

An impedance investigation of corrosion protection of copper by self-assembled monolayers of alkanethiols in aqueous solution

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Abstract: Self-assembled monolayers (SAMs) of three *n*-alkanethiols, 1-octadecanethiol (C18SH), 1-dodecanethiol (C12SH), and 1-hexanethiol (C6SH), were formed on fresh, oxide-free copper surfaces obtained by HNO₃ etching. The corrosion protection abilities of the three alkanethiol SAMs were evaluated in 0.2 mol cm⁻³ NaCl, 0.2 mol cm⁻³ HCl and 0.2 mol dm⁻³ H₂SO₄ solutions using the electrochemical impedance spectroscopy (EIS) method. The SAMs act as a hydrophobic barrier layer, which effectively prevents the copper substrate from contacting corrosive ions, thereby inhibiting corrosion of the copper to a considerable degree. A general equivalent circuit for the SAM-covered electrodes was proposed, by means of which the impedance behavior of the electrodes was interpreted and the corresponding electrochemical parameters were acquired. In addition, the quality of the SAMs and development of defects in the SAMs were also been evaluated based on the equivalent circuit. The dependence of the capacitance of the SAMs on the applied potentials was used to determine the stability of the SAMs at the applied potentials.

Keywords: electrochemical impedance spectroscopy (EIS), self-assembled monolayers (SAMs), alkanethiol, corrosion protection, equivalent circuit.

INTRODUCTION

The spontaneous self-assembly of alkanethiols on the surface of coinage metal (copper, gold and silver) is increasingly becoming a specific technique for the preparation of compact monolayers with controlled thickness and structure.¹ Self-assembled monolayers (SAMs) formed by chemisorption of alkanethiols onto these metal substrates are somewhat similar to ultrathin hydrophobic coatings,^{2,3} but the advantages of SAMs over common organic coatings are:⁴ (i) the ultrathin film is formed through a quite simple chemisorption process and strongly adheres to the metal surfaces and (ii) the film thickness can be controlled at the nanometer level by selecting adsorbates and (iii) the presence of the film does not significantly alter the appearance or most other characteristics of substrate, except the hydrophilicity of the metal surface.³ Therefore, SAMs provide a great possibil-

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ity of protecting metal substrates from corrosion under different corrosive environments. Despite some studies having been carried out in this field, to our knowledge, there have been only a few studies concerning the corrosion behavior of copper substrates treated with alkanethiols. Laibinis and Whitesides² first investigated the corrosion resistance of *n*-alkanethiol monolayer-covered copper in air under ambient conditions. Scherer *et al.*⁵, Feng *et al.*⁶ and Itoh *et al.*^{7,8} studied the corrosion protection by SAMs or modified SAMs of copper in aggressive electrolytes. A great deal of research needs to be done in order to gain a better understanding of the ability of alkanethiols to protect against corrosion and their gradual destruction in corrosive solutions.

Electrochemical impedance spectroscopy (EIS) provides a good means to monitor the stability and destruction process of SAMs in corrosive solutions. The aims of this study were to prepare SAMs on *n*-alkanethiols with different hydrocarbon chains on a copper surface and to study the corrosion protection ability of the SAMs in NaCl, HCl and H₂SO₄ solutions. A general equivalent circuit for SAM-covered metal electrodes is established in this paper.

EXPERIMENTAL

Chemicals

1-Hexanethiol (C6SH) (Aldrich, 95 %), 1-dodecanethiol (C12SH) (Aldrich, > 98 %), and 1-octadecanethiol (C18SH) (Aldrich, 98 %) were used as received. The three alkanethiols were dissolved in absolute ethanol to form 1 mmol dm⁻³ ethanolic solutions.

The electrolyte solutions used in this work, 0.2 mol dm⁻³ HCl, 0.2 mol dm⁻³ NaCl, 0.2 mol dm⁻³ H₂SO₄ and 7.0 mol dm⁻³ HNO₃ aqueous solutions, were prepared with analytical grade chemicals and triply distilled water.

Preparation of copper electrodes

A 3.1 mm-diameter copper rod (Aldrich, 99.999 %) was used to prepare the working electrode. The copper rod specimen was embedded in an epoxy resin mould, leaving only its cross-section exposed to the ethanolic alkanethiol solutions and the corrosive electrolyte solutions.

Formation of self-assembled monolayers

The copper surface was first ground with SiC abrasive papers of decreasing particle size to #2000 finish, rinsed with deionized water, degreased with acetone, followed by etching in 7.0 mol dm⁻³ HNO₃ solution for 30 s to obtain a fresh, oxide-free copper surface. The etched copper surface was rinsed with deionized water and anhydrous ethanol, and finally immersed in 1 mmol dm⁻³ deoxygenated ethanolic alkanethiol solutions. Before transfer and during immersion, the alkanethiol solution was purged with pure N₂. The immersion time was varied from 30 min to 8 h depending on the experimental requirements.

Electrochemical measurements

EIS Measurements were carried out in a conventional three-electrode cell at room temperature (≈ 22 °C) using a Zahner IM6 electrochemical workstation. A naked copper electrode or a SAM-covered copper one was used as the working electrode, a 2 cm \times 2 cm platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The reference electrode was led to the surface of the working electrode *via* a Luggin capillary. All the potentials reported in this paper are referred to the SCE.

