Journal of New Materials for Electrochemical Systems 19, 37-42 (2016)

Development of Gold Electrodes for Microbial Fuel Cells

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Received: December 22, 2015, Accepted: January 20, 2016, Available online: January 29, 2016

Abstract: *The microbial fuel cell (MFC) has been an important subject of study in the last decades because of its technological significance that one can produce hydrogen or electricity by wastewater treatment (bio-remediation). One of the main issues for the application of these devices on large scale is the processes and materials for the electrode fabrication. The cathode for MFC requires a catalyst to perform the reduction reaction and this work presents a simple technique to obtain thin layers of gold (TLG) supported on glass. This technique was employed to obtain TLG with different thicknesses from 848 nm to the thinnest of 137 nm. Since the gold of the TLGs presented adherence issues, a successful thermal treatment with different temperatures from 150-300 ºC was developed to avoid the gold detachment. The TLGs were tested as cathodes in a MFC and a maximum Voc of 431 mV and an Isc of 10 × 10^{-2} mA were obtained. The process to obtain TLGs presented here has probed to be a good option for this application since the thickness obtained and the accessible material (glass) employed as support offers a solution to the costs and the scaling issues.*

Keywords: Key words: gold layer, cathodes, microbial fuel cells

1. INTRODUCTION

The research in microbial fuel cells (MFC) has lately increased because of the fact that this technology allows the electrical energy production from waste water and the anodic reaction can be catalyzed with bacteria. One of the main goals of this research area is the development of the materials for electrodes to get good kinetic performances and low costs to make easier the scaling of this technology.

The design of the cathode for a MFC represents a challenge if the goal is to scale the technology. The difficulty resides in the fact that the electrons, protons and oxygen must all meet at the cathode in a tri-phase reaction (solid catalyst, air, and water) [1]. Besides the oxygen reduction at the cathode involves the transfer of four electrons, and therefore has a reduced probability of occurrence [2, 3].

Some materials that have been used as cathodes are carbon paper, carbon cloth, graphite, woven graphite, graphite granules, brushes, etc., and they are added with some precious metals as Pt that is the most commonly used one and it is available from different manufacturers (e.g., E-Tek, USA, 0.35 mg-Pt/cm^2).

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Carbon materials without Pt as catalysts have been tested as air-cathodes. Iron cathodes have been reported to produce up to 3.8 times the power obtained with plain woven graphite cathodes but they are not still compared to similar cathodes with Pt as catalyst [3].

It has also been reported the use of carbon with transition metal as cathode to avoid the use of precious metals. Zhao et al [4] reported that catalyst of iron (II) phthalocyanine (FePc) and cobalt tetramethoxyphenylporphyrun (CoTMPP) produced current densities comparable to Pt-based cathodes and up to 0.2 mA cm^{-2}. These materials presented good performances at a low pH but it represents an issue for the microbial population.

Among various catalysts based on non-precious metal for oxygen reduction reaction (ORR), carbon supported transition metal based nitrogen containing catalysts (M-N/C) have been considered as the most promising replacement for the existing platinum based catalysts for ORR in proton exchange membrane fuel cells [7]. Extensive researches have been conducted on M-N/C catalysts of carbon containing metalloporphyrin, metallophthalocyanine, metals, conducting polymers and others prepared by high temperature pyrolysis of metal salts, nitrogen sources and carbon [5, 6].

The results showed that the catalytic performance of M-N/C

catalysts for ORR is close to the metal type. However, a widely accepted consensus has not been achieved to date [7]. For catalysts applied in MFCs the requirements increase due to the vulnerability of the bacteria that cannot survive to acid pH and the possibilities of leaks through the membranes would make an extra issue to scale it and employ this devices.

In this work, the feasibility of the gold layers supported on glass was studied for its application as cathodes since its performance as catalyst is well known to be good.

