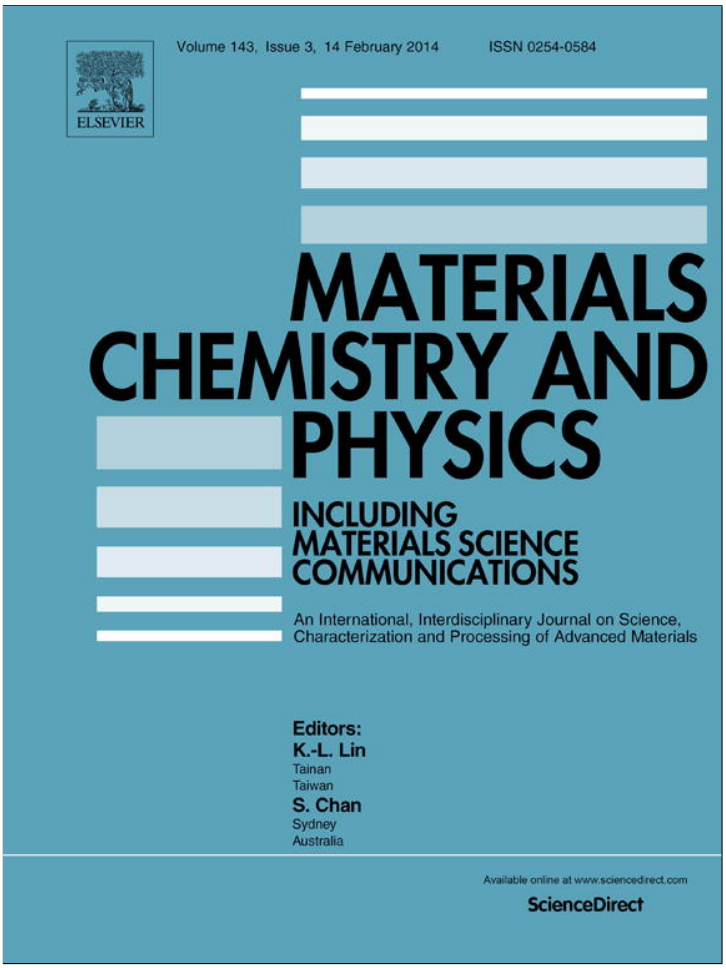

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Enhanced electrochemical oxidation of methanol on copper electrodes modified by electrocorrosion and electrodeposition

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HIGHLIGHTS

- We presented simple treatments to increase the response of copper electrodes.
- Copper electrodes were modified by electrocorrosion and electrodeposition.
- Scanning Electron Microscopy images reveal the effects of the different treatments.
- The response is enhanced by an area increase and/or intermediates concentration.
- For each treatment the concentration range of the diffusion control is analyzed.

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ABSTRACT

In this paper, we report a study of electrocatalytic oxidation of methanol on copper electrodes subjected to different surface treatments, either electrocorrosion or electrodeposition in the absence of strong hydrogen co-deposition. The surface morphology of treated electrodes was examined by Field Emission Scanning Electron Microscopy (FE-SEM). The effect of different treatment conditions and the methanol concentration dependence were evaluated by cyclic voltammetric technique. The results indicate that the oxidation of methanol can be enhanced by a suitable micro and nano structure generated by these treatments. This enhanced electrode activity is related to an increase of the effective surface area and/or to an increase of the surface concentration of electroactive molecules or intermediates.

