

Research of Self-assembled Monolayer of Alkanethiol for Corrosion Protection of Brass

Wei Liu¹, Weimin Cao^{2,*}, Xianqin Deng¹, Yulin Min¹, Qunjie Xu^{1,**}

¹Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai Engineering Research Center of Energy-Saving in Heat Exchange Systems, Shanghai University of Electric Power, 2588 Changyang Road, Yangpu District, Shanghai 200090, China

²Department of Chemistry, Shanghai University, 99 Shangda Road, Baoshan District, Shanghai 200444, China

* E-mail: cwm213@staff.shu.edu.cn

** E-mail: xuqunjie@shiep.edu.cn

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Self-assembled monolayers (SAMs) of alkanethiol have been fabricated on an anodized surface of brass. The inhibition behavior of SAMs of alkanethiol on brass in seawater had been investigated by electrochemical impedance spectroscopy (EIS) and polarization measurements. The results indicated that the pretreatment of anodizing on the surface of brass played a vital role in preparing of SAMs film. The anti-corrosion property of brass in seawater has been greatly improved by SAMs of alkanethiol. The inhibition efficiency is as high as 99.4% when the concentration of assemble solution was 10 mmol/L and the corresponding time was 4 h. The results have been discussed in terms of the structure of SAMs film and its performance of protection for brass in seawater.

Keywords: Anodizing, Brass, Self-assembled, Dodecanethiol, Corrosion resistance

1. INTRODUCTION

Self-assembled monolayers (SAMs) are useful for preparing well-ordered organic films on metal surface by chemical adsorption and self-organization, which could retard considerably the cathodic process of metal corrosion. Due to simple, feasible and stable, SAMs have been recognized to be a very promising anti-corrosion technique.

To date, one of the most studied SAMs for copper corrosion was compounds of alkanethiols [1]. It is found that oxides from self-passivation of Cu on copper surface have an impact effect on the mechanical and adhesive properties of SAMs of alkanethiols. Therefore, a pretreatment for substrates before the fabrication of SAMs has attracted much attention. Feng et al. [2] optimized the preparation

process of SAMs of dodecanethiol by comparing HNO₃ etching and other different pretreatment. Wen et al. investigated the inhibition effect of three kinds of alkanethiols SAMs for copper in 3% NaCl solution pretreated with HNO₃ etched for 15 seconds. Ma et al. [3] also employed alkanethiols to establish SAMs on copper substrates after etched in HNO₃ and achieved inhibition efficiency greater than 90% in 0.2 mol/L of NaCl solution. Disadvantages of etching are listed as large amounts of wasting of etching solution, uncontrolled corrosion reaction and serious destruction of substrates. It is desired to find some new pretreatments for fabrication of SAMs of alkanethiols. As a simple and effective pretreatment, anodization could construct a uniform surface structure on copper substrates. However, few reports on its application in the inhibition of copper corrosion have been studied.

Brass is an alloy (Cu-Zn) commonly used in almost all industries for cooling purposes [4-6]. In spite of the fact that brass is a relatively inert metal, it can susceptibly suffer various corrosion problems, such as pitting corrosion induced by chloride in seawater environment [7,8]. One of the most important anti-corrosion techniques is to use inhibitor. However, environmental restrictions to traditional inhibitor [8-12], due to toxicity (such as carcinogenic effects of chromates) require development of green inhibitors, for example alkanethiols [13-16]. In this paper, the surface of brass is firstly anodized in 3.5% NaCl solution and then rinsed in an ethanol solution of dodecanethiol to attain SAMs of alkanethiols. An attempt is also made to enhance the anti-corrosive performance of brass modified by SAMs of alkanethiol in 3.5% NaCl solution.

2. EXPERIMENTAL

2.1 Preparation

The brass electrodes (10mm×10mm) was polished with different grades of emery paper (1#, 4#, 6#), degreased with acetone in ultrasonic cleaner, washed with ethanol and deionized water, respectively, and then dried. The cleaned brass electrode were anodized under 0.25 V potential in 3.5% NaCl solution, rinsed in ultrapure water and ethanol, respectively, and then dried. Finally, the brass surfaces were modified in an ethanol solution of dodecanethiol at 35°C for a controlled period of time. The obtained samples were washed with ethanol and deionized water, respectively, and then dried and pending test.

