

COPPER PROTECTION BY PHOSPHONIC ACID SELF-ASSEMBLED MONOLAYERS

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Abstract

The formation and the protection properties against corrosion provided by self-assembled monolayers (SAMs) onto non-noble metals, such as copper, are described using molecules with long alkyl (decane) chains and phosphonate as anchoring group. The assembly of stable and densely packed monolayers has been achieved both on naked copper and on the metal after controlled anodic oxidation, conducted with the purpose to create different sorts of copper oxide thin films, simulating diverse possible situations. Surface characterisation techniques (contact angle measurements and atomic force microscopy) are employed to access the properties of the so-modified electrodes; in addition, the influence of each type of copper oxide on the proficiency of SAMs protection has been retrieved from comparative studies based on polarisation curves, carried out in sodium chloride.

Keywords: Copper, Anodic Copper Oxides, Alkane-Phosphonic Acid Self-Assembled Monolayers, Contact Angles, Atomic Force Microscopy, Polarisation Curves

PROTECÇÃO DE SUPERFÍCIES DE COBRE POR MONOCAMADAS AUTO-MONTADAS DE ÁCIDOS FOSFÓNICOS

Resumo

A formação e as propriedades de protecção contra a corrosão de monocamadas auto-montadas (SAMs) em metais não-nobres como o cobre, contendo uma cadeia alquila longa (decano) e fosfonato como grupo de ligação à superfície são descritas neste trabalho. SAMs estáveis e densas foram obtidas em cobre nu e no metal depois de oxidação electroquímica controlada, realizada com o objectivo de criar diferentes tipos de filmes finos de óxidos de cobre, simulando diversas situações possíveis. As propriedades dos eléctrodos modificados foram avaliadas recorrendo a técnicas de caracterização de superfície (medidas de ângulo de contacto e microscopia de força atómica). A influência de cada tipo de óxido de cobre na eficiência da protecção das SAMs foi também analisada a partir de estudos comparativos de curvas de polarização realizadas em cloreto de sódio.

Palavras-Chave: Cobre, Óxidos de Cobre Anodicamente Formados, Monocamadas Auto-Montadas de Ácidos Alcano-Fosfónicos, Ângulos de Contacto, Microscopia de Força Atómica, Curvas de Polarização

1. INTRODUCTION

Self-assembled monolayers, SAMs, are highly ordered and close packed layers formed by spontaneous adsorption of organic molecules onto solid substrates, as schematically represented in Fig. 1. The high stability and organiza-

tion is due to chemical bond between the head group (e.g. thiol, disulphide, phosphonate) and the solid substrate and to the Van der Waals interactions between the tail group (alkylchains) [1]. A functional group can be bind to the

tail group which can be important for the interaction of the monolayer with the environment and, being electroactive, also allows the electrochemical characterisation of the SAM [2].

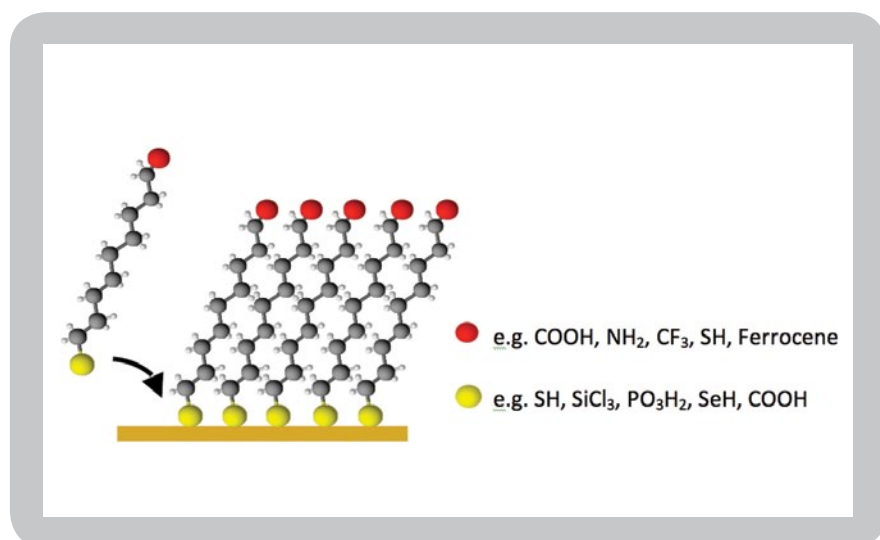


Fig. 1 – Schematic representation of a self-assembled monolayer on an electrode surface.

