Electrochemistry of copper in methanolic solutions: Anodic oxidation and fabrication of hydrophobic surfaces

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In the present study, hydrophobic surfaces have been fabricated in a one-step electrochemical process by anodic polarization of copper substrates in methanolic myristic acid solutions at relatively high applied potentials. These solutions have also been modified by the addition of tetraethylammonium tetrafluoroborate as a supporting electrolyte to improve their electric characteristics and enable the same fabrication in drastically milder working conditions. To elucidate the mechanism through which this fabrication occurs, various techniques, namely cyclic voltammetry, linear sweep voltammetry, chronoamperometry and electrochemical impedance spectroscopy, have been employed. The processes taking place during anodic oxidation of copper in methanol are electrodissolution and surface species formation depending on the presence of dissolved oxygen. Current oscillations resulting from the presence of these surface species have also been observed.

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1. Introduction

A number of electrochemical processes are accomplished in methanolic solutions, especially when the reactants are not readily soluble in water. Methanol is an amphiprotic solvent and exhibits the self-ionization reaction similarly to water [1],

\[ \text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^- + \text{CH}_3\text{OH}_2^+ \]  

(1)

According to the literature [2], the electrochemical window of methanol is about 2 V, with a cathodic limit determined by the hydrogen evolution reaction,

\[ 2\text{CH}_3\text{OH}_2^+ + 2\text{e}^- \rightarrow \text{H}_2 \text{+ 2CH}_3\text{OH} \]  

(2)

The anodic limit of the electrochemical window strongly depends on the anode material. Hence, for noble metals, it is determined by the methanol oxidation reaction, which can occur through several steps and reaction paths [3–6], and can be represented by the total reaction,

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]  

(3)

On the other hand, for electrodissolving metals, the anodic limit depends on the redox potential of the metal, the rate of electrodissolution, the formation of alkoxide precipitants etc.

Alcoholic solutions of saturated fatty acids, together with appropriate inorganic cations are often used for the fabrication of hydrophobic layers by a one-step cathodic process. Hydrophobic surfaces are characterized by static water contact angle above 90° while superhydrophobic surfaces have a contact angle of above 150°. The hydrophobic property is a result of the combination of specific surface morphology and chemical composition of the layer. In the case of cathodic fabrication, the resulting layer is an organo-metallic salt composed by the organic anion and the inorganic cation provided from the solution. The fatty acids commonly employed are stearic and myristic acid and the inorganic salts are lanthanum(III), nickel(II), manganese(II), and cobalt(II) chlorides [7–10].

In many cases, though, the anode material is the reactant itself. An example, which is of interest in the present study, is the fabrication of hydrophobic or even superhydrophobic surfaces on metals in a single step, either spontaneously upon immersion [11–14] or by anodic polarization [15–19]. By employing the second procedure, an organo-metallic hydrophobic layer is formed on the metal substrate. The metal to be covered by the hydrophobic layer is immersed in a methanolic solution containing the intrinsically hydrophobic organic compound that provides the anion of the corresponding organo-metallic salt and it is polarized anodically. Anodic polarization of the metal anode promotes the
electrodissolution of the metal and the formation of metal cations in the vicinity of the electrode. When the solubility product of the organo-metallic salt is satisfied, the salt precipitates on the metal substrate thus forming the hydrophobic layer. Due to the relatively low electrodissolution rate and the high ohmic resistance of the methanolic solutions, this method requires an applied potential difference of up to 100 V for several hours in order to fabricate a layer of about 1 cm² area and 20 μm thickness (details concerning the fabrication of copper myristate hydrophobic layers are presented in Sec. 3).

As shown in the next sections, this one step process becomes possible in milder conditions, in terms of applied potential, by improving the electric characteristics of the electrolytic solution. Moreover, the addition of a supporting electrolyte permits the study of the process by conventional electrochemical techniques. Thus, the effect of the addition of a supporting electrolyte is studied, both on the operating conditions and the resulting hydrophobic layer in a system consisting of a copper anode and a methanolic solution of myristic acid. In order to elucidate the process, an electrochemical study is required to determine the occurring reactions depending on the anode material (copper), the solvent (methanol) and the combination of both. For this purpose, cyclic voltammetry, linear sweep voltammetry, chronoamperometry and electrochemical impedance spectroscopy are employed.