The use of precious metals like Au would represent expensive to scale up a MFC but it certainly be less expensive than Pt. A high efficiency performance of MFC with a good yield of Au could compensate the use of this catalyst. The Au was selected due to their conductivity characteristics and its resistance to the bacterial activity. To obtain thin layers of Au the metal evaporation technique was employed for this research. The metal evaporation technique was selected since one of the aims of this research is to determine the optimal thickness of the Au layer to obtain high ORR rates.

The Au as catalyst in MFCs devices has also been used successfully with carbon paper to fabricate anodes. The anode performance had an increase of 47 % with Shewanella oneidensis MR-1 [8]. Thin films of Au can also been employed for anode fabrication. For this research the anode was only catalized with bacteria and it was fabricated with the method described by Verea et al [9].

2. MATERIALS AND METHODS

2.1. Gold Deposition

The gold was deposited on glass substrate with predetermined uniform dimension of 2 × 2 cm^2 that was delimited by adhesive tape. The glass substrate was previously washed with deionized water. The excess of particles was removed with hot air. Each Au deposit was made triplicate. The evaporation technique was performed with the Balzers BAE 250 coating system provideding a current of 6 A and a vacuum of $1x10^{-6}$ mbar.

2.2. Heat treatment

The gold thin layers obtained from the Au evaporation on glass substrates were subjected to a heat treatment at different temperatures in order to prevent the detachment of gold. The temperatures of the treatment were 150, 250 and 300ºC. The treatment was applied through an electric furnace with a periodically intermittence of 5 minutes between each treatment. The detachment of the gold thin layer was evaluated with a cotton rubbed on the surface. Subsequently, the thickness was measured with profilometry technique.

2.3. X-ray and SEM Measurements

The gold thin layers were analyzed using X-ray diffraction method to obtain the structure and the size of the gold particles deposited. The morphology of the cathode surface and its composition was characterized with scanning electron microscope (SEM-EDS SU-1510) with a magnification of 20 k and multiple working distance from 2 μm to 500 nm.

2.4. Electrochemical Measurements

The cathode reduction capability was analyzed with cyclic voltammetry technique (CV). The analysis was performed in a three electrode cell of 100 ml. The Ag / AgCl electrode was used as the reference electrode. The thin layer of Au on the surface of the glass substrate was the work electrode and carbon cloth was used as the counter electrode. The electrolyte composition was 88 mM of carbonate buffer ($NaHCO_3$ and Na_2CO_3). The analysis was recorded with a sweep from the potential of -0.1 V to -0.7V vs Ag/AgCl at different scan rates of 10, 50,100 and 200 mVs^{-1}.

3. Microbial Fuel Cell

The cathodes made with the thin layer of Au were placed in a single chamber air cathode microbial fuel cell and it was assembled as reported by Liu et al [10]. The MFC consisted of an 80 ml volume glass cell. The anode electrode was made of carbon cloth with a biofilm of bacteria as it has been reported by Verea et al [9] and was placed in the cell under anaerobic conditions. The proton exchange membrane (PEM Nafion 115, Dupont) was previously boiled in deionized water at 30 % of H_2O_2 and 0.5 M of H_2SO_4. The medium consisted of 70 ml of synthetic wastewater (SWW) composed of 1 g/L NH_4Cl, 1 g/L $NaHCO_3$, 1 g/L Na_2CO_3 , 0.2 g/L K_2HPO_4 and 10 μL of vitamin and 10 μL mineral solutions [11]. The medium was maintained at a pH of 9 at anaerobic conditions and it was maintained at 37 ºC. The voltage was measured with a data acquisition system Keithley 2400 source meter.

4. RESULTS AND DISCUSSION

4.1. Deposition of Au

From the evaporation technique, different thicknesses of the thin layer of Au (TLG) were obtained with the evaporation of different weights of Au under the same conditions. As it was expected the results of the TLG showed a direct positive relation between the TLG thickness of 137, 225, 350, 500 and 848 nm and the weight of Au evaporated.

These results are comparable with those obtained with the sputtering technique employed for a thin film of 300 nm of Au deposited on Si/SiO_2 substrates witch also needed a thin film of titanium (10 nm) as the adhesion layer [12]. Since the Au was deposited on the glass substrate without any other thin film for adhesion effect, the detachment of the TLG was evaluated through the friction of the cotton against Au surface. In all cases it was observed that the TLG was detached with cotton and there was no effect on the thickness of the Au layers related with the detachment issue.