1. Introduction

Fabrication of materials with specific functionalities in efficient three-dimensional architecture is still a great challenge. Metal electrodeposition is an efficient way of producing unique self-supported 3-D foams with highly porous structures [1–9]. The geometry is a critical factor in the development of porous materials for use as electrodes in electrochemistry applications [1,10–12]. It has been shown that an ideal porous electrode should have micro and nanoscale features, where the pore size in the bulk of the material decreases with the distance to the surface. Also, porosity on the nanoscale increases the surface area and electrode apparent activity [1]. While several electrochemical studies have been done on Pt, Pd, Au and Ag surfaces [2,5,8,13–15], copper has received smaller attention due to its high sensitivity and reactivity towards oxygen. Although metals such as Pt, Au and Ag are suitable electrodes for anodic oxidation and cathodic reduction, they are too expensive [10,14,16]. The catalytic activity of other metals was studied, such as nickel [17–20] or copper [21–32]. The catalytic action of copper has been reported to take place through the Cu(II)/Cu(I) redox couple. At a very high positive potential the Cu(III)/Cu(II) redox couple is involved instead [21,22]. Thus, the copper electrodes have been studied for practical applications. Copper is of particular interest due to its use in detection of carbohydrates and related compounds [23–29], nitrites [30], and heterogeneous catalysis for the oxidation of hydrocarbons [11,31]. The catalytic degradation of these compounds is a matter of concern for environmental control.

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Electrodeposition of copper at very high overpotentials in aqueous solutions results in the formation of porous foams with a huge concentration of dendrites. The deposition mechanism and the influence of the experimental conditions on copper morphology were investigated [33,34]. Because of its hierarchical structure, this kind of materials, which provides high specific areas for charge and mass transfers in electrochemistry, is important for technological applications in catalysis, fuel cells, batteries, sensors, etc. The potential of 3-D structures is very attractive, but key issues for practical applications of these structures still remain, including the control of the microstructure (such as pore size and wall density) for better utilization of internal surfaces.

The electrochemical oxidation of fuels requires the use of a catalyst to achieve the high current densities necessary for practical applications [35]. Among the different small organic molecules, methanol is considered an ideal molecular fuel because it is widely available and easy to handle and to store [14,36–38]: it is the basis for the design of a direct methanol fuel cell (DMFC) [10,14]. However, compared to hydrogen based fuel cells, DMFC still remains to be further developed to improve the kinetics of the anodic methanol oxidation [10,13,16].

The aim of this work was to develop a reliable and simple surface treatment to enhance the current response of copper electrodes. Electrodeposition and electrocorrosion of copper, which are attractive techniques because of their simplicity, low cost and possibility of making large area electrodes, were applied in different experimental conditions to obtain micro-nano structured surfaces for which the catalytic oxidation of methanol was evaluated. Cyclic voltammetric and amperometric techniques were used for this purpose.

2. Experimental

2.1. Reagents and instrumentation

Methanol and other reagents were of analytical grade without further purification. All solutions were prepared with Milli-Q water. Electrochemical measurements were carried out in a conventional three-electrode cell controlled by a μAUTOLAB type III potentiostat/galvanostat. The system was run on a PC using GPES software. Copper wires with a diameter of 0.5 mm were used as working electrodes. A copper sheet was employed as the counter electrode. In this way the area of the counter electrode was much larger than the area of the working electrode. Ag/AgCl (saturated KCl) served as reference electrode. This electrode showed a reproducible reference value before and after the experiments even in alkaline medium. All the potentials reported in this work are versus Ag/AgCl electrode. All experiments were performed at room temperature (25 ± 2 °C).

2.2. Preparation of modified copper electrodes

Copper wires were coated with an insulating polymeric resin so that only the wire section remained uncovered. The surface of the copper electrode was mechanically polished, first with sand papers 400 and 1200 and then with 0.5 μm, 0.3 μm and 0.05 μm alumina. Finally it was rinsed with Milli-Q water. Inset in Fig. 1a shows an image of the electrode after this preparation. Then, the electrode was placed in the treatment solution indicated in Table 1 which also summarizes current densities and types and times of treatments. The current density was calculated dividing the applied current by the geometrical area of the electrodes (i.e. approximately 0.2 mm^2).

The catalytic efficiency of the different electrodes was checked using 0.1 M NaOH solutions, with addition of 0–100 mM methanol. A single electrode was used for one series of measurements at different methanol concentrations. Afterward, new measurements were performed with 0 and 100 mM methanol, without significant change compared to previous ones. However, after a larger number of experiments (more than 15), the electrode response appeared to deteriorate somehow, evidencing a limited lifetime.