2.2 Characterization

The morphologies of the samples were observed on a SU-1500 scanning electron microscopy (Japanese Hitachi company) and the corresponding element distributions were determined by an energy dispersive X-ray spectroscopy (Japanese HORIBA company). The contact angle was measured by JC2000C1 CA system at ambient temperature.

2.3 Electrochemical measurements

AC impedance and potentiodynamic polarization measurements were carried out in a three-electrode electrochemical cell with a Pt electrode as the counter electrode and a saturated calomel

electrode as the reference electrode. Electrochemical measurements were carried out on EG&G PARC Model 273 Potentiostat/Galvanostat and PARC M1025 frequency response detector. For the measurement of EIS, M398 software was used. The frequency range was 100 kHz - 0.05 Hz; the amplitude was 5 mV and the scan rate of Tafel curves was set between -0.25 and 0.25 V(vs OCP) at 1 mV/s. The electrolyte was 3.5% NaCl solution.

3. RESULTS AND DISCUSSION

3.1 The basis for anodization

Figure 1 showed the cyclic voltammetry curve of brass in 3.5% NaCl solution. As shown in figure 1, two anodic peaks corresponded to the oxidation of Cu(0) to Cu(I) on brass surface in 3.5% NaCl solution. Accordingly, When the negative electrode potential gradually moved around 0 V, Cu(I) began to be restored to Cu(0) on the brass electrodes with producing the Faraday current. As more and more negative potential, the Cu(I) concentration in the surface of the electrode decreased, resulting in an increase of current in the brass electrode surface. When the surface concentration of Cu(I) dropped to near 0, the current also increases to a maximum (i_{pc}), then gradually decrease the current. However, CuO appeared when the potential increased to about 0.42 V. Similarly, with the electrode potential is gradually being shifted, when the potential approaches and passes through 0 V, the electrochemical equilibrium on the electrode surface should be more conducive towards the direction of the development of the Cu(I) generated. Whereupon Cu(0) began to be oxidized, and the oxidation current increases to the peak current (i_{pa}). And subsequently, as a significant consumption of Cu(0) causing the current decline down. Therefore, the high activity of Cu₂O film obtained after anodized for 120 s on the brass surface would be benefit for the adsorption of monolayer of dodecanethiol molecules.

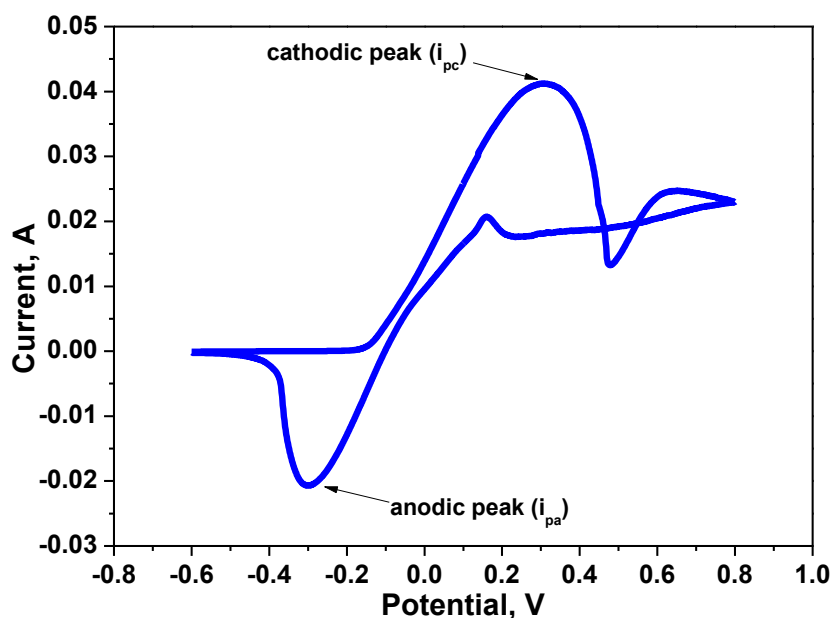


Figure 1. The CV of brass in 3.5% NaCl solution

3.2 Effects of assemble time on inhibition of SAMs

It was suggested that SAMs of alkanethiols usually take a longer time to assemble [17,18]. The inhibition of SAMs for brass in 3.5% NaCl solution with different assemble time has been studied in this work, respectively in 5 mmol/L and 10 mmol/L assemble solution.