To avoid the detachment of the TLG they were treated with temperatures of 150, 250 and 300 ºC for 5 minutes without successful results. The same treatment was applied during 1 minute with intermittence of 4 minutes. The TLG submitted to the intermittent thermal treatment (ITT) of 300 ºC resulted in a TLG with no detachment. The same treatment was applied to TLG with different thicknesses and it was not observed any differences on the effectiveness of the ITT.

4.2. Intermittent Thermal Treatment

Since one of the goals of this study was to develop low cost materials for their application as electrodes, it was tested the ITT at lower temperatures and with different thicknesses of the TLG to obtain the best characteristics. It was observed that with the thickness of 848 nm and 500 nm presented good TLG adherence to the glass with both the ITT of 250 ºC and also with 150 ºC. For the TLG with 350 nm the detachment was avoided with the ITT of 300 ºC. The ITT was also effective in thinner TLG of 225 nm with ITT

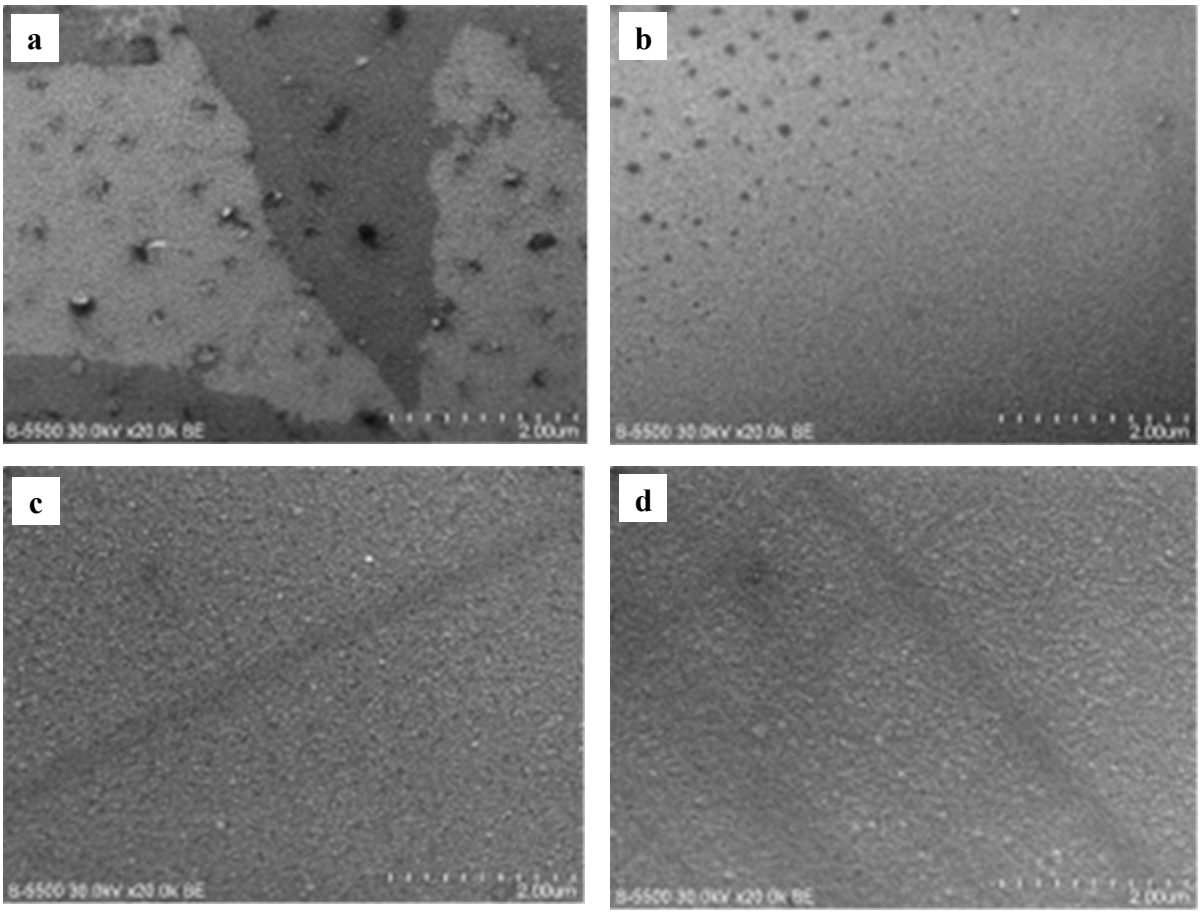

Figure 1. a. SEM image of the TLG with thickness of 137 nm and ITT at 150 ºC. b. SEM image of the TLG with thickness of 137 nm and ITT at 300 ºC. c. SEM image of the TLG with thickness of 500 nm and ITT at 150 ºC. d. SEM image of the TLG with thickness of 500 nm and ITT at 300 ºC.

of 300 ºC and also at 250 ºC. The thinnest layer of gold tested with 137 nm presented good adherence with the ITT at 300 ºC and 250 ºC.

The images of the TLG obtained with the SEM technique revealed that with the ITT at 300 ºC the surface was more homogeneous compared to the surface of a similar TLG with an ITT at 150 ºC (figure 1). It also showed that the characteristic of the homogeneity increased with a higher thickness of 500 nm (Figure 1c. and Figure 1d.).