Each impedance spectrum was measured at the open-circuit corrosion potential (E_{OC}) in the frequency range from 60 kHz to 10 mHz with ten points per decade under excitation of a sinusoidal wave of ± 5 mV amplitude. The impedance data were analysed with IM6 impedance analysis software and fitted to the appropriate equivalent circuits. The fitting results gave the values of elements in the equivalent circuits.

RESULTS AND DISCUSSION

Corrosion protection ability of alkanethiol SAMs

Figures 1–3 show the Nyquist impedance plots for naked and *n*-alkanethiol SAM covered copper electrodes in 0.2 mol dm^{-3} NaCl, 0.2 mol dm^{-3} HCl and 0.2 mol dm^{-3} H_2SO_4 solution, respectively. Before the EIS measurements, the naked copper and SAM modified copper electrodes were immersed in the corrosive solutions for 6 min so that their corrosion

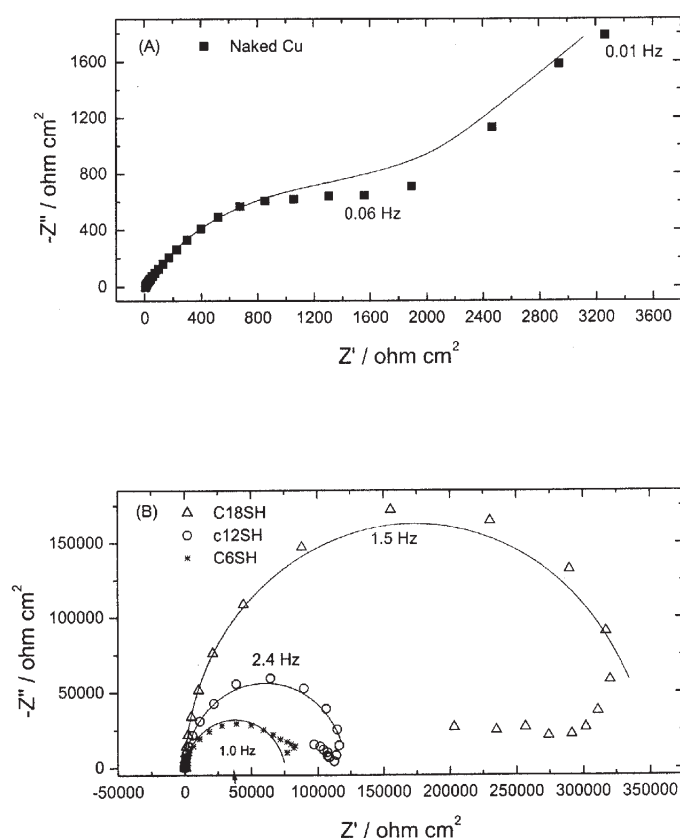


Fig. 1. Nyquist impedance spectra for naked (A) and alkanethiol SAM-covered (B) copper electrodes in 0.2 mol dm^{-3} NaCl solutions at the corrosion potentials. Formation time of the SAMs was 4 h. Symbols: measured data; solid line: fitted curve.

potentials tended to a stable value. The common feature of the Nyquist spectra of the naked copper electrode is that they display a small semicircle at high frequencies and a straight line at low frequencies (see Figs. 1A, 2A and 3A). Especially, for the Cu/HCl system, the high frequency semicircle is so small that it is almost hidden by the straight line. The high frequency semicircle is associated with the relaxation of the electrical double-layer since the charging and discharging process are rapid processes.^{6,9,10} The low frequency straight line, *i.e.*, the Warburg impedance, is attributed to the diffusion of soluble reactant or product species. This indicates that mass transfer has a great influence on the corrosion reactions of cop-

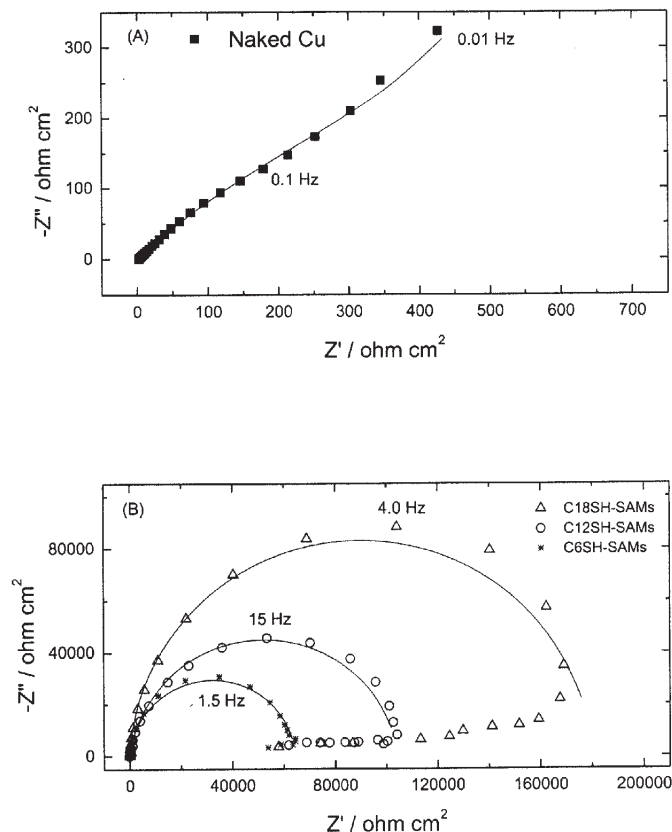


Fig. 2. Nyquist impedance spectra for naked (A) and alkanethiol SAM-covered (B) copper electrodes in 0.2 mol dm^{-3} HCl solutions at the corrosion potentials. Self-assembling time of the alkanethiol monolayers at copper was 4 h. Symbols: measured data; solid line fitted curve.

per in the three solutions because the anodic dissolution of copper in chloride-containing solutions and the cathodic reduction of dissolved oxygen are diffusion controlled.