3. Results and discussion

3.1. Characterization of morphological properties

Fig. 1 shows the Field Emission Scanning Electron Microscopy (FE-SEM) images of copper wires after B, C and D treatments. The achieved morphology is different for each treatment, but the morphology achieved after D treatment differs more significantly from the two others. B treatment produces localized micrometric pores with nanometric roughness, evidencing pitting corrosion. Although the wire is also corroded in C treatment, its morphology is different from that achieved after B treatment; in particular, it produces fewer and smaller pores. D treatment generates micrometric irregular features and nanometric hierarchical structures that highly increase the surface area. Dendrites can be clearly seen for this treatment. Although the current density applied in this treatment was much larger than the estimated limiting current density (−0.02 mA mm^{-2}), no strong hydrogen evolution was observed, contrarily to experiments reported in Ref. [34]. Indeed, the typical “craters and holes” morphology reported in this paper was not observed in D treatment.

As mentioned in Section 2, all surface treatments were applied for 1000 s. Times of treatment larger or smaller than 1000 s were also investigated, but they did not give significant results: electrodes treated for 500 s were not markedly different from untreated electrodes, whereas electrodes treated for more than 1000 s appear to be unstable and the results were hardly reproducible. Altogether, current values and time of treatment were chosen in order to get the best catalysis improvement and reproducibility.

Following ref. [24], the electrochemical behaviors of treated copper electrodes were evaluated performing cyclic voltammetry (CV) carried out in a 100 mM phosphate buffer with pH 7. Voltammograms were measured just after electrode treatments. For all three treatments a reduction peak at about −0.100 V ($CuO \rightarrow Cu^0$) and an oxidation peak at about 0.050 V vs. Ag/AgCl were observed [39]. Fig. 2 shows the obtained voltammograms for A and D treatments. Table 2 summarizes the peak intensity ratios and the peak area ratios for B, C and D treatments: the intensity and the area of the peaks for B and C treatments are close to each other, and only slightly larger than those for the untreated electrode. On the other hand, they are much larger for D treatment, evidencing a greater increase of the electrode surface area.

Voltammograms were measured again before evaluation of catalytic methanol oxidation, which could be performed a few days later: no change was noticed, indicating a good stability of the electrodes.

3.2. Catalytic methanol oxidation

The thermodynamic potential for methanol oxidation to CO_2 lies very close to the equilibrium H^+/H_2 potential [13]. However, compared with hydrogen oxidation, this reaction is several orders of magnitude slower. As suggested [10,13] for electrooxidation of methanol a catalyst is required. This process, involving adsorption of methanol molecules, requires several adsorption sites at the surface of the catalyst: this should depend on its morphology. We will now present the results obtained for the different electrode treatments described above.

In this study, the electrodes, untreated and treated, were placed in 0.1 M NaOH and the electrode potential was cycled between

