes were coated with SAM$_{\text{DT}}$ and SAM$_{\text{max}}$, indicating the formation of the compact “insulating” coatings, which inhibit the production of such corrosion products as CuCl$_2$.

### 3.1.2. Potentiodynamic polarization measurements

The polarization curves for Cu in 0.10 mol dm$^{-3}$ NaCl solution were also measured with and without SAMs (Fig. 3). The oxide film on the bare copper is reduced, or the reduction of oxygen takes place [10,26] during the cathodic process, while the copper ions are formed first and then consumed subsequently to produce the cuprous chloride as a slightly soluble salt layer and/or cuprous chloride complexes [27] during the anodic process.

In the presence of SAM$_{\text{HL}}$, the anodic current decreases (Fig. 3b), compared with that of the bare copper (Fig. 3a). However, both the cathodic and the anodic currents decrease significantly with the presence of SAM$_{\text{DT}}$ (Fig. 3d), which indicates that SAM$_{\text{HL}}$ inhibits the anodic process only while SAM$_{\text{DT}}$ inhibits both the anodic and the cathodic processes. The $\eta$% are calculated as Eq. (2) [28,29]:

$$\eta = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100$$

where $i_{\text{corr}}^0$ and $i_{\text{corr}}$ are the corrosion currents of the electrodes without and with SAMs. The informative parameters obtained from the polarization curves (Fig. 3) are summarized in Table 2. The $\eta$% for SAM$_{\text{HL}}$ is 41% and for SAM$_{\text{DT/HL}}$ is 76% while it is 89% for SAM$_{\text{DT}}$ and 96% for SAM$_{\text{HL/DT}}$. indicating that SAM$_{\text{DT}}$ and SAM$_{\text{HL/DT}}$ are more compact and stable than SAM$_{\text{HL}}$ and SAM$_{\text{DT/HL}}$.

The difference in the inhibition efficiency between SAM$_{\text{HL}}$ and SAM$_{\text{DT/HL}}$ obtained by polarization plots and EIS measurements, can be explained by the effect of cathodic desorption [30,31] and anodic oxidation [31] during the polarization. So, the results support the conclusion obtained from EIS that SAM$_{\text{HL/DT}}$ is the best protective film.

### 3.1.3. Surface morphology measurements

The surface morphologies of the electrode before and after the polarization (Fig. 4) were obtained by SEM in the absence and the presence of SAMs. Compared with the electrode before the experiment (Fig. 4a), dense pits with small radii were induced on the surface of the untreated electrode after the polarization (Fig. 4a'). With the presence of SAM$_{\text{HL}}$, the surface of copper was coated with a protective film (Fig. 4b). After the polarization, the film was severely damaged and one pit with a large radius emerged (Fig. 4b') in the observed area, while the number of the pits decreased dramatically. After SAM$_{\text{HL}}$ was modified by DT, the film was relatively more homogeneous (Fig. 4c') than that formed with HL, resulting in an almost defect-free coating (Fig. 4c').

The results obtained by EIS, potentiodynamic polarization and SEM all indicate that SAM$_{\text{HL/DT}}$ is the most protective film, followed by SAM$_{\text{DT}}$, SAM$_{\text{DT/HL}}$, and SAM$_{\text{HL}}$. The quality of SAM$_{\text{max}}$ is determined by the structure of the substances and their assembly sequence. As mentioned above, the classical electrochemistry (EIS and potentiodynamic polarization) characterization can only provide global information about the inhibitive behavior of SAM$_{\text{max}}$. To observe the degradation processes of the films in situ, SECm is an essential technique that can be used.