After the copper surface had been modified by the alkanethiol monolayers, the impedance spectra of the copper electrode changed significantly in both size and shape Figs. 1B, 2B and 3B all display a large capacitive loop, the diameter of which strongly depends on the corrosive electrolyte used. It is worth noticing that their low frequency impedance behavior is very peculiar, quite different from the usual inductive loops.

In theory, the hydrophobic alkanethiol SAMs are ionic insulators,¹¹ being able to isolate the metal surface from the corrosive solutions. If SAMs are defect-free insulators and are able to resist corrosion attack by the corrosive ions, the Nyquist impedance spectrum for a SAM-covered electrode should be a straight line normal to the real axis. However, recent results have shown that electrons can penetrate SAMs¹² even though they are defect-free; moreover, SAMs have been found to contain moleculesized defects.^{3,13–15} Therefore, SAMs usually behave as leaky capacitors, instead of perfect ones. Accordingly, the impedance spectra for the SAM-covered electrodes give a slightly depressed semicir-

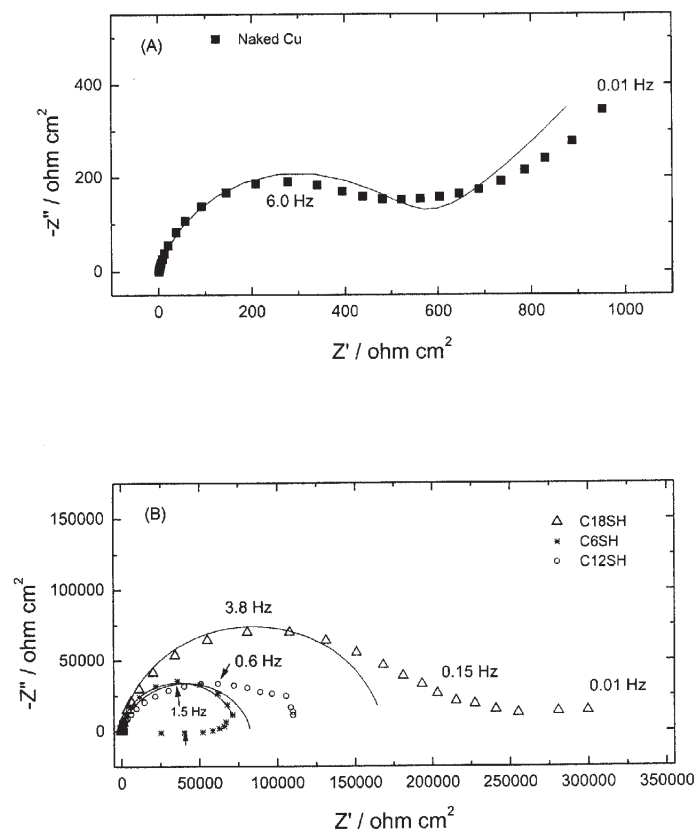


Fig. 3. Nyquist impedance spectra for naked (A) and alkanethiol SAM-covered (B) copper electrodes in $0.2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solutions at the corrosion potentials. Alkanethiol monolayers were self-assembled for 4 h. Symbols: measured data; solid line: fitted curve.

cle at high frequencies. Zamborini and Crooks³ proposed a corrosion reaction model for electrodes coated by defect-containing SAMs. In this model, corrosive ions, such as halide ions, can permeate the SAMs through the defect sites and directly contact the surface of the bare metals, giving rise to corrosion of the metal substrate and leading to further destruction of the SAMs; long hydrocarbon chains within the SAMs might partially heal the defects. It is inferred that the whole electrode process occurring at the surface of a SAM-covered copper electrode involves not only the electrochemical corrosion reactions at the defective sites, the transfer of electrons across the monolayers by means of the tunneling effect¹² and ions/water migration within the SAMs,¹⁶ but also the local breakdown and self-repair of the SAMs.⁴ The peculiar low frequency impedance behavior shown in Figs. 1B, 2B and 3B may be associated with these various features.

General equivalent circuit for SAM-covered metal electrodes

The impedance spectrum for the naked copper electrode can be fitted by the equivalent circuit shown in Fig. 4. In this circuit, R_s is the solution resistance between the working

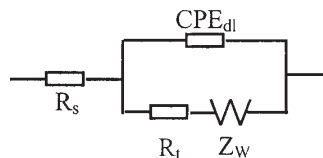


Fig. 4. The equivalent circuit used to fit the impedance spectra, consisting of a high frequency capacitive loop and a Warburg impedance.

electrode and the reference electrode, R_t is the charge transfer resistance for the corrosion reaction and CPE_{dl} represents the double-layer capacitance at the copper/solution interface. Here a constant phase element (CPE) is substituted for the capacitor to fit the depressed semicircle more exactly. The admittance and impedance of a CPE are, respectively, defined as

$$Y_{CPE} = Y_0(j\omega)^n \quad (1)$$

and

$$Z_{CPE} = \frac{1}{Y_0}(j\omega)^{-n} \quad (2)$$

where Y_0 is the modulus, ω the angular frequency and n the phase.^{17,18} For a highly polished electrode, the value of n is always less than 1.0. The lower the value of n is the rougher is the electrode. In addition, the value of n is also related to the inherent physical and chemical heterogeneous nature of the solid surface,¹⁹ the presence of a porous corrosion product layer,^{20,21} the development of a solid corrosion product within the defects,²² and the non-uniform distribution of the current density on the surface.²³