2. Experimental

Two electrode experiments were performed in a homemade setup consisting of a copper anode (geometric area A = 1 cm²) and a platinum mesh as the cathode. The distance between the two electrodes was 2 cm and the volume of the methanolic solution about 20 mL. The potential difference between the two electrodes was controlled by a potential source.

Three electrode experiments were performed using a PAR RDE0018 Analytical cell kit. A Cu disk electrode (99.9% Alfa Aesar) of geometric surface area A = 0.0176 cm² embedded in an epoxy cylinder was employed as the working electrode. A Pt wire (99.95% Alfa Aesar) served as the counter electrode whereas an Ag/AgCl (sat. LiCl in ethanol) was used as the reference electrode. All measured potentials in this study are reported versus this electrode, having a potential of 0.143 V at 25 °C vs. the SHE. Prior to each experiment the working electrode was polished by a series of wet SiC sandpapers. The final polishing was performed using methanol instead of water to minimize the oxidation of the copper surface. The pretreated electrode was washed with methanol and transferred to the cell while keeping a droplet of methanol on the surface. The reproducibility of the surface pretreatment was ensured by the appearance of cyclovoltammetric peaks of similar current densities at the same electrode potentials.

Linear sweep voltammetry, cyclic voltammetry and chronoamperometry where performed with a BioLogic SP-150 potentiostat (EIS-capable with a low-current option). Stereoscopic images where acquired using a Leica MZ6 stereoscope equipped with a Leica DFC290 camera. SEM images where acquired using a FEI QUANTA 200 SEM with an Energy Dispersive X-ray (EDX) spectroscopy option. XRD measurements were performed by a Siemens D-5000 XRD with monochromatic Cu-Kα radiation source. FT-IR spectra were obtained by a Jasco 4200.

Methanol (analytical reagent grade, Fischer Scientific, with water content 0.014%) was used as the solvent and tetraethylammonium tetrafluoroborate, Et₄NBF₄ (99%, Alfa Aesar) as the supporting electrolyte. Myristic acid was purchased by Dae Jung Reagents Chemicals (98.5%) and sulfuric acid from Fisher Scientific (>95%, analytical reagent). The solutions were naturally aerated or, when mentioned, deaerated by nitrogen purging for at least 20 min.

3. Results and Discussion

Hydrophobic surfaces of copper myristate are typically produced in a two electrode arrangement consisting of a copper anode and an appropriate cathode [15–19]. An example of a hydrophobic surface produced using a copper anode (geometric surface area A = 1 cm²) and a Pt cathode in a methanolic solution of 0.1 M myristic acid (specific conductivity 25.1 μS/cm) at 20 °C is presented in Fig. 1. This rather uniform characteristic blue layer is fabricated by applying a potential difference of 100 V for 9000 s. The current density during electrolysis (after some initial transients) was constant at about 0.8 mA/cm². FT-IR and XRD measurements, Fig. 2, indicate that the layer consists of copper(II) myristate [15], produced possibly through the precipitation reaction, Eq. (5), following the dissolution of copper, Eq. (4).

\[
\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \tag{4}
\]

\[
\text{Cu}^{2+} + \text{CH}_3\text{(CH}_2\text{)}_{12}\text{COO}^- \rightarrow \text{Cu(CH}_3\text{(CH}_2\text{)}_{12}\text{COO})_2 \tag{5}
\]

As can be seen from the SEM images, the layer features a “star-like” structure having a characteristic length of 5–10 μm. This kind of structure along with the intrinsic hydrophobic properties of the organic part of the salt are responsible for the hydrophobic properties of the surface since it is capable of trapping air, thus impeding the contact of water with the metal substrate [20,21].

Even though the layer is generally uniform, some flaking defects can be observed, Fig. 1 (a). These flaking defects permit an estimation of the layer thickness at about 20 μm from SEM images. The mean wt% composition of the layer, as determined from EDX analysis, is 76% C, 14% O and 10% Cu. These values support the hypothesis that the layer consists of copper(II) myristate. An image.
of a 10 µL water droplet on the hydrophobic surface is shown in the inset of Fig. 1 (b). The static water contact angle, as estimated by a homemade setup, is 145°.