3.2.1 Inhibition of SAMs in a low assemble concentration

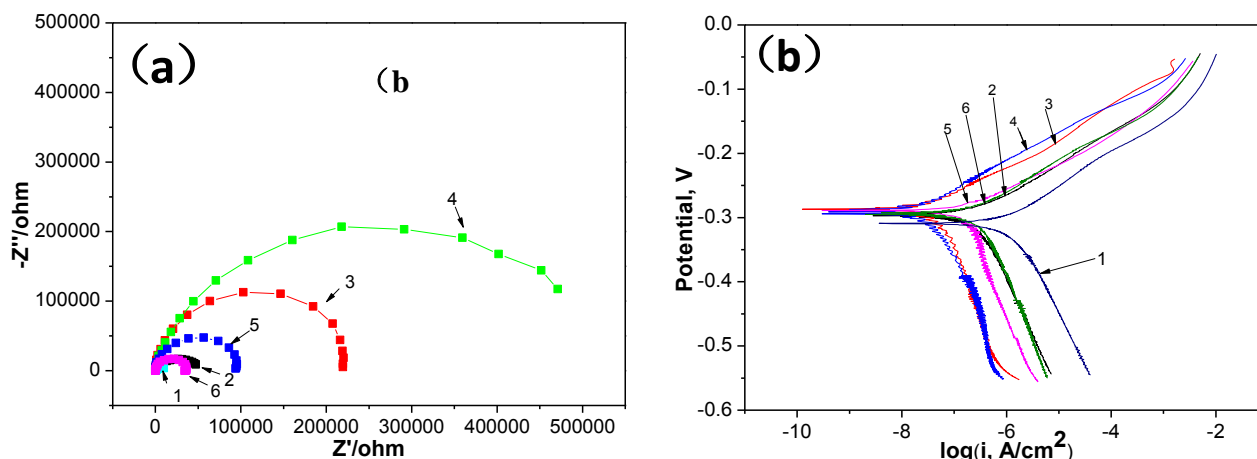


Figure 2. Nyquist plots (a) and Polarization curves(b) of brass surface in 3.5% NaCl solution with different assemble time; (1) bare, (2) 2h, (3) 4h, (4) 6h, (5) 8h, (6) 12h

Table 1. Electrochemical parameters of brass surface in 3.5% NaCl solution with different assemble time

assemble time/(h)	$E_{corr}/(V)$	$i_{corr}/(\mu A \cdot cm^{-2})$	IE(%)
0	-0.33	4.2	/
2	-0.30	0.99	76.4
4	-0.29	0.14	96.5
6	-0.29	0.038	99.1
8	-0.30	0.41	90.2
12	-0.30	0.12	70.4

Figure 2 showed the Nyquist plots (a) and Polarization curves (b) of the filmed brass with low assemble concentration in 3.5% NaCl solution. As shown in figure 2(a), the corrosion resistance properties became better with the increasing assemble time, while it got worse as it exceeded 6 h. Table 1 showed the electrochemical polarization parameters, i.e. corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), corrosion inhibition efficiency (IE) obtained from figure 2(b). It is noted that

the corrosion current density decreased considerably with the increasing assemble time, and inhibition might change a little weaker when it exceed 6 h. The result might be explain that the dissolution of metal emerged in assemble solution for a long immersed time. Therefore, 6 h was the optimal assemble time in a low concentration.