For metal electrodes without coatings, the diameter of the high-frequency semicircle is treated as the charge-transfer resistance (R_t),^{6,9} which can be used to evaluate the electrochemical corrosion rate of metals. The smaller is the value of R_t , the faster the corrosion reaction proceeds. However, for coated electrodes, the high frequency capacitive loop is related to the barrier and protective properties of the coating,²⁴ and the relaxation time constant originating from the Faradaic reactions, which usually appear at low frequencies since the time constant is relatively large. Different equivalent circuits have been established to interpret the impedance behavior of SAMs-coated electrodes.^{4,6,11,12,16,25,26} However, these circuits are inconsistent with each other in their interpretation of the physical meaning of the elements and in their explanation of the origin of the high frequency semicircle. Seeing that SAMs behave somewhat like organic coatings, on the basis of Deflorian and co-workers' model²⁴ for protective coatings, a general equivalent circuit for SAM-covered electrodes was established (see circuit A in Fig. 5.)

In the equivalent circuit A in Fig. 5, R_s , R_t , CPE_{dl} and Z_w have the same physical meaning as in Fig. 4, and CPE_{sam} characterizes the capacitance of the SAM, and R_{sam} represents the transfer resistance of electrons through the monolayers, which reflects the protective property of the SAM. When the influence of the mass transport process is insignificant, Z_w can be ignored and circuit A can be simplified to circuit B. Circuit B can be further simplified to circuit C in Fig. 5 under the condition that $R_{sam} \gg R_t$.⁴

The impedance spectra for the naked copper electrode and the SAM-coated ones

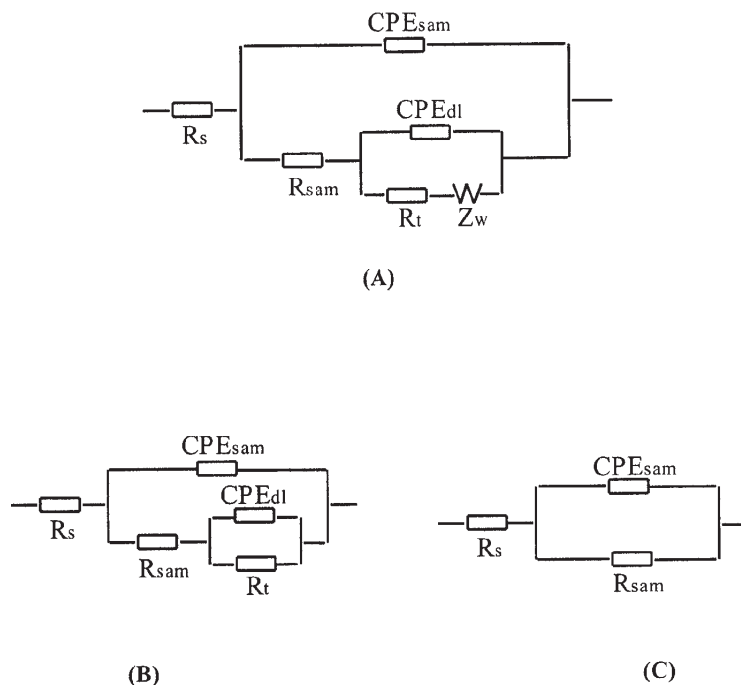


Fig. 5. Equivalent circuits of metal electrodes covered by SAMs with defects under varying conditions.

were fitted using the circuit in Fig. 4 and circuit C in Fig. 5, respectively. Here, only the high frequency capacitive loops of the SAM-covered copper were fitted (see solid lines in Figs. 1 to 3). The values of the elements of the equivalent circuits obtained by fitting are given in Table I. The capacitance values of the SAMs and the electrical double-layer were calculated by means of a previously proposed method^{17,27} and are also listed in this Table.

By comparing the values of R_{sam} and C_{sam} for C18SH, C12CH and C6SH monolayers it can be seen that with increasing length of the hydrocarbon chain, the value of R_{sam} increases and the value of C_{sam} decreases. The quality of SAMs can be evaluated by R_{sam} and C_{sam} .⁶ In general, the more densely packed and the thicker a monolayer is, the higher are the R_{sam} values and the lower are the C_{sam} values. It is evident that the long hydrocarbon chain is favorable for the corrosion protection by SAMs. In corrosion studies, the n value of a CPE reflects the roughness of the electrode surface.^{15,17} The n values of CPE_{dl} describing the double-layer capacitance of bare copper in NaCl, HCl and H₂SO₄ solutions are 0.66, 0.49 and 0.80, respectively. In particular, the value of 0.49 suggests diffusion impedance. The deviation from unity is ascribed to the surface roughness of the copper electrode caused by the corrosion reactions, whereas most n values of the CPE_{sam} element are over 0.90. This shows that an electrode surface modified by alkanethiol SAMs remains smooth due to the good corrosion protection of the alkanethiol SAMs.