The fabrication of this hydrophobic surface can be accomplished in milder conditions, in terms of applied potential, by increasing the conductivity of the solution by the addition of a supporting electrolyte. A cyclic voltammogram in the potential region from 0.27 to 1.2 V of a system consisting of a copper working electrode (geometric area A = 0.0176 cm²), a Pt wire counter electrode and a methanolic solution of 0.1 M myristic acid, 0.1 M tetraethylammonium tetrafluoroborate (Et₄NBF₄) with specific conductivity 6 mS/cm is presented in Fig. 3 (a). The first cycle, n = 1, for a scan rate of 10 mV/s, consists of an anodic peak at 0.97 V during the forward scan and an anodic peak at 0.78 V during the backward scan. These features disappear for the following cycles, n > 1, while the cyclic voltammogram consists of a monotonically increasing (decreasing) current during the forward (backward) scan. The chronoamperogram of this system for E = 0.5 V is presented in the inset of Fig. 3 (a). As can be seen, the current rapidly attains the value of 3.5 mA/cm², resulting in a blue hydrophobic layer (see Fig. 3 (b)). The layer has the desired “star-like” structure, presented in Fig. 3 (c). An image of a 10 µL water droplet on the hydrophobic surface is shown in the inset of Fig. 3 (c). The static water contact angle is 141°. It is evident that the micro-nano structure as well as the hydrophobic character of the layer are preserved under these conditions.

The processes taking place during the anodic oxidation of copper in methanol can be elucidated by performing cyclic voltammetry in the region from 0.27 to 1.2 V in the absence of myristic acid. In this potential region the current attains only positive values. A typical example is presented in Fig. 4 (a) for a scan rate of 5 mV/S. During the first cycle (black curve, n = 1) of a freshly polished copper electrode, an anodic peak appears at 0.83 V during the forward scan, followed by an anodic peak at 0.58 V during the backward scan. While the number of cycles increases, both transitions from high to low current densities and vice versa tend to coincide at E = 0.75 V (red curve, n = 6). These transitions are rather abrupt and resemble those of an active/passive transition, poisoning or transition due to precipitation. In addition, the color of the copper surface turns from typical reddish to yellow during the first cycle (even at low current densities) and remains yellow during anodic cycling. This yellow color resembles the color of cuprous oxide, Cu₂O, which can be formed anodically in the

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**Fig. 2.** (a) FT-IR spectrum and (b) XRD pattern of a hydrophobic surface of copper myristate on copper after 9000 s of electrolysis at 100 V.

**Fig. 3.** (a) Cyclic voltammogram of copper in 0.1 M myristic acid, 0.1 M Et₄NBF₄ in methanol. Scan rate v = 10 mV/s. The arrow indicates increasing number of cycles n. Inset: Chronoamperometric curve for E=0.5 V in the same solution. (b) Stereoscopic image and (c) SEM image of the hydrophobic surface corresponding to the chronoamperometric experiment. Inset: water droplet of 10 µL on the hydrophobic surface.

**Fig. 4.** Cyclic voltammogram of (a) copper in methanol, black curve: first cycle, red curve: sixth cycle. Blue curve: Platinum in methanol. Supporting electrolyte 0.1 M Et₄NBF₄. (b) Copper in methanol containing 0.5 M H₂SO₄. Full line: forward scan, dashed line: backward scan and scan rate 5 mV/s in all cases.
The anodic cyclic voltammograms could be attributed to the oxidation of methanol on the Cu electrode. Actually, the potentials where the oxidation peaks and transitions are recorded are rather similar to those observed for the oxidation of aqueous solutions of methanol on noble metals [4–6]. Moreover, oxidation of formaldehyde and methanol has been observed on copper electrodes, but in rather strong basic aqueous solutions of the corresponding organic molecules [25,26]. However, the hypothesis of methanol oxidation in the present system cannot be supported if the cyclic voltammogram of Fig. 4 (a) is compared with the one of Fig. 4 (b), where the methanolic solution is acidic, containing 0.5 M H2SO4 (specific conductivity 32.2 mS/cm at 20 °C). It can be noticed that in acidic methanolic solutions there is no evidence of surface blockage during anodic oxidation of the copper electrode as well as no sign of methanol oxidation in this potential region [27]. The high current densities observed in this case are attributed to the active dissolution of the copper anode. A similar conclusion can be drawn by comparing the cyclic voltammograms of Cu (black and red curves) with that of Pt (blue curve) in methanol, containing 0.1 M Et4NBF4, Fig. 4 (a) for a scan rate of 5 mV/s. As can be seen, in the anodic potential region extending up to 1.2 V, there is no evidence of an oxidation process on Pt at any considerable rate while the anodic current density does not exceed the value of 0.06 mA/cm2. Thus, it can be concluded that the processes corresponding to the cyclic voltammograms of copper in Fig. 4 (a) are due to the oxidation of the Cu electrode only. The oxidation of copper can lead to either the formation of copper oxides in the presence of an oxidant together with metal cations or the precipitation of alkoxides due to the reaction of metal cations (produced by electrode dissolution) with the alkoxide group in the solution [28–30].