### 3.2. SECm measurements

The SECm analysis can not only lead to a global evaluation of SAMs, but also a very accurate characterization of the degradation of the grafted films [12,32]. Fig. 5 shows the j-$\bar{E}$ curves of the SECm tip above the specimens with different assembly films measured in 0.10 mol dm$^{-3}$ NaCl + 1.0 mmol dm$^{-3}$ ferrocene-methanol solution at the scan rate of 10 mV s$^{-1}$. These curves describe the electrochemical reactions associated with the dissolved Cu(I) and Cu(II) in the electrolyte. The tip current above the copper electrode with SAMs (Fig. 5b-e) is much lower than that above the bare copper (Fig. 5a). With the presence of SAM$_{\text{HL/DT}}$ (Fig. 5e), the tip current decreases the most. The results show that the compactness, the stability or the thickness of the SAM$_{\text{HL}}$ may improve significantly after being modified by DT molecules. In other words, among the four types of SAMs or SAM$_{\text{max}}$, SAM$_{\text{HL/DT}}$ offers the best protecting coat for the copper electrode against corrosion.

While traditional electrochemistry experiments can only provide general information, a SECm technique, called “Repetitive Runs”, is able to detect the corrosion of the substrate via the feedback current on a micrometric scale [33,34]. The redox mediator of FcMeOH molecules can reach the substrate surface mainly at
Table 2
Polarization parameters and inhibition efficiencies obtained from copper electrodes with different assembly conditions in 0.10 mol dm⁻³ NaCl solution.

<table>
<thead>
<tr>
<th></th>
<th>0 min</th>
<th>HL(60 min)</th>
<th>DT(30 min) HL(30 min)</th>
<th>DT(60 min)</th>
<th>HL(30 min) DT(30 min)</th>
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<tr>
<td>-Ecorr (V)</td>
<td>0.18</td>
<td>0.13</td>
<td>0.19</td>
<td>0.19</td>
<td>0.17</td>
</tr>
<tr>
<td>icorr (µA cm⁻²)</td>
<td>1.50</td>
<td>0.89</td>
<td>0.36</td>
<td>0.17</td>
<td>0.06</td>
</tr>
<tr>
<td>δEcorr (mV)</td>
<td>—</td>
<td>41</td>
<td>76</td>
<td>89</td>
<td>96</td>
</tr>
</tbody>
</table>

Fig. 4. SEM images obtained before and after 50 min polarization at the potential of −0.080 V for Cu samples with different assembly conditions. Before polarization a: 0 min; b: HL 60 min; c: HL 30 min + DT 30 min
After polarization a’: 0 min; b’: HL 60 min; c’: HL 30 min + DT 30 min.

Fig. 5. The j-E curves of the SECM tip towards the pre-treated Cu electrodes with different assembly conditions in 0.10 mol dm⁻³ NaCl + 1.0 mmol dm⁻³ FcMeOH solution at the scan rate of 10 mV s⁻¹; the copper being polarized at −0.080 V.

pinholes or non-covered areas [12]. Therefore, the SECM response will be mostly sensitive to reactions at defects, which will enable the capturing of the current peaks of pitting processes. In other words, it is expected to yield suppressed feedback current peaks in the case of well-ordered films [35,36].

As Fig. 6A shows, the bare copper was roughly attacked by the chloride ions. At 5 min (A1), no peak was observed. However, 10 min after the potential (−0.08 V) was applied (A2), the first peak appeared. At 35 min (A3), two fresh ones emerged while the first one disappeared. Then, they developed (A4), and the electrode was completely active at 98 min (A5). The dynamic processes of the pitting on copper were thus successfully observed by SECM.

Fig. 7B-E show that the coated electrodes exhibit obviously different behavior. After the electrode was pre-treated in HL containing solution for 60 min, the first current peak appeared at 35 min (B3) and was replaced by two fresh ones at 58 min (B4). Three more emerged at other places 98 min after (B5). When the copper was coated with SAMDT, the first peak appeared as late as 58 min (C4), and was then replaced by two fresh ones at 98 min (C5). When the copper was coated with SAMDT/HL, a tiny pit was induced at 35 min (D3), but it soon disappeared. No other pits came into existence until 98 min (D5). When the copper was protected with SAMmix/HLDT, no peak was observed at all throughout the scanning process (E1-E5).

It is obvious both SAMs and SAMmix can inhibit pitting though in different degrees and manners. Of the four types of coatings, SAMmix yields the most ideal result, which proves that the assembly sequence has a great impact on the quality of SAMmix.