In view of the ordered arrangement of alkanethiol SAMs on gold, silver and copper surfaces, the capacitive behavior can be described approximately by the Helmholtz model of an electrical double-layer. Taking the C6SH SAM on copper as an example, if the SAM

acts as an ideal capacitor, the capacitance per unit area is:

$$C = \epsilon \epsilon_0 / d \quad (3)$$

where d is the thickness of the C6SH monolayer, ϵ_0 is the permittivity of vacuum, a fundamental constant with the value of $8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$,²⁸ and ϵ is the relative permittivity. Based on the data reported in Lange's Handbook of Chemistry,²⁹ the length of a C–C bond is about $1.541 \times 10^{-10} \text{ m}$ and that of a C–S bond is $1.817 \times 10^{-10} \text{ m}$. It can be roughly estimated that the length of a C6SH molecule is $9.52 \times 10^{-10} \text{ m}$, which is treated as the approximate thickness of a C6SH monolayer. The relative permittivity of C18SH (3.0) was used as the reference value for C6SH. With these values, the capacitance of C6SH SAMs is calculated to be about $2.79 \times 10^{-2} \text{ F m}^{-2}$, *i.e.*, $2.79 \mu\text{F cm}^{-2}$. Within experimental error and the theoretical treatment, this value can be considered to be in good agreement with the value listed in Table I, thereby confirming that the equivalent circuits for a SAM-coated electrode are creditable and the analysis and treatment of the impedance data are reasonable.

Formation process of C12SH SAMs

As indicated in the experimental section, the C12SH monolayers were formed on the copper surface by immersing the copper electrode in 1 mmol dm^{-3} ethanolic solution of C12SH for different times. The Nyquist impedance spectra for an electrode covered by a C12SH monolayer in 0.2 mol dm^{-3} NaCl solution at the respective corrosion potential are

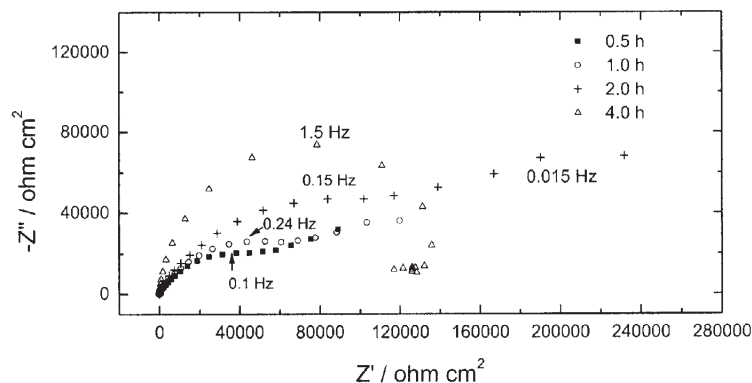


Fig. 6. Effect of self-assembling time of C12SH SAMs on copper on their impedance behavior. Impedance measurements were carried out in 0.2 mol dm^{-3} NaCl solution at the corrosion potentials.

given in Fig. 6. When the formation time of the C12SH monolayer was short (0.5 h, 1 h), the corresponding impedance spectra displayed an obvious Warburg impedance. This implies that the C12SH monolayers were not sufficiently dense to completely avoid corrosion reactions over the whole copper substrate. However, after 2 h of immersion in the C12SH solution, the low frequency impedance behavior changed greatly and the impedance spectrum evolved into one diagram composed of two capacitive loops. In this case, the C12SH monolayer was more compact and better ordered, but still had some defects

TABLE I. Values of the elements of the equivalent circuits in Fig. 4 and Fig. 5 C to fit the impedance spectra of the Bare electrode and electrodes covered by alkanethiol SAMs, as well as the calculated values of C_{dl} , C_{sam}

	$R_{sam}/\Omega\text{cm}^2$	$R_f/\Omega\text{cm}^2$	CPE_{sam}		CPE_{dl}		$C_{dl}/\mu\text{Fcm}^{-2}$	$W/\Omega\text{cm}^2$
			$Y_0/\Omega^{-1}\text{cm}^{-2}\text{s}^n$	n	$Y_0/\Omega^{-1}\text{cm}^{-2}\text{s}^n$	n		
0.2 mol dm ⁻³ NaCl								
Bare Cu	-	1.99×10^3	-	-	4.22×10^{-4}	0.66	385.4	1.52×10^{-5}
C18SH	3.47×10^5	-	3.40×10^{-7}	0.98	-	-	0.33	-
C12SH	1.21×10^5	-	5.24×10^{-7}	0.97	-	-	0.48	-
C6SH	7.5×10^4	-	2.26×10^{-6}	0.91	-	-	1.90	-
0.2 mol dm ⁻³ HCl								
Bare Cu	-	8.65×10^2	-	-	4.89×10^{-3}	0.49	2.20×10^3	4.10×10^{-5}
C18SH	1.79×10^5	-	1.92×10^{-7}	0.97	-	-	0.17	-
C12SH	1.04×10^5	-	1.29×10^{-7}	0.92	-	-	0.09	-
C6SH	6.44×10^4	-	1.68×10^{-6}	0.96	-	-	1.53	-
0.2 mol dm ⁻³ H ₂ SO ₄								
Bare Cu	-	5.49×10^2	-	-	1.07×10^{-4}	0.80	52.9	3.82×10^{-5}
C18SH	1.68×10^5	-	2.94×10^{-7}	0.93	-	-	0.23	-
C12SH	8.28×10^4	-	1.33×10^{-6}	0.92	-	-	0.99	-
C6SH	7.35×10^4	-	1.51×10^{-6}	0.97	-	-	1.41	-