The formation of surface species on the copper surface due to anodic oxidation can be explored by performing cathodic linear sweep voltammetry after anodic oxidation. Such cathodic linear sweep voltamograms of different scan rates, v, obtained by independent experiments are presented in Fig. 5 (a). The voltammetric curves have been recorded after an anodic scan from open circuit potential to 0.5 V, followed by a potentiostatic oxidation (potential hold) at this potential for t0 = 60 s. In this figure, the anodic cyclic voltammogram for v = 20 mV/s (obtained by an independent experiment) is also included for reasons of comparison.

As can be seen, an intense cathodic peak C1 is observed at the potential region from -0.8 to -1.1 V, with peak potential Ep depending on the scan rate, its value being more cathodic as v increases. Additionally, the peak current Ip also depends on v, its absolute value increasing as v increases. The mean charge corresponding to the cathodic peak is Qc = 76.5 mC/cm2, as determined by dividing the peak area by the scan rate. The corresponding concentration of surface species \( \Gamma^* \) is about \( 8 \times 10^{-7} \) g eq/cm², as determined by applying Faraday’s law. On the other hand, the mean charge corresponding to the anodic process is Qc = 962 mC/cm². The difference between the anodic and the cathodic charge is an indication that the anodic current at \( E = 0.5 \) V mainly corresponds to the electrode dissolution of the electrode surface whereas only a small amount corresponds to the formation of surface species.

Two additional peaks are observed during the cathodic scans, the least cathodic of which, C3, in the potential region close to 0 V and a more cathodic one, C2, close to -0.5 V. In order to determine the origin of the C3 peak, the voltammetric curve obtained for a scan rate of 40 mV/s directly after anodic oxidation at \( E = 0.5 \) V for \( t_0 = 60 \) s (solid curve in Fig. 5 (b)) is compared with the corresponding curve obtained after stirring (dashed curve in Fig. 5 (b)). Stirring is performed in order to homogenize the solution, thus removing dissolved species from the vicinity of the electrode. As can be seen, a homogeneous solution results in the disappearance of peak C3. Moreover, the cathodic peak C1 becomes smaller. The above facts indicate that peak C3 is due to the reduction of free (solution) species produced during anodic oxidation. These species are in turn reduced to the immobilized species which contribute to peak C1. An additional indication for the above scenario is that the charge corresponding to peak C3 is about 15 mC/cm² whereas the decrease of the charge corresponding to peak C1 is almost the same (11 mC/cm²).

A justification of the fact that the cathodic peak C1 corresponds to the reduction of surface species is the plot of the dependence of the peak current \( i_p \) on the scan rate, v. As can be seen in Fig. 6 (a), this dependence is linear, as expected for an irreversible reduction of immobilized species. The dependence of the peak potential (corrected for the IR-drop), \( E_p \) on the logarithm of the inverse scan rate is shown in Fig. 6 (b). The relation is linear with a slope of 0.059 V, serving as an estimate of \( \alpha_n \). An estimation of \( \alpha_n \) from the half-peak potential is 0.33. This underestimation is attributed to the deformation of the peaks at more cathodic potentials due to the occurrence of the hydrogen evolution reaction. The concentration of surface species \( \Gamma^* \) can be estimated from the slope \( \beta \) of the \( i_p \) vs \( v \) curve, based on the equation \( \beta = 0.368 \alpha_n F^2 AT^0/RT \). Assuming \( \alpha_n = 0.43 \) and taking into account the slope 4.15 \( \times 10^{-3} \) A s/V, an estimation of the surface concentration is \( 4 \times 10^{-7} \) g eq/cm². This value is close to the one determined from the reduction charges.