For the last decade, there has been an increasing interest in the preparation of monolayer structures with thickness controllable at molecular level using self-assembly with different functional subunits. There are a large variety of applications for these systems, from electronic devices [3] to sensors and biosensors [4,5], electrocatalysis [6], and of course corrosion protection [7,8], as it is the current purpose. The formation of a densely packed structure, consists on a barrier to the transport of oxygen and water to the surface, and therefore contributes to avoid the metal corrosion. Depending on the terminal group better protection can be achieved; hydrophobic terminal groups, causes a reduction in the contact area of water with the surface due to the repulsion of water molecules [9]; the thickness of the film can also be tailored by design and synthesis of adsorbates [10]. The presence, stability and organisation of SAMs are usually assessed using spectroscopic methods [11], X-ray diffraction [12] and XPS [13], but in what concerns their ability for corrosion protection, contact angle measurements [14,15], electrochemical information retrieved from different methods, such as cyclic voltammetry [16], polarization curves [17] and impedance spectroscopy [18], as well as scanning electronic microscopy (SEM) [19] or atomic force microscopy (AFM) [20] to analyse the surface morphology, are the most employed.

It is well known that reactive metals exposed to the environment suffer rapid oxidation with an increase in surface roughness [21]. Besides the metal surface pre-treatment, which influences the amount of oxide and the surface morphology [21], the self-assembly process is influenced by the possible reactions among the metal and the substances present in the adsorption solution, including the solvent [22]. For instance, for alkylthiols, it has been reported that ethanol has a negative effect on SAM formation on copper, due to its chemical reactivity towards this metal [23]. Notwithstanding, providing appropriate solvent and thiol concentration, high-quality alkylthiol SAMs might be formed on thin Cu oxide layers [24]. Another interesting comparison is between different linking groups. As thiols, selenol molecules act as a cleaner and reduce the copper oxide before adsorption. Recent work has shown the effect of selenol compared to thiol when they react with oxidised electroplated copper [25]. In what concerns the corrosion protection ability, polarisation curves carried out in aggressive environment containing chloride showed that the corrosion current density is about 50 times lower than shown by the unprotected substrate whereas the pitting corrosion potential is displaced towards more anodic value by about 300 mV [25]. Also, thiol and phosphonic acid molecu-

lar anchors have been employed to protect ZnO [26]. The hexane phosphonic acid modified surface is more uniform and hydrophobic (contact angle $\pm 115^\circ$) than the correspondent prepared with the thiol.

In the present work, to illustrate the corrosion protection properties of SAMs, the behaviour of copper, naked and anodically oxidised at different potentials, is contrasted to that shown by the samples coated with decane-phosphonate monolayers produced from butanol solutions. The change in the contact angle, AFM imaging and polarization curves in alkaline solutions have been used in this study.

2. METHODOLOGY

All the chemicals were analytical grade and used as received, and the aqueous solutions were prepared with Millipore-Q water (nominal resistivity of 18 M Ω at 25 °C).