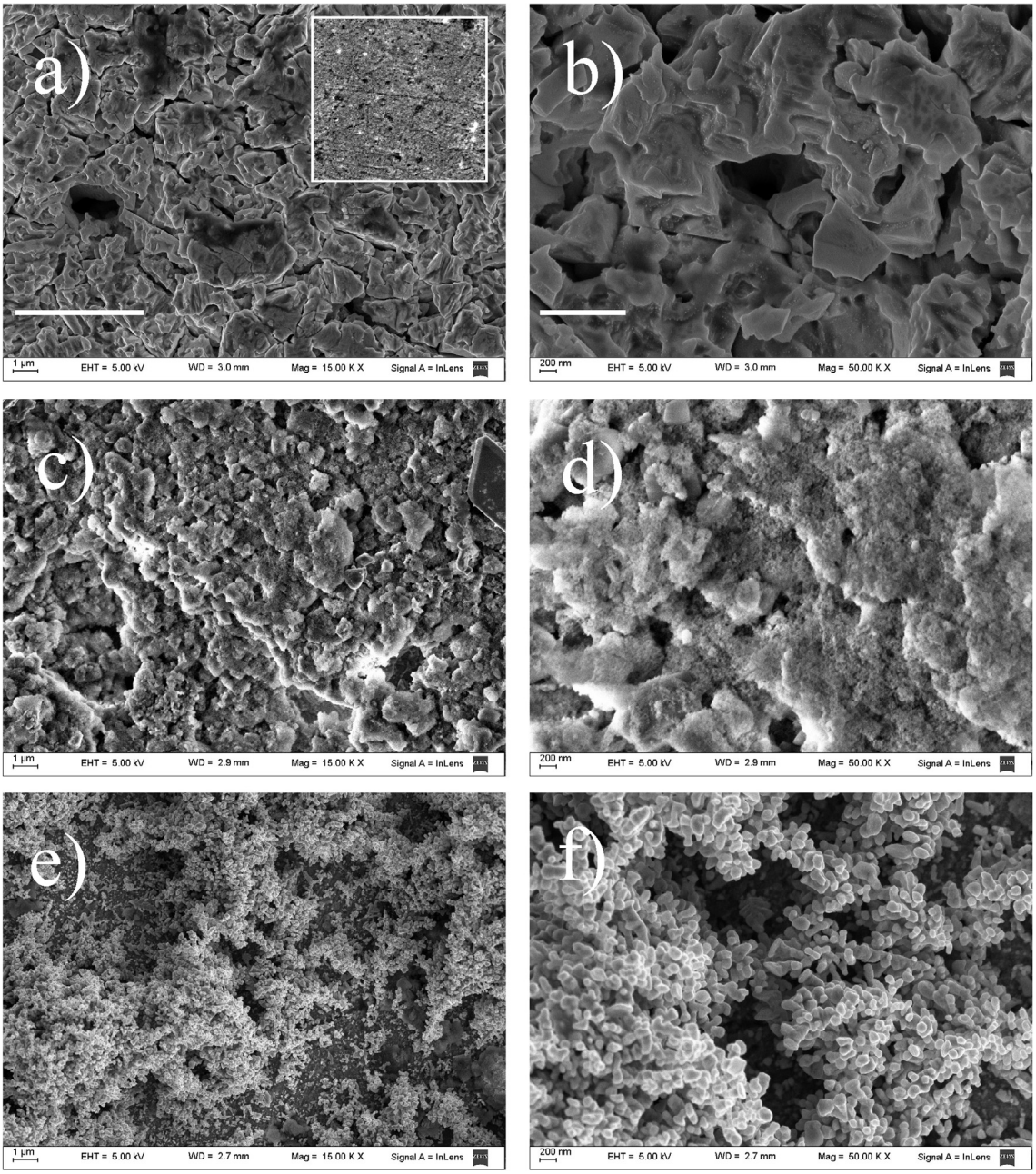

Fig. 1. FE-SEM images at two different magnifications: a) and b) B treatment; c) and d) C treatment; and e) and f) D treatment. The white bars shown in Fig. 1a and b are respectively 5 µm and 1 µm long. The same scale applies to Fig. 1a, c and e on the one hand, and to Fig. 1b, d and f on the other. Inset in a): untreated electrode surface.

0 and 1 V at a scan rate of 0.05 V s^{-1} for 2 cycles. See Figs. 3–5. The procedure was repeated after different additions of methanol, evaluating the current response at a potential of 0.75 V [10] for methanol concentrations ranging from 0 to 100 mM.

Table 1
Surface treatments.

Treatment	Type	Treatment solution	Applied *j*	Time
A	No treatment	–	–	–
B	Corrosion	KCl 10 mM/H_2SO_4 10 mM	0.51 mA mm^{-2}	1000 s
C	Corrosion	$CuSO_4.5H_2O$ 10 mM/H_2SO_4 10 mM	0.51 mA mm^{-2}	1000 s
D	Deposition	$CuSO_4.5H_2O$ 10 mM/H_2SO_4 10 mM	−0.51 mA mm^{-2}	1000 s

Fig. 3 shows the typical behavior for the electrodes obtained after the different treatments. All experiments were carried out in 0.1 M NaOH containing 40 mM methanol. The inset compares the response in regular and deoxygenated solutions for A and B treatments: both present the same behavior and current values are approximately the same, within experimental uncertainty. The response for B and D treatments is seen to be larger than the response for the untreated electrode, whereas the response for A and C treatments is very similar. The difference between B, C and D treatments will be analyzed further.