As shown in Fig. 4 (a), for potentials more positive than 0.75 V, the current attains a low value, indicating some kind of blockage of the electrode surface. The nature of the copper electrode surface for those anodic potentials can be explored by recording the

\[
2\text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^{-}
\]
chronocoulamperometric transients at 0.85 V, followed by cathodic linear sweep voltammetry. As can be seen in Fig. 7 (a), the chronocoulamperometric curves consist of two different stages. During the first stage, $s_1$, lasting for about $t_1 = 75$ s, the current attains a constant value of about 50 mA/cm$^2$. The second stage, $s_2$, appears after an abrupt transition to a low current value, between 6 and 10 mA/cm$^2$ and has a duration of $t_2$. It is evident that a rather slow process occurs during the stage $s_1$ producing surface species that impede the current flow.

The cathodic voltammetric curves, for $v = 20$ mV/s and for different durations $t_2$ of stage $s_2$ are presented in Fig. 7 (b). The anodic part of these curves seems to be, more or less, independent of $t_2$. Thus, at the beginning of the cathodic scan from 0.85 to -1.6 V, the current forms an anodic peak at $E \approx 0.63$ V. As the potential becomes more cathodic, three cathodic peaks are formed. The peak $C_1$ is identical to the one presented in Fig. 5 and thus must be associated with the surface species formed at stage $s_1$. The cathodic peak $C_4$ does not appear when anodic oxidation is performed at 0.5 V (see Fig. 5), thus it can be associated to surface species formed during stage $s_2$. It must be noticed that even though $t_1$ is almost the same across different anodic oxidations at 0.85 V, the charge corresponding to the $C_1$ peak decreases as $t_2$ increases. Finally, the peak $C_2$ still appears at potentials close to -0.5 V.

The appearance of the $C_4$ peak is an indication that new surface species are produced at high anodic potentials. Moreover the increase of $C_4$ current peak and the decrease of $C_1$ current peak indicates that during the anodic oxidation, new surface species are produced in expense of the previously formed surface species. The production of new surface species is proved by plotting the dependence of the peak current of $C_4$ as a function of $v$, after anodic oxidation at $E=0.85$ V for $t_0=300$ s, Fig. 7 (c). As can be seen in Fig. 7 (d), the dependence is linear, as it should be in the case of immobilized (surface) species. It must be also noted that in the experiments presented in Fig. 7, peak $C_3$ is actually absent indicating that the rate of electrolysis at high anodic potentials drastically decreases.

It is interesting to explore the oxidation processes at intermediate values of the anodic potential. A typical example of a chronocoulamperometric curve for $E=0.7$ V is presented in Fig. 8. It is evident that the current does not reach a steady state but oscillates almost periodically between stages. The oscillations are rather slow, having a period of about 200 s. Based on the previously presented data, the higher state of the oscillatory cycle

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**Fig. 6.** Dependence of (a) $C_1$ peak current versus the scan rate and (b) $C_1$ peak potential (corrected for the IR-drop) versus the logarithm of the inverse scan rate.

**Fig. 7.** (a) Chronocoulamperometric curves of copper in methanol for $E=0.85$ V for different oxidation intervals and (b) corresponding cathodic linear sweep voltammograms. (c) Cathodic linear sweep voltammograms after anodic oxidation at $E=0.85$ V for $t_0=300$ s and (d) corresponding dependence of $C_4$ peak current on the scan rate. Supporting electrolyte 0.1 M Et$_4$NBF$_4$. 

corresponds to the formation of surface species accompanied by a high rate of electrode dissolution whereas the lower state corresponds to the formation of new surface species and a low rate of electrode dissolution. Oscillatory electro-oxidation of copper under potentiostatic conditions has been reported for several aqueous electrolytic media, including chloride solutions [31–34], phosphoric acid [35], acetate solutions [36,37], trichloroacetic acid [38] and trifluoroacetic acid [39,40]. On the other hand, galvanostatic oscillations during the electro-oxidation of methanol have been also observed on noble metals [41,27] and direct methanol fuel cells [42]. The influence of Cu²⁺ ions on the oscillatory response during the oxidation of small organic molecules has been also observed in the past [43]. Preliminary experiments (not shown in this work) reveal that the oscillatory response persists in the presence of myristic acid, at least for low concentrations. There is some evidence suggesting that the hydrophobic properties of the resulting layer are inferior, but additional experiments are required in order to justify this preliminary observation.