The TLG obtained can be employed as cathode. The Au as catalyst on the glass surface is a proportion from 1 mg cm^{-2} to 1.5 mg cm^{-2}. This range is similar to the one reported for the platinum catalyst supported on carbon materials reported to be 0.5 mg cm^{-2} for MFC applications [13] and from 0.5 mg cm^{-2} to 2 mg cm^{-2} for electrolysis applications [14, 8]. For MFC devices the Au as catalyst has been mainly employed at the anode to increase the bacterial performance [8].

The effect of the ITT to avoid the Au detachment from the glass support was analyzed with the XRD technique. Figure 2 shows that as it was expected the layer is composed of cubic crystal system. The size of crystal was also analyzed with the same technique and the results showed that the TLG with no detachment presented crystal sizes from 10.2 nm to 10.8 nm and crystal sizes up to 11.3 nm in TLG presented the detachment effect. Figure 2 also shows a comparison of the ITT at 250 ºC and 300 ºC applied to the TLG without detachment and it was observed an effect on the increase of the intensity of the Au (220) for the TLG with 225 nm and 350 nm (figure 2a and figure 2c). For the TLG with 137 nm of thickness the increase of the temperature favored the increase of the intensity of the Au (111) (figure 2b). These different configurations of thickness and ITT can be employed to obtain the combination of the crystal systems that better suit for a determined application.

Since it is been reported that Au nanoparticles of 10 nm deposited on diffusion layers with the sputtering technique provide high power density in a fuel cell [15] the TLG with good adherence to the glass substrate was analyzed with the cyclic voltammetry technique (VC) to evaluate their capability in reduction reactions since one of the goals of this work it is to apply the TLG as cathode in microbial fuel Cells.

4.3. Kinetic Parameters

The cyclic voltammetry (CV) analysis shows that that the reduction peaks in the voltammograms appear close to the theoretical potential (-0.23 V) calculated with the Nernst equation [16] for the