3.2.2 Inhibition of SAMs in a high assemble concentration

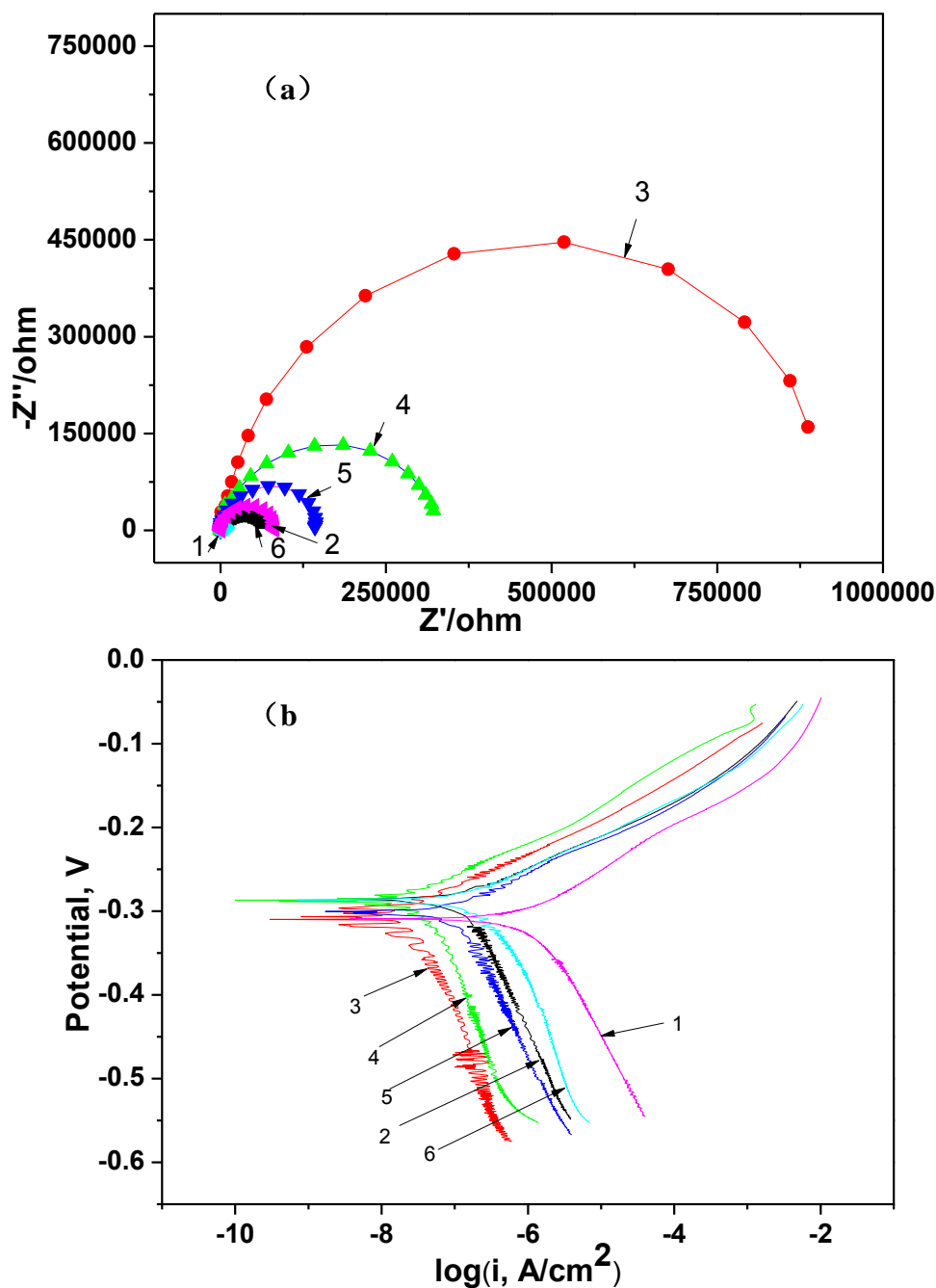


Figure 3. Nyquist plots (a) and Polarization curves(b) of brass surface in 3.5% NaCl solution with different assemble time; (1) bare, (2) 2h, (3) 4h, (4) 6h, (5) 8h, (6) 12h

Table 2. Electrochemical parameters of brass surface in 3.5% NaCl solution with different assemble time

assemble time/(h)	$E_{corr}/(V)$	$i_{corr}/(\mu A \cdot cm^{-2})$	IE(%)
0	-0.33	4.2	/
2	-0.29	0.58	86.1
4	-0.31	0.025	99.4
6	-0.29	0.076	98.2
8	-0.30	0.28	93.2
12	-0.30	0.61	85.4

Figure 3 showed the Nyquist plots (a) and Polarization curves (b) of the filmed brass with high assemble concentration in 3.5% NaCl solution. As shown in figure 3(a), the corrosion resistance properties became better with the increasing assemble time, while it get worse as it exceeded 4 h.