The nature of the cathodic peak C2 has not been discussed so far. In order to identify the origin of this process, cyclic voltammetry was employed in the region from 0.1 to -1 V, presented in Fig. 9 (a). During the cathodic scan, the cathodic peak C2 is observed, with \( E_p \) and \( i_p \) depending on \( v \). The characteristics of this cathodic peak do not depend on the oxidation charge, as can be seen in Fig. 9 (b). In these curves, the electrode is oxidized at \( E = 0.1 \) V for different \( t_p \). Apparently, the reduction peak does not depend on \( t_p \), in other words, the reduction peak is not associated with the concentration of surface species resulting from the oxidation of copper at \( E = 0.1 \) V. Moreover, peak C2 can be associated with free (solution) species due to the fact that \( t_p \) varies linearly with \( v^{1/2} \) as can be seen in Fig. 9 (c). An additional indication of the reduction of free species during the C2 peak is the impedance spectra presented in Fig. 9 (d) for different cathodic potentials. It is evident that a diffusion process occurs together with a faradaic reduction at low cathodic potentials whereas at high cathodic potentials the faradaic reduction is rapid and the rate is controlled by diffusion.

As there is no other free species in the solution apart from the naturally dissolved oxygen during the experiments presented in Fig. 9, C2 peak is attributed to the irreversible reduction of these species according to the reaction,

\[
\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}
\]  

The equilibrium potential of this reaction is both pH, water and oxygen activity dependent. It is evident that this reaction can supply water in order to form cuprous and/or cupric oxides during the anodic oxidation of copper in methanol, even in the absence of water in the initial solution formulation. According to the above observations, copper immersed in the aerated methanolic solution can be considered as a mixed electrode where both copper oxidation and oxygen reduction occur at the same rate. This fact explains why copper oxides can be formed even in the absence of a cathodic scan, leading to the surface blockage presented in Fig. 4.
It could be argued that, since methanol has not been further purified prior to the experiments, traces of water would have the same effect as dissolved oxygen. However, removal of dissolved oxygen results in a complete different picture during the anodic oxidation and the cathodic reduction of Cu in a 0.1 M Et₄NBF₄ methanolic solution. As can be seen in Fig. 10, during the anodic oxidation by cyclic voltammetry with a scan rate of \( v = 20 \) mV/s and supporting electrolyte 0.1 M Et₄NBF₄, the current increases monotonically due to the active dissolution of copper in methanol. On the other hand, during the cathodic linear sweep voltammetry, immediately after anodic oxidation, there is no sign of reduction of surface species. The above experiments support the hypothesis that water resulting from dissolved oxygen is responsible for the oxidation of copper in methanol to surface species instead of traces of remaining water. The monotonic increase of current in the absence of dissolved oxygen also indicates that the formation of alkoxides in this potential region does not occur.

4. Conclusions

1. Hydrophobic surfaces based on methanolic solutions of myristic acid can be fabricated in mild conditions, when a supporting electrolyte is present. The resulting layers have the desired ‘star-like’ structure.

2. Hydrophobic surfaces can be fabricated for applied potentials where electrode dissolution of a passive layer is rapid.

3. High anodic potentials are not necessarily desirable for the fabrication of hydrophobic layers due to the blockage of the metal surface by insulating surface species.

4. The anodic oxidation of copper in methanolic solutions of a supporting electrolyte results in two types of surface species as well as electrode dissolution.

5. The anodic dissolution of copper in methanolic solutions of a supporting electrolyte exhibits an instability resulting in current oscillations. The oscillations have a large period and take place between two states, both involving the presence of surface species.

6. The surface species created during the anodic oxidation of copper in a naturally aerated methanolic solution may be similar to the ones observed during the anodic oxidation of copper in mild basic aqueous solutions.

7. Dissolved oxygen is responsible for the anodic oxidation of copper to its oxides.

8. The oxidation of copper in deaerated methanolic solutions results only in metal dissolution.

References


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