The role of Cu(III) species in the oxidation of organic substances [16,22,26] has been largely advocated. This species, which is generated at positive potentials in alkaline medium, has been reported to have the role of a redox mediator in the oxidation of several compounds on copper electrodes: the electrode reaction

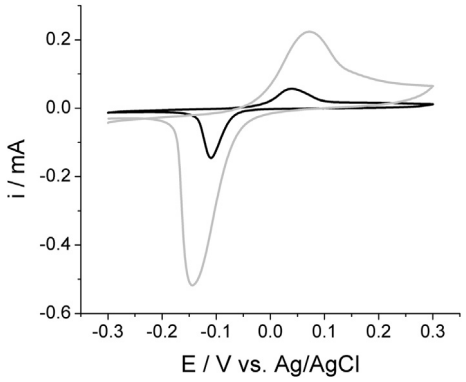

Fig. 2. Cyclic voltammetry carried out in a 100 mM phosphate buffer with pH 7, voltage scan rate 0.05 V s^{-1}. Black line: untreated electrode, gray line electrode after D treatment.

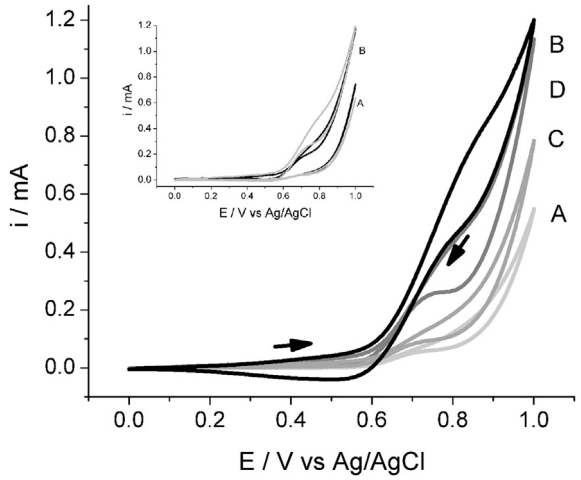

Fig. 3. Cyclic voltammograms for methanol oxidation catalyzed on copper wires with different treatments: A (light gray), B (black), C (medium gray) and D (dark gray). Methanol concentration is 40 mM. Inset: Cyclic voltammograms for methanol oxidation catalyzed on A and B treated copper electrodes in 0.1 M NaOH containing 40 mM methanol, for regular (black) and deoxygenated solutions (light gray).

may take place with a mechanism involving a rate limiting step where a reaction intermediate is formed upon a chemical reaction process. The formation of Cu(III) depends not only on the hydroxide concentration but also on the history of the electrode surface [26].

Fig. 4 shows voltammograms recorded in 0.1 M NaOH solution for the different treated copper electrodes before the addition of methanol. In the inset of Fig. 4, the voltammograms obtained for these electrodes before treatment are presented for comparison: in this case the slight differences between the three curves only originate from the fact that after preparation, untreated electrodes are not strictly identical. The signal seen at 0.7 V corresponds to the formation of Cu(III) species, which is only generated in a relatively highly concentrated NaOH solutions [26]. For instance, no current peak was observed in the positive potential range when voltammograms were performed with copper electrodes at supporting electrolyte concentration lower than 0.1 M NaOH [26]. Fig. 4 reveals that B and D treated electrodes present a higher signal in the region of Cu(III) formation than untreated and C treated electrodes.

By adding methanol in the electrochemical cell, an irreversible process is observed in the region corresponding to the electrochemical formation of Cu(III) shown in Fig. 4. Fig. 5 evidences the influence of methanol concentration on voltammograms: the results for D treatment are shown in this figure. Voltammograms were performed on the same electrode with successive additions of a given amount of methanol to reach concentrations between 0 and 100 mM. The results indicate that the anodic current around 0.8 V increases with concentration.