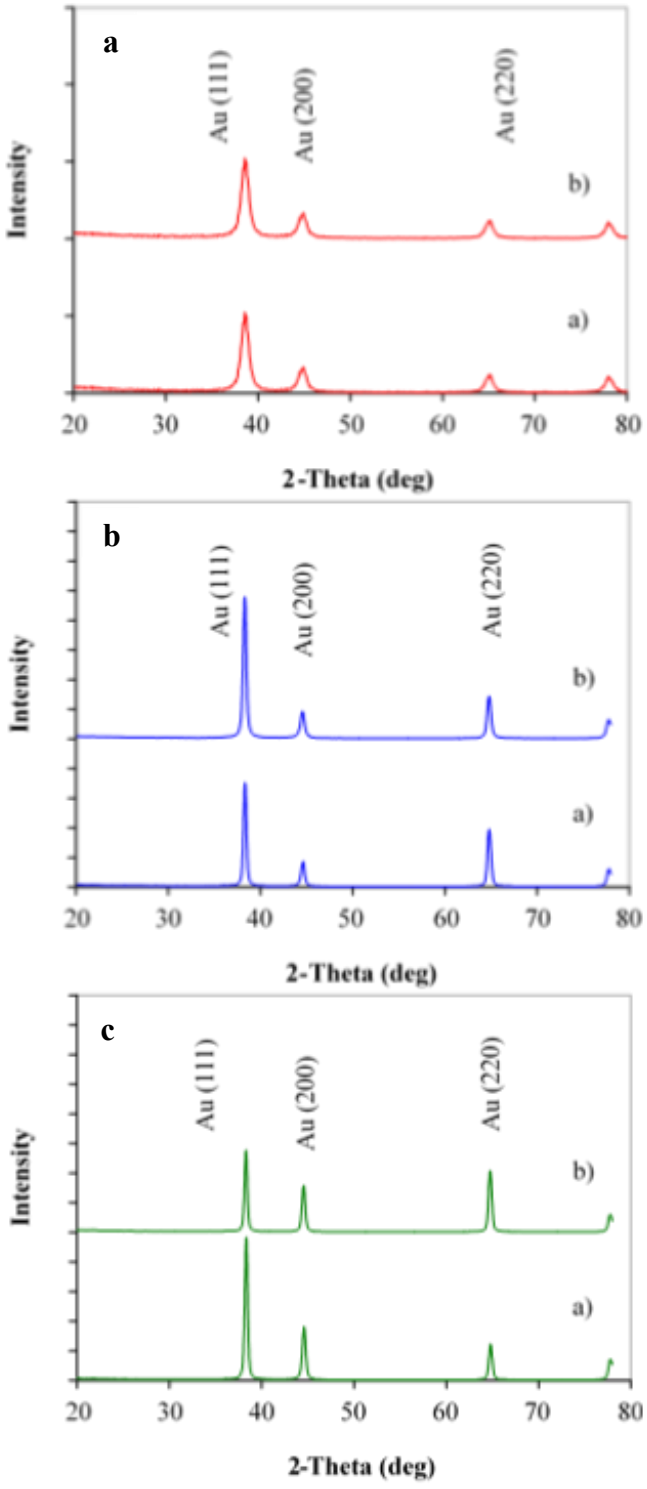

Figure 2. a. XRD Pattern of the TLG of 137 nm with ITT at a) 250º C and b) 300 º C. b. XRD Pattern of the TLG of 225 nm with ITT at a) 250º C and b) 300 º C. c. XRD Pattern of the TLG of 350 nm with ITT at a) 250º C and b) 300 º C.