Table 2 showed the electrochemical polarization parameters, i.e. corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), corrosion inhibition efficiency (IE) obtained from figure 3(b). It is noted that the corrosion current density decreased considerably with the increasing assemble time, and inhibition might change a little weaker when it exceed 4 h. Therefore, 4 h was the optimal assemble time in a high assemble concentration, and the best inhibition efficiency arrived to 99.4%.

3.3 Effects of assemble concentration on inhibition of SAMs

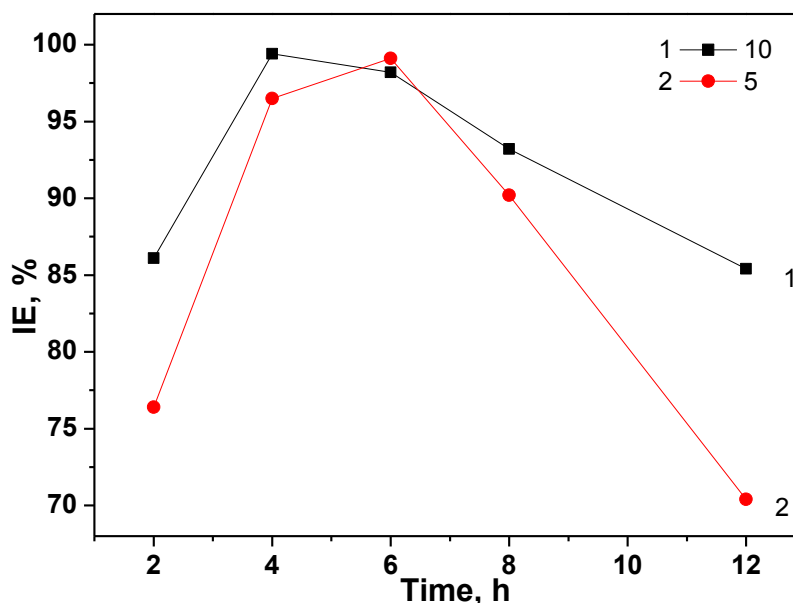


Figure 4. Inhibition of SAMs for brass in 3.5% NaCl solution with different assemble concentration

The relation between inhibition efficiency and the self-assembly time in different assemble concentrations was shown in Figure 4, obtained according to the electrochemical parameters in Table 1 and Table 2. As shown in Figure 4, 10 mmol/L generally showed better inhibition performance than 5 mmol / L with same assemble time, and also the optimal filmed time was shorter. It should point out

that high concentration would be conducive to the density of dodecanethiol SAMs formed spontaneously by chemical adsorption.[18-22]