The cyclic voltammetric measurements were performed on a potentiostat (Wenking LB 75L) with a voltage scan generator (Wenking VSG83), coupled to a Recorder X-Y Model 2000 (The Recorder Company) and the polarisation curves were carried out using a PAR-STAT 2263 (Perkin Elmer) potentiostat controlled by a computer which makes use of a PowerSuit software. For all the electrochemical studies a one-compartment Teflon cell was used. Copper slides were used as working electrodes, with an exposed area of 0.57 cm², while a Pt foil (1 cm²) and a saturated calomel electrode (SCE) were employed as counter and reference electrode, respectively. Before each experiment, a mirror-finishing copper surface was obtained by hand-polishing the electrode in diamond paste and aqueous suspension of successively finer grades of alumina (from 5 down to 0.3 μ m), rinsed with ethanol and water, ultrasonically cleaned in Millipore-Q water, and then dried using a N₂ (purity > 99.99997%) flow. All the solutions were deoxygenated directly in the electrochemical cell with a stream of N₂ for at least 20 minutes prior to each experiment and the measurements

were carried out at room temperature.

The copper substrate was characterised in a 0.1 M NaOH (Panreac), solution by cycling the potential from -1.300 V to +0.300 V, at a scan rate of 20 mV s⁻¹.

The anodically oxidised copper surfaces were attained in the same alkaline solution by linearly scanning from -1.300 V to -0.350, -0.150 and 0.060 V, and waited for 5 seconds at these final potentials till the current densities reached the value of 0 mA cm⁻².

The different copper surfaces were immersed for 18 hours in 1 mM butanolic solutions with decane-phosphonic acid, CH₃(CH₂)₉PO₃H₂, especially synthesised for self-assembling, and illustrated in Fig. 2. After self-assembling the modified substrates were thoroughly rinsed with butanol and Millipore-Q water and kept under N₂ till further use.

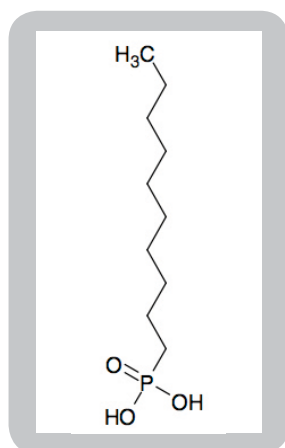


Fig. 2 – Decane-phosphonic acid [CH₃(CH₂)₉PO₃H₂].

The contact angles of water on the different copper substrates were measured by the Sessile drop method using a Contact Angle Measuring Instrument DSA30 (Krüss Co., Germany), at room temperature. Millipore-Q water droplets (about 1 µL) were dropped automatically onto the sample surface by a computer-controlled system. The average contact angles were obtained with a maximum error of measurement of ± 3°.

The morphology of bare and modified copper electrodes were also examined by tapping mode Atomic Force Microscopy, using a Nanoscope IIIa Multi-mode AFM (Digital Instruments, Veeco). The AFM images were obtained in air

at room temperature, using etched silicon tips (TAP-300, BudgetSensors) with a resonance frequency of ca. 300 kHz. The images were taken at scan rate of ca. 1.8 Hz.

The polarisation curves of the copper surfaces in 0.5 M NaCl (Merck) solutions were performed using a potential range of 250 mV, regarding the open circuit potential, at a scan rate of 0.166 mV s⁻¹.

3. RESULTS AND DISCUSSION

The typical electrochemical response of a polished copper substrate in 0.1 M NaOH solution is shown in Fig. 3, and is in agreement with the widely accepted behaviour reported in the literature [27-29]. The first oxidation processes (peak I), corresponds to the formation of a Cu₂O layer, followed by the generation of Cu (II) species associated with the formation of CuO (peak II) and of a mixed layer of CuO/Cu(OH)₂ (peak III) at higher potentials [30]. On the reverse scan the cathodic processes IV and V are attributed to the reduction of Cu (II) species to Cu (I) and of Cu (I) back to metallic copper, respectively. In order to study the protection ability of a phosphonic acid SAM on copper substrates with distinct oxide layers, the electrode potential has been swept, at 20 mV s⁻¹ from -1.300 to -0.350 V (peak I), -0.150 V (peak II) and 0.060 V (peak III), and waited at the final potentials approximately 5 seconds till the current reaches zero value.