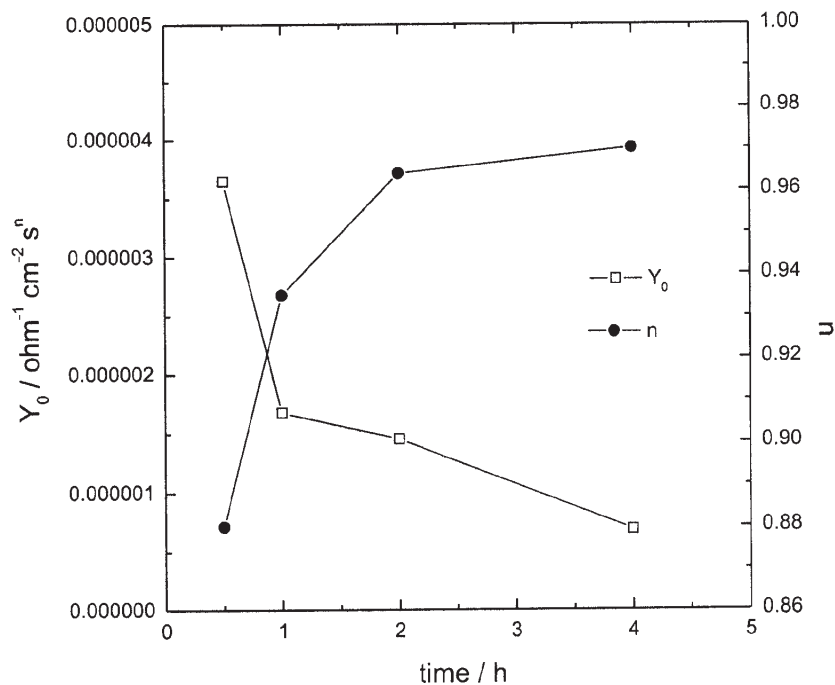


Fig. 7. The dependence of Y_0 and n for CPE_{sam} on the formation time of C12SH SAMs.

through which corrosion reactions could occur at the bare substrate. On further increasing the self-assembling time, the C12SH monolayer on the copper had become even more ordered and the defect sites were healed and repaired by the long hydrocarbon chains. The impedance spectrum obtained after 4 h of immersion shows a nearly regular semicircle with a larger diameter, which indicates the corrosion reactions had been significantly inhibited. The evolution of the high frequency capacitive loop with the time of self-assembling time reflects the improvement of the SAMs in respect of ordered state and compact structure. Using the equivalent circuit C in Fig. 5 to fit the high frequency capacitive loop, variations of Y_0 and n of CPE_{sam} with the immersion time are plotted in Fig. 7. It can be seen from Fig. 7 that the longer the immersion time is, the smaller are the Y_0 values and the higher are the n values. Variation of n with the immersion time indicates that the C12SH monolayer tends to behave like a perfect capacitor with increasing self-assembling time.

The destruction of C12SH SAMs in NaCl

The C12SH monolayers were self-assembled on the copper surface under identical conditions as above. The impedance spectra for the copper electrode modified with a C12SH monolayer after various time of immersion in 0.2 mol dm^{-3} NaCl solution at the corrosion potentials are shown in Fig. 8. With increasing exposure time to NaCl solution, the high frequency capacitive loop gradually decreased in size and the Warburg impedance appeared at low frequencies. This kind of changing trend, contrary to that shown in Fig. 6, reveals that the protection ability of the SAMs against corrosion decreases with immersion

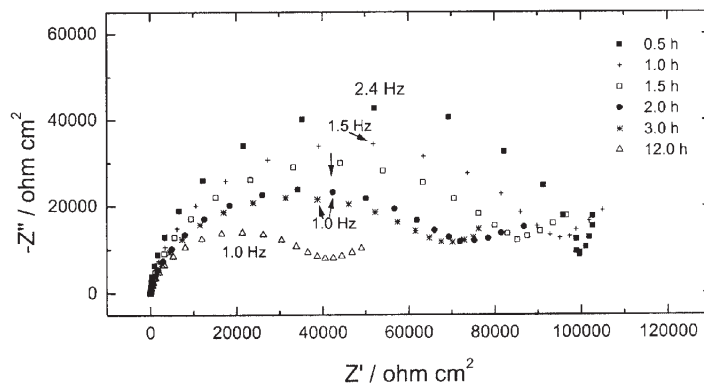


Fig. 8. Variation of Nyquist impedance spectra for the C12SH-SAM-coated copper electrodes on immersion time in 0.2 mol dm⁻³ NaCl solution. The C12SH monolayers were self-assembled for 4 h.

time. Theoretically, the defect sites in SAMs are attracted by the corrosive ions first,³ followed by growth of defect sites which leads to a local breakdown of the SAM. The capacitive loops were fitted by circuit C in Fig. 5 and then the values of Y_0 and n of CPE_{sam} were plotted as function of immersion time (see Fig. 9). Figure 9 shows that n decreases but Y_0 increases with the time of immersion in the NaCl solution. The decrease in the n values reflects that the C12SH SAMs gradually deviate from a relatively perfect capacitor because of their destruction in the corrosive solution.