3.4 Effects of anodization on inhibition of SAMs

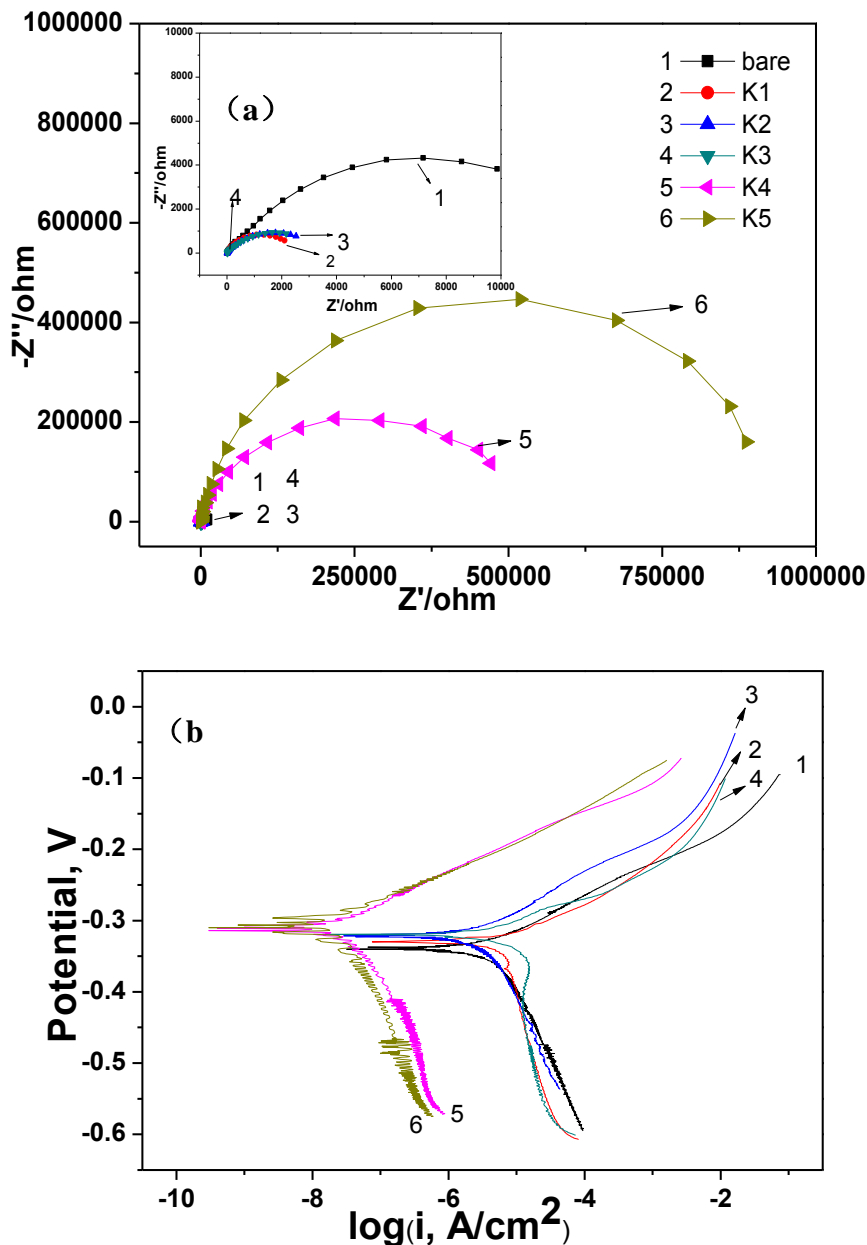


Figure 5. Nyquist plots (a) and Polarization curves(b) of different brass sample in 3.5% NaCl solution; (1) Bare surface, (2)Anodized surface K1, (3) Self-assemble surface with no anodizing in 5 mmol/L alkanethiol solution K2, (4) Self-assemble surface with no anodizing in 10 mmol/L alkanethiol solution K3, (5) Anodized brass self-assemble in 5 mmol/L alkanethiol solution K4, (6) Anodized brass self-assemble in 10 mmol/L alkanethiol solution K5

The optimal inhibition effective film prepared in 5 mmol/L (K4) and 10 mmol/L (K5) has been obtained by above research. In this paper, the inhibition of the modified brass surface assembled in 5 mmol/L (K2) for 6 h and 10 mmol/L (K3) for 4 h with no anodization has also been researched. Figure

5 showed Nyquist plots (a) and Polarization curves (b) of different modified brass surface in 3.5% NaCl solution. Electrochemical polarization parameters obtained from figure 5(b) were listed in Table 3. As shown in Figure 5 and Table 3, self-assemble with no anodization (K2, K3) could not prepare film with good corrosion resistance on brass surface. On the contrary, the dissolution of metal during self-assemble process led to worse corrosion resistance than bare brass. It should be noted that self-assemble with anodization (K4, K5) could fabricate good corrosion resisting film on brass surface. Compared bare sample and anodized surface (K1), it was clear that anodization does not have any contribution to improve the corrosion resistance of brass, but it was helpful to self-assemble.

So it appeared reasonable to conclude that as a pretreatment, anodization played a vital role in preparing film on brass surface.[22-25]

Table 3. Electrochemical polarization parameters of different brass sample in 3.5% NaCl solution

Brass sample	$E_{\text{corr}}/(\text{V})$	$i_{\text{corr}}/(\mu\text{A}\cdot\text{cm}^{-2})$	$\eta(\%)$
bare	-0.33	4.2	/
K1	-0.32	7.3	/
K2	-0.32	5.1	/
K3	-0.31	8.6	/
K4	-0.30	0.038	99.1
K5	-0.31	0.025	99.4