By observing carefully the changes in SECM images in Fig. 6 and Fig. 7, a self-recovering phenomenon can be detected: some pits disappear during the scanning process. This may have been caused by the blocking of the active zones by the precipitation of the corrosion products such as copper oxide [33], and possibly the rearrangement [37] of the physical adsorption of organic molecules.

Fig. 6. SECM images of untreated Cu electrode (1000 µm x 1000 µm) in 0.10 mol dm⁻³ NaCl + 1.0 mmol dm⁻³ FcMeOH solution at −0.080 V.
3.3. XPS measurements

As shown in Fig. 8, the peaks give clear evidence that N, S, Cu, and O exist in the mixed films. The atomic% of the five elements extracted from XPS data is listed in Table 3.

The presence of N and S indicates that SAMmix is formed with HL and DT molecules by chemical adsorption. On the basis of all the experimental results, it is proposed that the organic molecules can fill in the defects on the pure SAMs and form high quality protective films. Due to the large chemical steric hindrance of the HL molecules and the relatively high density of SAMDT, SAMDT/DL is not as compact as SAMHL/DL.

The interaction models of HL and DT molecules with copper substrates are presented in Fig. 9. As Fig. 9a shows, when the copper surface is covered with HL molecules, the monolayer is poorly packed or organized. When DT comes in to act as the filling substance, the film density is greatly improved. And the pinholes shrink both in number and size, leading to the obvious increase of the inhibition efficiency (Table 1 and 2). But when the assembly sequence is switched over, the compactness of SAMDT/DL (Fig. 9b) is not as good as that of SAMHL/DL. However, N is still found on the surface of SAMDT/DL, which may be due to the rearrangement of DT on SAMDT in absolute ethanol solution and the competitive adsorption between HL and DT molecules [37–40], which in turn explain

![Fig. 7. SECM images of pre-treated Cu electrodes (1000 µm × 1000 µm) in 0.10 mol dm⁻³ NaCl + 1.0 mmol dm⁻³ FcMeOH solution at -0.080 V with different assembly conditions. B: HL 60 min; C: DT 60 min; D: DT 30 min + HL 30 min; E: HL 30 min + DT 30 min.](image)

![Fig. 8. XPS of copper samples covered by (a) SAMDT/DL; (b) SAMHL/DL.](image)

![Fig. 9. The adsorption models of SAMmix (a) SAMHL/DL; (b) SAMDT/DL.](image)

<table>
<thead>
<tr>
<th>Name</th>
<th>C (%)</th>
<th>Cu (%)</th>
<th>S (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMDT/DL</td>
<td>75.34</td>
<td>13.41</td>
<td>4.63</td>
<td>1.06</td>
<td>5.57</td>
</tr>
<tr>
<td>SAMHL/DL</td>
<td>73.71</td>
<td>14.83</td>
<td>5.60</td>
<td>1.24</td>
<td>4.62</td>
</tr>
</tbody>
</table>
why the ηf % (87%) for SAMDTTH is slightly lower than that of SAMDT (89%) (Table 1). Some of DT on SAMDT may be replaced by HL after the electrode with SAMDT has been immersed in HL solution for 30 min, and the inhibitive ability of SAMHL is much lower than that of SAMDT. As a result, the ηf for SAMDTTH is slightly lower than that (89%) of SAMDT. For the same reason, some of HL on SAMHL may be replaced by DT, and the inhibitive ability of SAMDTTH is improved.

4. Conclusions

Summarizing the results of SAMmax on copper surface and its anticorrosion behavior by SECM and other electrochemical measurements as well as surface analysis, following conclusions can be drawn.

(1) SAMMUDTH has higher compactness and stability than SAMDTTH, indicating that the assembly sequence has a great impact on the quality of SAMmax. The filigree role played by DT molecules result in a defect-free film, which prevents the copper surface from being attacked by chloride ions and improves the inhibition efficiency markedly.

(2) SECM has demonstrated its advantage over the traditional techniques by capturing transient details concerning the formation and the propagation of the pits on SAMmax.

(3) The re-arrangement and the competitive adsorption of DT and HL molecules in absolute ethanol solution during the assembly process lead to lower inhibition efficiency of SAMDTTH than that of SAMDT.

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References