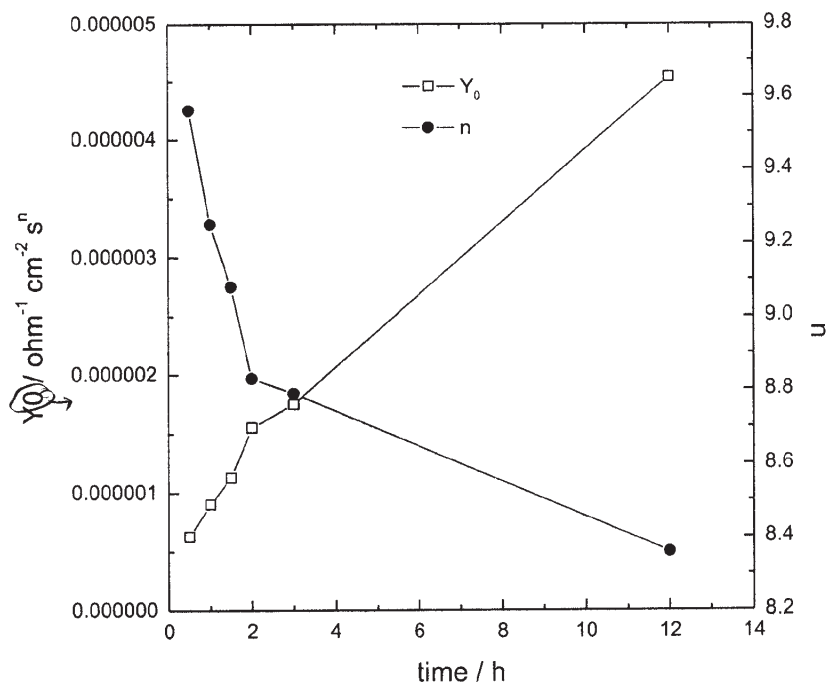


Fig. 9. Variation of Y_0 and n for CPE_{sam} on the immersion time in 0.2 mol dm⁻³ NaCl. Before the test, the copper electrode had been immersed in 1 mmol dm⁻³ ethanolic solution of C12SH for 4 h.

Stability of alkanethiol SAMs as a function of applied potential

The dependence of the capacitance of the SAMs on the applied potential in 0.2 mol dm^{-3} NaCl solution was measured to detect the development of defects in the SAMs at the applied potentials. The capacitance value measured at certain potential is the total electrode capacitance of the SAM solution interface, which is dependent on both the frequency and the applied potential. Therefore, selecting the appropriate frequency to deduct the contribution of the double-layer capacitance is the key in measuring the capacitance curves of SAMs against the applied potential. After repeated attempts, it was found that the top frequency of the high frequency capacitive loop is the optimum frequency to perform this kind of experiment. The immersion time of the SAM covered copper electrode in the NaCl solution was 6 minutes before the capacitance measurements.

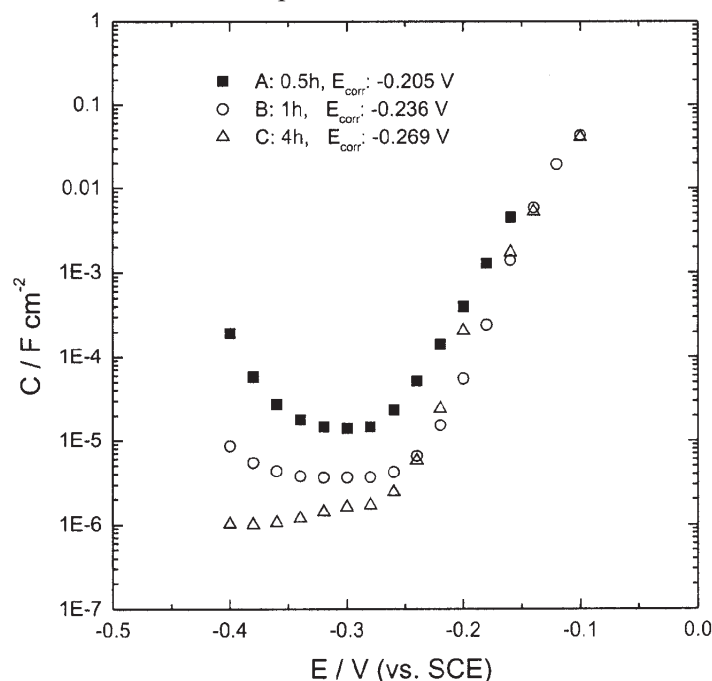


Fig. 10. Values of C as a function of applied potentials in 0.2 mol dm^{-3} NaCl solution for copper electrodes coated with C12SH SAMs formed during various times of immersion in a 1 mmol dm^{-3} ethanolic solution of C12SH. The self-assembling time of the C12SH SAMs and the corrosion potentials of the electrodes before the capacitance measurements are indicated in the figure.

Three capacitance curves vs. the applied potential for C12SH SAM-coated copper electrodes are shown in Fig. 10. The formation times of the C12SH SAMs on the copper surface were 0.5 h, 1 h and 4 h, respectively. The corrosion potential of the SAM modified electrode decreased with increasing time of formation of the C12SH SAMs. In the case of a short self-assembling time, the capacitance value first decreased and then increased with increasing potential (curve A). The relatively high capacitance values reveal that they include a large contribution from the double layer capacitance. As mentioned earlier, when