Before SAM deposition the polished copper electrode as well as the anodically

modified copper surfaces have been morphologically characterised by AFM and through the measurement of water contact angles, as illustrated in Fig. 4.

It is clear that the imposed electrochemical conditions deeply influence surface topography and respective roughness of copper substrates, as revealed by the AFM images and also by the root-mean square roughness values, R_q. In the case of Cu₂O globular features, with distinct diameters (15 to 150 nm) can be denoted; however, the most drastic differences regarding bare polished copper surface are obtained immediately upon Cu (II) species generation [22,27,28]. The appearance of elongated structures, together with triangular and globular crystallites are responsible for the increase in surface roughness (R_q = 16 nm). At higher potentials, where the presence of a mixed CuO/Cu(OH)₂ layer is expected, the surface becomes smoother, possibly due to the process of redissolution/precipitation of copper corrosion products [27,29].

The water contact angle obtained for the copper surface immediately after polishing reveals the hydrophobic nature of this metallic substrate; the value decreases when Cu₂O is present and the surface becomes even more hydrophilic after CuO and CuO/Cu(OH)₂ formation, confirming the different copper oxidation states electrochemically generated.

The naked and anodically modified copper electrodes were also characterised by AFM and water contact angle measurements, after immersion in a butanolic solution of decane-phosphonic acid

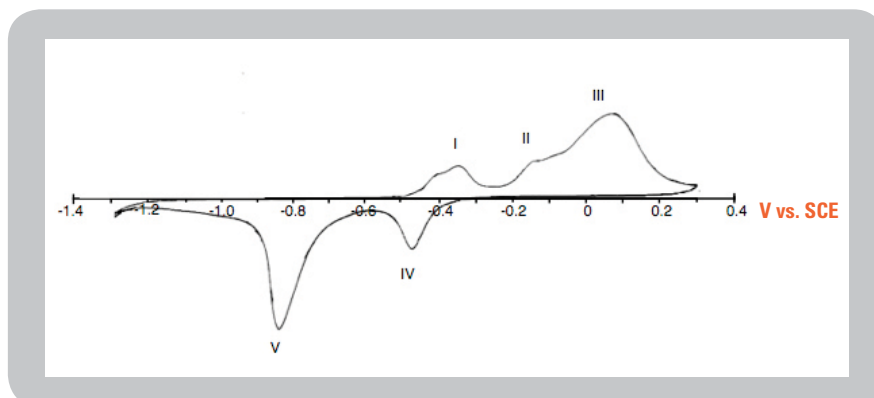


Fig. 3 – Cyclic voltammogram obtained for a polished copper surface in 0.1 M NaOH, between -1.300 and 0.300 V, at 20 mV s⁻¹.

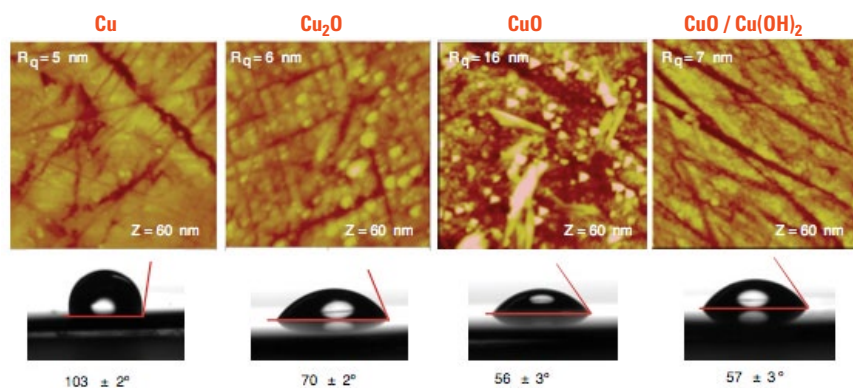


Fig. 4 – AFM images ($2 \times 2 \mu\text{m}^2$), root-mean square roughness (R_q) and water contact angle values obtained for bare and anodically oxidised copper at different potentials.