Fig. 6 compares the results for different treatments as a function of methanol concentration. For A and C treatments, the current response only slightly increases with methanol concentration. On the other hand we observe that both for B and D treatments the current increases significantly with methanol concentration. The relative increase is similar for both treatments. Comparing the response of the electrodes before and after treatment, an electrocatalytic efficiency of 3–5 may be deduced for B and D treatments.

Table 2
Effect of different treatments evaluated from cathodic peak on cyclic voltammetry carried out in a 100 mM phosphate buffer with pH 7.

Treatment	a_t/a_u	i_t/i_u
B	1.2 ± 0.6	1.2 ± 0.3
C	1.8 ± 1.0	1.3 ± 0.6
D	6.0 ± 1.0	3.5 ± 0.4

a_t: peak area of treated electrode – a_u: peak area of untreated electrode.
i_t: peak current of treated electrode – i_u: peak current of untreated electrode.

For untreated electrodes and for treatment C (no hierarchical structure – see Fig. 1) the current increases almost linearly with methanol concentration in the whole concentration range. For treatments B (with pitting structures) and D (with hierarchical structures), the current first linearly increases with concentration, then increases more slowly for concentrations above 60 mM suggesting that an adsorption step is involved.

In a catalytically enhanced reaction, an area increase should induce a larger number of adsorbed intermediates, enhancing the response of the global reaction if the obtained area is able to offer a large number of appropriate sites to the adsorption step. Although the obtained areas for B and C treatments are similar (see Table 2) B treatment appears to offer a more suitable surface for electrocatalytic oxidation of methanol. Without methanol addition, Figs. 4 and 6 show a high signal in the region of Cu(III) formation for B treatment. It suggests that the higher catalytic activity for B treatment would originate from higher concentration of Cu(III) related to the history of this surface [26]. Both B and C treatments consist in

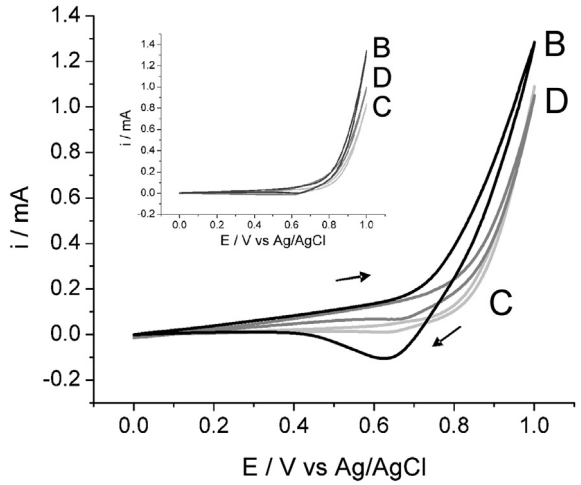

Fig. 4. Cyclic voltammograms recorded in 0.1 M NaOH solution with different treated copper electrodes before the addition of methanol, B (black), C (medium gray) and D (dark gray). Inset: Cyclic voltammograms in same conditions for the same electrodes before treatment.

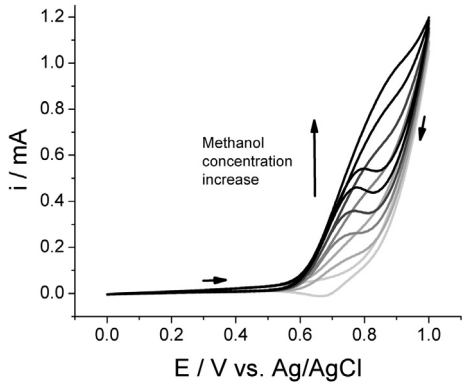

Fig. 5. Cyclic voltammograms for methanol oxidation catalyzed on a copper electrode treated by electrodeposition (D treatment) for methanol concentration between 0 and 100 mM.

anodic reactions: their main difference comes from the nature of the electrolyte, KCl 10 mM/H_2SO_4 for B treatment, $CuSO_4 \cdot 5H_2O$ 10 mM/H_2SO_4 for C treatment: corrosion in copper sulfate then appears to be less effective in enhancing the catalytic activity of copper electrodes for oxidation of methanol.