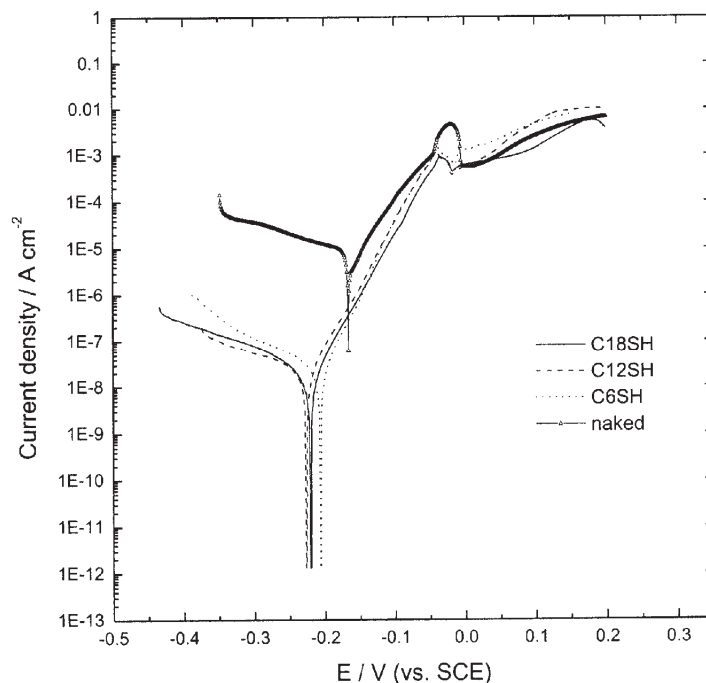


Fig. 11. Polarization curves for a naked copper electrode and SAM-coated copper electrodes in 0.2 mol dm^{-3} NaCl solutions at 0.2 mV s^{-1} . The copper electrodes had been immersed in 1 mmol dm^{-3} ethanolic solutions of alkanethiol for 4 hours to obtain the SAMs.

the self-assembling time is short, some defects in the C12SH SAMs exist where corrosion reactions occur at the bare copper substrate; moreover, the applied potential will further induce the development of the defects.¹⁶ The capacitance–potential curve (B) for a SAM-coated electrode assembled for 2 hours was similar to curve A, but the values of the capacitance were lower by one order of magnitude. With further extension of the self-assembling time, curve C shows that the capacitance values are lower compared to curves A and B; in addition, the capacitance increased monotonously with increasing potential, *i.e.*, with no minimum in the capacitance (see curve C). This implies that the defects in the SAM had been repaired with extension of the self-assembling time. In this case, the SAM remained stable at least at the cathodic polarization potential. Small capacitance values at cathodic polarization potentials are somehow related to the significant cathodic inhibition of the SAM, which is supported by comparison of the polarization behavior of naked copper and SAM coated copper electrodes in NaCl solution (Fig. 11). It can be seen from Fig. 11 that when the copper electrodes were covered by C6SH, C12SH and C18SH SAMs, both the anodic and cathodic currents were simultaneously inhibited. Especially, the cathodic currents were inhibited more significantly, being reduced by two orders of magnitude.

Our recent results have shown that increasing of the potential causes alkanethiol SAMs to be gradually stripped off from the copper substrate *via* electrochemical desorption, resulting in an expansion of the defect sites and, this the anodic copper dissolution

occurs more remarkably at higher anodic potentials.³⁰ Therefore, it is believed that the rapid increase in the electrode capacitance with increasing potential, shown in Fig. 10, may be attributed to the extension of the defects in the SAM caused by the anodic potentials, followed by electrochemical desorption of the SAM.

CONCLUSIONS

The self-assembled C18SH, C12SH and C6SH monolayers (SAMs) on copper provide significant protection against corrosion of the underlying copper in different corrosive solutions, such as NaCl, HCl and H₂SO₄. The length of the hydrocarbon chain has a great influence on the corrosion protection of alkanethiol SAMs. The longer the carbon chain, the better is the corrosion protection efficiency of the SAM.

A general equivalent circuit for a SAM-covered electrode is proposed. The high frequency capacitive loop originates from the transfer of electrons across the monolayer *via* the tunneling effect and the impedance behavior at low frequencies is related to the corrosion reaction at the bare copper/solution interface. The value of the capacitance of the SAM calculated from the equivalent circuit is in good agreement with the theoretical value. The n and Y_0 values of the CPE_{sam} element in the equivalent circuit may be used to evaluate the quality of the SAM and the development of the defect in the corrosive solution. The closer the value of n is to 1, the smaller is the Y_0 value, the higher is the quality of the SAM.

For SAM-covered electrodes, the plots of capacitance *versus* the applied potential offer a convenient method to determine the stability of a SAM under the applied potentials.

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ИЗВОД

ИМПЕДАНСНА ИСПИТИВАЊА ЗАШТИТЕ БАКРА САМООБРАЗУЈУЋИМ МОНОСЛОЈЕВИМА АЛКАНТИОЛА ОД КОРОЗИЈЕ У ВОДЕНОЈ СРЕДИНИ

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Самообразујући монослојеви (SAM) три n -алкантиола, 1-октадекантиола (C18SH), 1-додекантиола (C12SH) и 1-хексантиола (C6SH) начињени су на свежој површини (без оксида) бакра добијеној нагризањем у HNO₃. Заштитна моћ три алкантиола испитивана је у растворима 0,2 mol dm⁻³ NaCl, 0,2 mol dm⁻³ HCl и 0,2 mol dm⁻³ H₂SO₄, коришћењем методе електрохемијске импедансне спектроскопије (EIS). SAM монослојеви делују као хидрофобна баријера која ефикасно спречава контакт корозивних јона са бакарним супстратом и тиме у знатној мери инхибира корозију бакра. Предложено је еквивалентно електрично коло за електроду превучену са SAM које описује понашање електрохемијске импедансе и које је послужило за израчунавање одговарајућих електрохемијских параметара. Такође, уз помоћ еквивалентног кола процењен је квалитет SAM и стварање дефеката у SAM-у. За оцену

стабилности SAM на одређеном потенцијалу коришћена је зависност капацитета SAM од примењеног потенцијала.

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