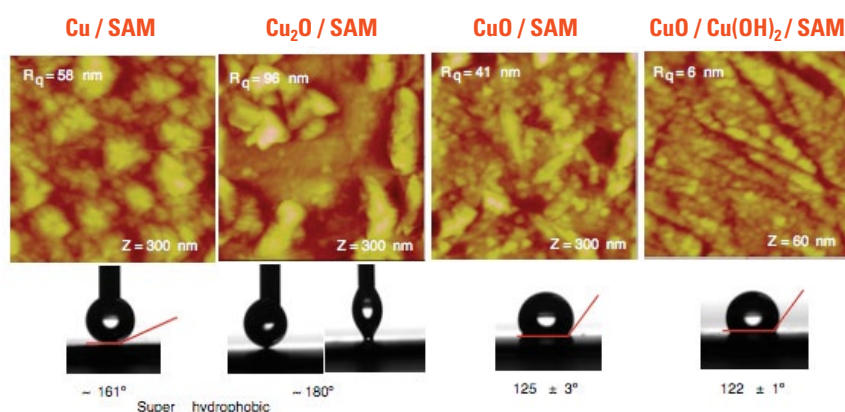
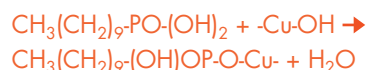


Fig. 5 – AFM images ($2 \times 2 \mu\text{m}^2$), root-mean square roughness (R_q) and water contact angle values obtained for bare and anodically oxidised copper at different potentials, modified with a $[\text{CH}_3(\text{CH}_2)_9\text{PO}_3\text{H}_2]$ SAM.

(Fig. 5). The presence of a hydrophobic top layer after the self-assembling process is undoubtedly revealed by the general increase of contact angle values, even for the more hydrophilic layers [CuO and $\text{CuO}/\text{Cu(OH)}_2$]. In fact, for bare copper and Cu_2O surfaces a super hydrophobic behaviour could be observed (contact angle $> 160^\circ$). After the self-assembling deposition the more accentuated morphological changes (Fig. 5), namely in terms of a roughness increase, is achieved for the super hydrophobic surfaces, which could be explained by the adsorption process of the phosphonic acid molecules on bare copper and Cu_2O . In spite of the great improvement of the water contact angles observed for CuO/SAM and $\text{CuO}/\text{Cu(OH)}_2/\text{SAM}$, 125° and 122° , respectively, the topography is only affected in the first case, where R_q value changed from 16 to 41 nm. When mixed oxides are present, in particular

hydroxyl species, the surface roughness is practically unchanged upon the adsorption of phosphonic acid, indicating that in this case a monolayer is most probably deposited. In fact, it has been reported that phosphonates undergo a condensation reaction with surface bound copper-hydroxyl species establishing a bidentate interaction, as confirmed by XPS [15], through the formation of Cu-phosphonate and H_2O . In the present work the adsorption of phosphonate SAM should follow the reaction:



The water contact angles obtained in this work for the CuO/SAM and mixed $\text{CuO}/\text{Cu(OH)}_2/\text{SAM}$ agree with the reported value ($119 \pm 2^\circ$) for chemically induced copper oxides, by exposure of the bare electrode to hydrogen peroxide, also modified with decane-phos-

phonic acid [15].

The protection ability of self-assembled phosphonic acid films on bare and anodically prepared copper oxides has been investigated electrochemically through the plot of polarisation curves in NaCl, as illustrated in Fig. 6. The electrochemical parameters, E_{corr} and i_{corr} , obtained from the Tafel slopes of Fig. 6 are compiled in Table 1.