3.5 Characterization of brass surface

Surface morphology of the modified brass was observed using a SU-1500 scanning electron microscopy (Japanese Hitachi company). Figure 6 showed the SEM images of the modified brass, (a) bare surface of brass, (b) bare surface of brass immersed in 10 mmol/L self-assemble solution for 4 h with no anodization, (c) bare surface of brass anodized for 120 s, (d) bare surface of brass immersed in self-assemble solution for 4 h and anodized for 120 s. The changes of wettability were observed from the drop shape of water placed on Figure 6(b) and 6(d) as showed in Figure 8. It is noted that surface structure such as pits appeared after anodization (as shown in Figure 6a and 6c). The dodecanethiol SAMs was found to be easily prepared on anodized surface but difficult on bare surface when comparing Figure 6(b) ($CA=81^\circ$) and 6(d) ($CA=136^\circ$). This result also indicated that the anodization was conducive to prepare dodecanethiol SAMs.[25-29]

The chemical compositions of different modified brass surface were analyzed by EDX.[29-34] Figure 8 showed the EDX spectrum of the distributed elements of different brass samples, and the elements content were listed in Table 5, Figure 8(a), (b), (c), (d) was bare surface, anodized surface, self-assemble sample without anodization, self-assemble sample with anodization, respectively. As shown in Figure 8 and Table 4, in good agreement with the theory of anodization, O elements content was found increasing to 15.33% in the anodized brass. Compared S content in self-assemble sample without anodization and self-assemble sample with anodization, it is noteworthy that it increased from 0.11% in Figure 8(3) to 1.23% in Figure 8(4). Based on the above analysis, it was much easier to

prepare SAMs on anodized surface than that on bare surface, which was in good agreement with the electrochemical test results.

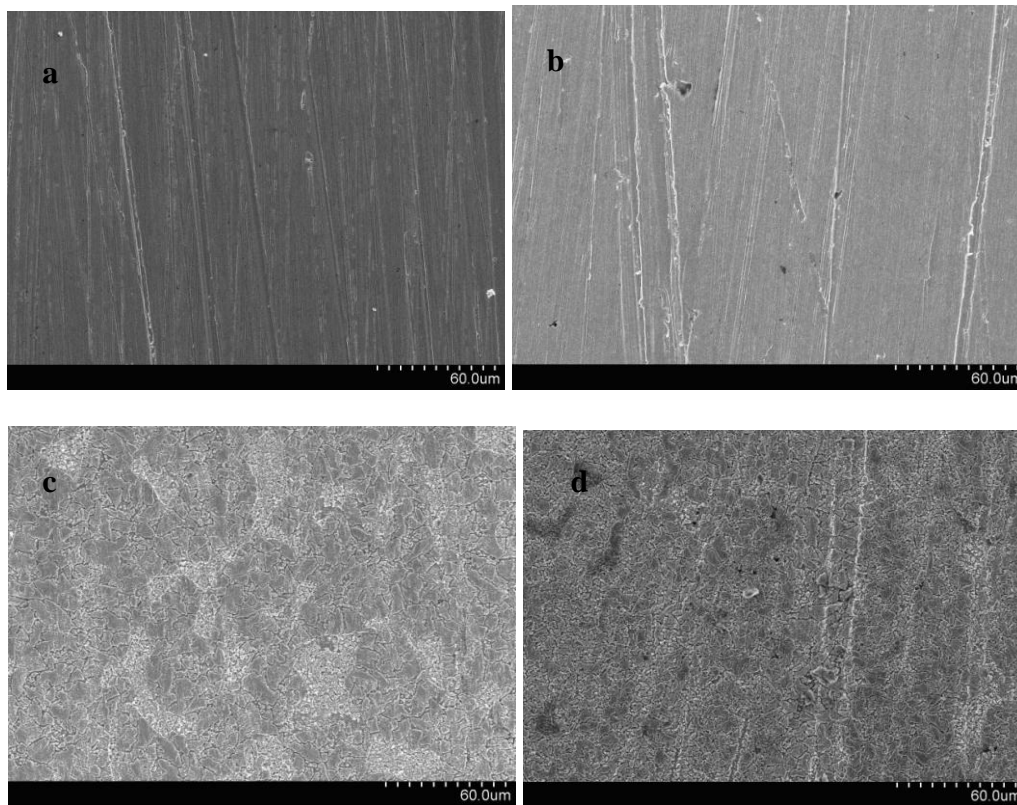


Figure 6. SEM images of modified brass surfaces. (a) Bare surface; (b) Self-assemble surface without anodization; (c) Anodized surface; (d) Self-assemble surface with anodization