The measurements shown in Fig. 6 for treated electrodes have a sigmoid shape in the investigated concentration range. More than one phenomenon could be involved in such a behavior: the saturation of the active sites above 60 mM related to the voltage scan rate, the transport rate inside/outside the pores and the rate of the electrochemical reaction, including adsorption step. A stronger limitation in the peak current is expected for voltammograms, where a higher current density is forced by the voltage scan rate. As mentioned earlier, there is ample evidence regarding the involvement of Cu(III) species in the electrochemical oxidation of methanol [16,22,26,29,32]. This species is generated at positive potentials (see Fig. 4): it has the role of a redox mediator in the oxidation of several compounds at copper electrodes. A similar process, involving Ni(III), was also evidenced in the case of nickel [17,20]. Disappearance of the Cu(III) reduction peak in the negative sweep of the voltammograms confirms that the oxidation of methanol occurs via a chemical reaction with Cu(III) species. However, the high value of the current density suggests that part of the current could be due to methanol oxidation on the surface of the oxide layer by direct electrooxidation, where Cu(III) is used as an active surface site for methanol oxidation: an analogous mechanism was proposed in Refs. [18,19] for methanol oxidation on nickel. Besides, the small or null cathodic current observed at the reduction potential of Cu(III) species may be due to the interfering high anodic current of methanol or to an intermediate oxidation process occurring at the same potential. Therefore both proposed mechanisms depend on Cu(III) species generation. Above 60 mM, concentration of methanol does not affect the current response, indicating that the active area, for adsorption or reaction, is saturated. The Cu(III) generation seems to limit the oxidation of methanol and current response remains constant.

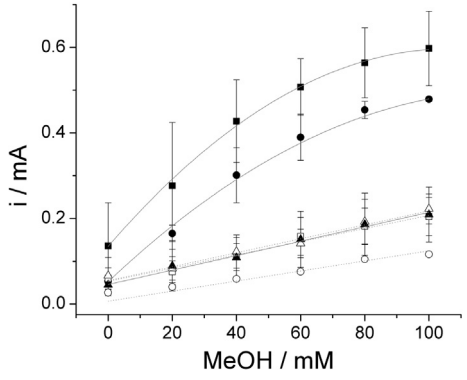

Fig. 6. Current variation vs. MeOH concentration at 0.750 V, for different treatments: B (solid square), C (solid triangle) and D (solid circle). Empty symbols represent the response of the same group of electrodes before treatment. Lines (dotted lines for untreated electrodes, solid lines for treated electrodes) are drawn to guide the eye. Error bars represent the standard deviation from 3 independent experiments.

Fig. 7a shows the cyclic voltammogram for B treated electrode at various scan rates (0.005, 0.01, 0.02, 0.05, 0.1, 0.25, 0.5 V s^{-1}), obtained in 0.1 M NaOH containing 50 mM methanol. It can be noted from this figure that the potential corresponding to the catalytic oxidation of methanol does not vary significantly with scan rate. Also the voltammogram at 0.5 V s^{-1} (black solid line) shows a catalytic current comparable to that at 0.25 V s^{-1} (black dashed line). Figs. 7b–c show the variation of the normalized catalytic current as a function of: b) scan rate, and c) square root of scan rate