There is a significant increase in the corrosion potential of the bare copper after immersion in the phosphonic acid solution, in agreement with the presence of a super hydrophobic surface, as revealed by the contact angle measurements. However, regarding the Cu_2O substrate (Fig. 6a) there is only a slight decrease in i_{corr} and no difference on E_{corr} after being modified with the phosphonic layer, even though there is a slight improvement on the corrosion potential relative to the bare copper surface. The weak protection verified in the case of the $\text{Cu(I)}/\text{SAM}$ is apparently in contrast with the super hydrophobic behaviour observed for this modified surface. This might be explained by the presence of porous layer permeable to the chloride ions [27,31,32], with weekly bounded phosphonic acid film, since as mentioned above, the chemisorption of phosphonates on oxidised copper is strongly dependent on the hydroxylation state of the oxide layer, and in this situation, the major copper species initially present is Cu_2O .

The polarisation curve obtained for the anodically modified CuO before self-assembling of phosphonates, shown in Fig. 6b, clearly revealed that the presence of this oxide, containing Cu^{2+} and O^{2-} species, increases copper corrosion. After modification by adequate immersion in phosphonic acid solution, even though the corrosion potential remains practically unchanged, there is an increase of i_{corr} indicating that SAM does not provide an effective protective barrier. A distinct behaviour was achieved for the $\text{Cu}/\text{CuO}/\text{Cu(OH)}_2$ (Fig. 6c): there is a drastic increase of the E_{corr} after decane-phosphonic acid deposition, revealing that, in this particular case with hydroxyl species available at