Figure 7. Shape of water drops placed on brass surface. (a) Self-assemble surface without anodization; (b) Self-assemble surface with anodization

Table 4. Chemical composition of different brass surface

	Sample	C	O	S	Cu	Zn
a	Bare surface	0	0	0	60.70	39.30
b	Anodized surface	0	15.33	0	54.23	30.44
c	SAM without anodization	20.47	0	0.11	50.28	29.14
d	SAM with anodization	35.53	3.48	1.23	37.15	22.61

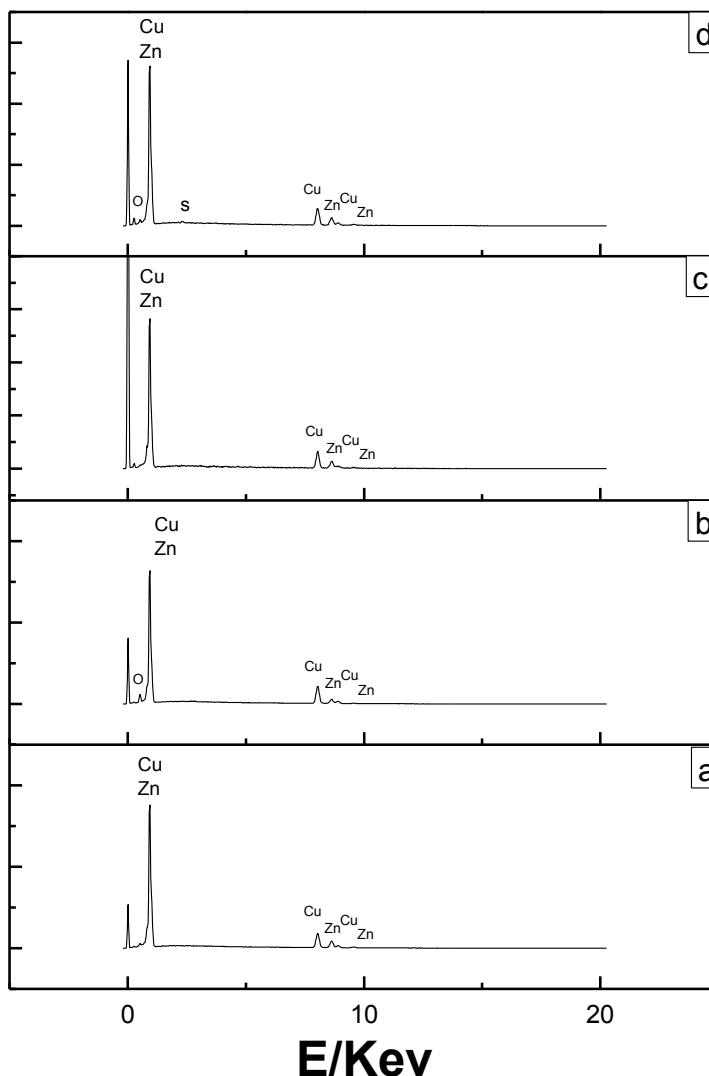


Figure 8. EDX spectrums of brass surface. (a) Bare surface; (b) Anodized surface; (c) Self-assemble surface without anodization; (d) Self-assemble surface with anodization

4. CONCLUSIONS

In the present work, self-assembled monolayers (SAMs) of alkanethiol have been fabricated on an anodized surface of brass. The anti-corrosion property of brass in seawater has been greatly improved by SAMs of alkanethiol. The optimal assemble time was 6 h in 5 mmol/L assemble solution, while 4 h in 10 mmol/L, and the inhibition efficiency had arrived to 99.1% and 99.4%, respectively. High concentration would be conducive to corrosion inhibition of SAMs of alkanethiol adsorbed on brass surface spontaneously. The composition and structure on the anodized surface played a key role in the preparation of SAMs of alkanethiol on brass substrates.

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