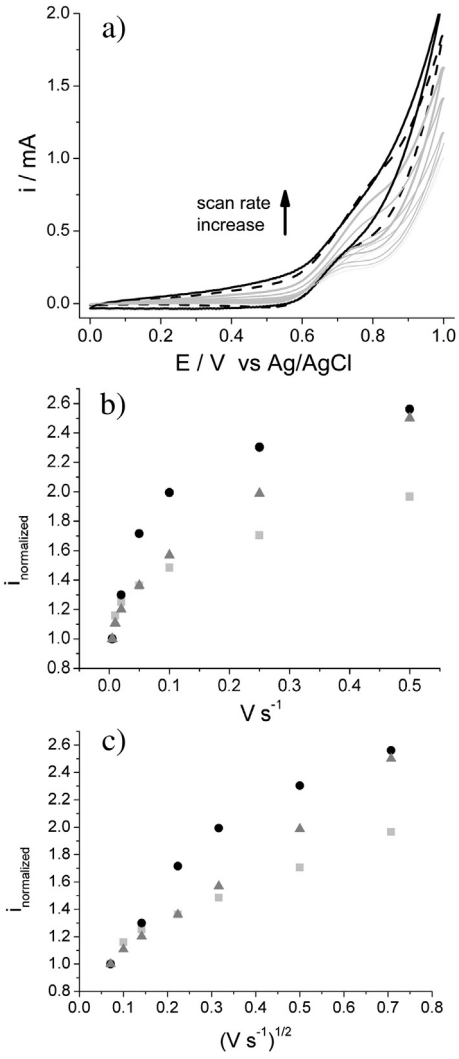

Fig. 7. a) Scan rate dependence of cyclic voltammetric response of methanol oxidation on treated electrode by corrosion in KCl solution (B treatment); variation of the normalized catalytic current with b) scan rate and c) square root of scan rate for different electrode treatments: A (square – light gray), B (circle – dark gray) and D (triangle – medium gray). The experiments were carried out in 0.1 M NaOH containing 50 mM methanol. Scan rates: 0.005, 0.01, 0.02, 0.05, 0.1, 0.25, 0.5 V s^{-1}.

for different electrode treatments: A (square – light gray), B (circle – dark gray) and D (triangle – medium gray). The current was divided by the current at the lowest scan rate in order to facilitate comparison.

For B treatment, the response increases linearly with square root of scan rate below 0.1 V s^{-1}. For D treatment the response increases linearly with square root of scan rate in the whole investigated range, suggesting that the surface is used more efficiently, and that the range of diffusion control is extended. For untreated electrodes diffusion control is observed at scan rates above 0.01 V s^{-1}. These results suggest that an increase of the electrode areas by electrodeposition allows keeping diffusion-controlled methanol oxidation at low concentration and/or scanning rate. Further work is in progress to clarify this point.

The present results evidence an enhanced catalytic behavior of methanol oxidation on B and D treated copper electrodes (electrocorrosion from KCl solution and electrodeposition from $CuSO_4$ solution, at low hydrogen co-deposition): this enhancement is comparable with values reported in Refs. [10,16]. About D treatment, Refs. [33,34] establish that hydrogen evolution is produced mainly at high current density to get suitable foams. Our experiments are far from this condition, but the results indicate that in spite of lower hydrogen evolution, the morphology of copper electrodeposited in our conditions increases significantly the area available for catalytic oxidation of methanol.

4. Conclusion

We have presented simple and robust electrochemical treatments to increase the electrochemical response of copper electrodes enabling to enhance methanol oxidation. The electrochemical treatments B and D presented in this work proved to be an effective alternative method to obtain an increase of 3–5 times in peak current of methanol oxidation. Other applications could be considered, such as the oxidation of carbohydrates, which present similar mechanisms [23,24].

SEM images and reported voltammograms reveal the effects of the different treatments. The electrodes treated by electrocorrosion from KCl solution (B treatment) have morphology with localized pores, evidencing pitting corrosion, but they do not show an increase of electrochemical area. B treated electrodes present a high signal of Cu(III) electrochemical formation, which might be responsible for the enhancement of methanol catalytic oxidation. Electrodeposition from $CuSO_4$ solution (D treatment) produces a dendritic deposit, with nanometric hierarchical structure. Its higher surface area might be responsible for the higher electrochemical response related to the formation of Cu(III) and for the methanol oxidation process. Both B and D treated electrodes have a better catalytic response than untreated electrodes. On the other hand, an electrode treated by electrocorrosion from $CuSO_4$ solution (C treatment) does not exhibit similar features. Its catalytic response is very similar to that of untreated electrodes.

The results for D treatment seem to be related to effective micro-nanostructures which increase the electroactive area and in this way the concentration range of the diffusion control is extended. The results for B treatment suggest that it is possible to increase the catalytic behavior of copper without increasing the electrochemical area of the electrodes. In this case, we assume that the formation of Cu(III) species is increased: the diffusion controlled range and the reaction rate would be limited by adsorption of methanol and/or Cu(III) regeneration steps.

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