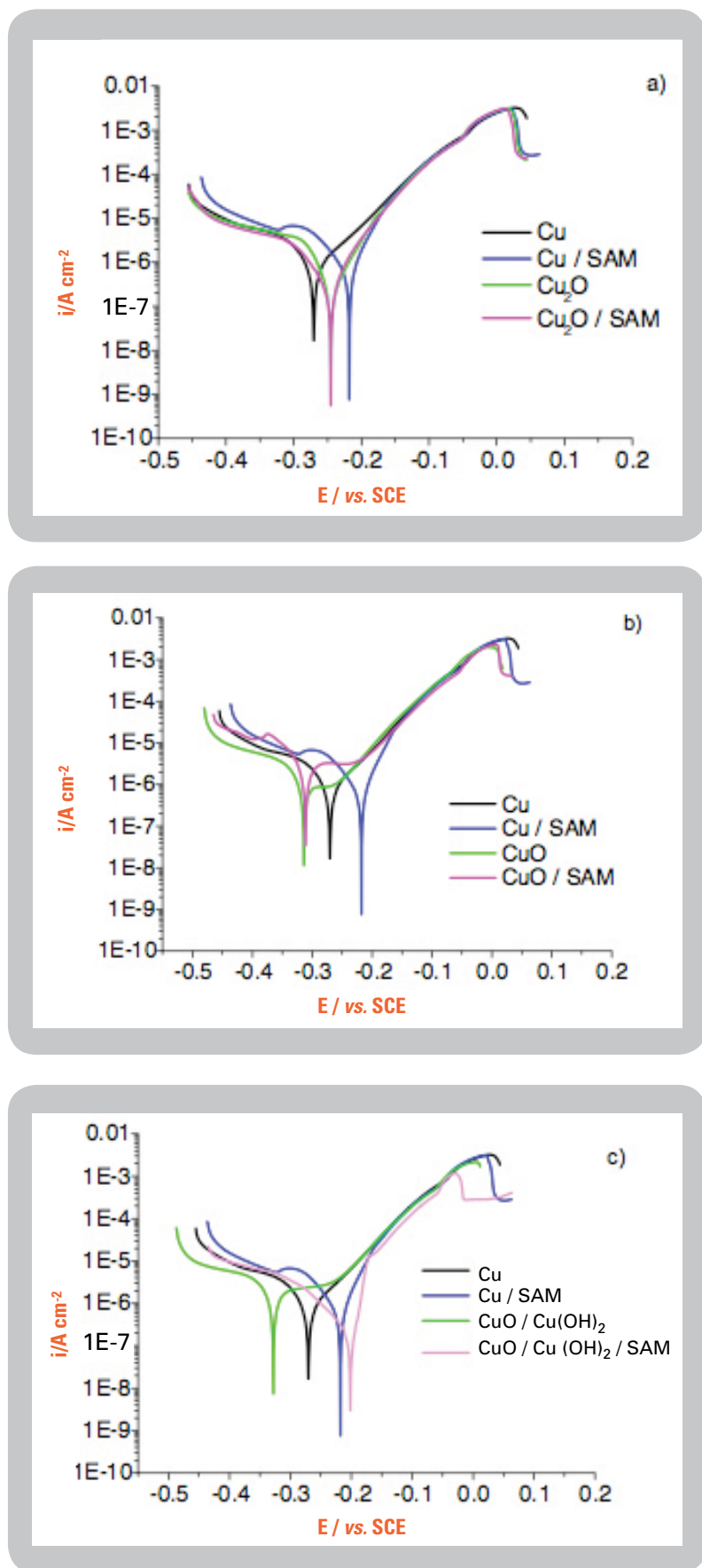


Fig. 6 – Polarisation curves of distinct copper modified surfaces in the presence and absence of decane-phosphonic acid layer in 0.5 M NaCl solution, a) Cu_2O ; b) CuO ; c) $\text{CuO}/\text{Cu}(\text{OH})_2$. Polarisation curves for bare copper in the presence and absence of phosphonic acid SAM are included in the graphs for better comparison.

the surface, chemisorption is favoured and should occur with the formation of densely packed layers, clear protecting the copper substrate.

4. CONCLUSIONS

A comparative study on the protection ability of self-assembled monolayers of a decane-phosphonic acid onto bare and controlled anodically oxidised copper surfaces has been here reported. The morphological characterisation by atomic force microscopy and water contact angle measurements have confirmed the formation of the distinct copper oxides. Upon modification by self-assembling of phosphonate molecules the surfaces became rougher and very hydrophobic, in particular bare Cu/SAM and $\text{Cu}_2\text{O}/\text{SAM}$ exhibited contact angles greater than 160° . A distinct morphological behaviour was obtained for the $\text{Cu}/\text{CuO}/\text{Cu}(\text{OH})_2/\text{SAM}$ since its surface roughness was practically unchanged after SAM adsorption, even though its water contact angle has increased significantly. This was attributed to the favoured interaction between phosphonic acid and surface hydroxyl groups, regarding the O^{2-} species present in other oxides (Cu_2O and CuO), with the formation of compact monolayers. The protection proficiency of $\text{CuO}/\text{Cu}(\text{OH})_2/\text{SAM}$ modified copper electrode has been clearly demonstrated by polarization essays in corrosive chloride medium, where a large positive shift of the corrosion potential together with a decrease in the i_{corr} was observed. A lower but still significant improvement was also observed for the direct deposition of phosphonic acid SAM on bare Cu, while the presence of phosphonate films in Cu_2O and CuO does not apparently inhibit the corrosion process of the underlying copper. This study reveals the potential application of this simple and efficient procedure to protect naturally oxidised copper surfaces containing both oxide-hydroxide species.

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Table 1- Corrosion potential (E_{corr}) and current density corrosion values (i_{corr}) obtained for the bare and anodically oxidised copper substrates in the presence and absence of decane-phosphonic acid SAM in 0.5 NaCl.

Substrate	E_{corr} (V vs. SCE)	i_{corr} (A cm^{-2})
Bare Cu	-0.268	2.0×10^{-6}
Cu / SAM	-0.218	2.1×10^{-6}
Cu_2O	-0.244	2.2×10^{-6}
Cu_2O / SAM	-0.244	1.5×10^{-6}
CuO	-0.314	7.7×10^{-7}
CuO / SAM	-0.311	1.8×10^{-6}
CuO / $\text{Cu}(\text{OH})_2$	-0.282	2.5×10^{-6}
$\text{CuO}/\text{Cu}(\text{OH})_2$ / SAM	-0.202	2.1×10^{-7}