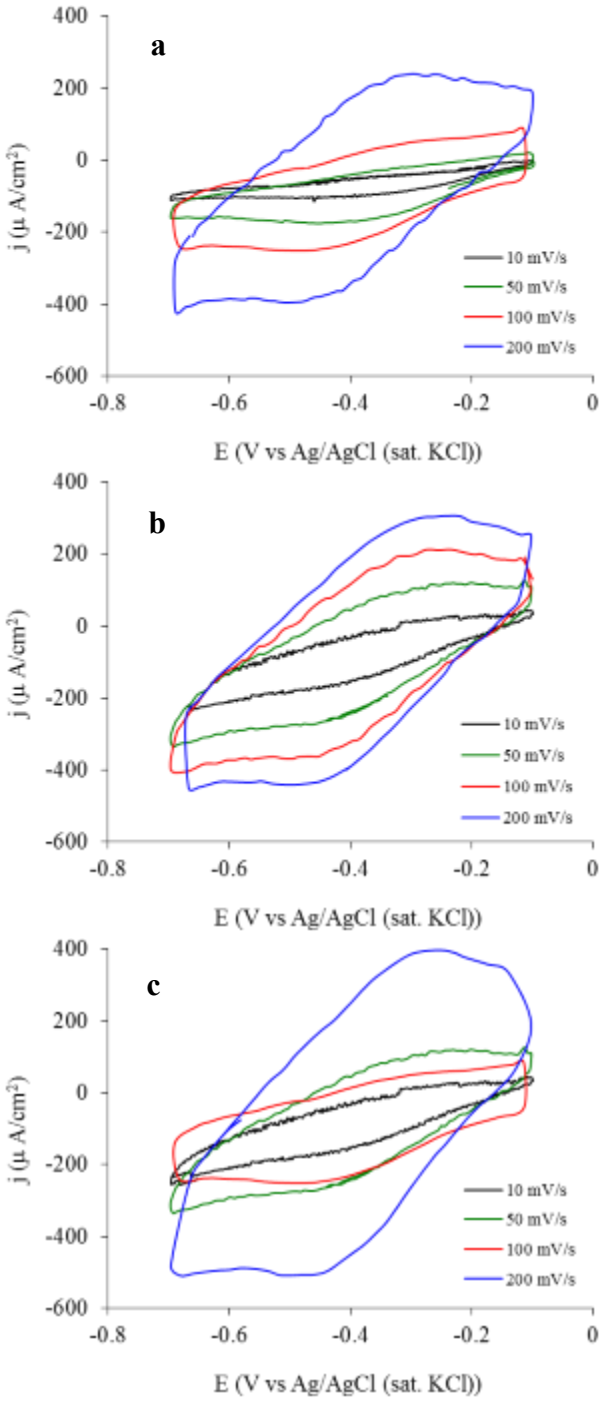

Figure 3. a. Cyclic Voltammogram of the TLG at different scan rates of 10, 50, 100, and 200 mV/s of the TLG of 225 nm with ITT of 250 ºC. b. Cyclic Voltammogram of the TLG at different scan rates of 10, 50, 100, and 200 mV/s of the TLG of 225nm with ITT of 300 ºC. c. Cyclic Voltammogram of the TLG at different scan rates of 10, 50, 100, and 200 mV/s of the TLG of 350 nm with ITT of 300 ºC.

reaction eq.(1) at pH=9.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1)$$

The kinetic response of the TLG was analyzed from the CV developed at different scan rates of potentials. The kinetic parameters like the transfer coefficient (α) and the exchange current (i_0) were calculated with the Tafel plot and eq. (2) and eq. (3) [16]. The results of the CV are shown in figure 3.

$$\eta = E - E^0 = \alpha - b \log i \quad (2)$$

$$\eta = \frac{2.303RT}{\alpha nF} \log i_0 \frac{2.303RT}{\alpha NF} \log i \quad (3)$$

Where η is the over-potential, E is the potential of an electrode versus a reference, E^0 is the standard electromotive force of a half reaction, i is the current and i_0 is the exchange current, α is the transfer coefficient, n is the stoichiometric number of electrons involved in an electrode reaction (see eq. (1)), R is the gas constant and T is the absolute temperature.

The CV analysis showed that the TLG tested can be applied for both the oxidation and the reduction reactions. There was observed an effect on the increase of the current density for both reactions when the TLG of 225 nm with an ITT of 250 ºC was analyzed and compared with a similar TLG with ITT of 300 ºC (figure 3a and figure 3b.). The performance for the TLG of 225 nm and the TLG of 350 nm both with ITT of 300 ºC was similar for the electrochemical reactions (figure 3b and figure 3c). Then there is possible to obtain similar performances with less material and the right ITT.

The results are summarized in table 1 and they show that the exchange current normalized by the surface area j_0 is similar for TLG of 350 nm and 225 nm at ITT of 300 ºC and 250 ºC respectively and the same transfer coefficient which means that in both cases the reduction reaction predominates but they need larger overpotentials than the TLG of 225 nm with ITT at 300 ºC. Then the best performance was obtained with the TLG treated at 300 ºC but it was also proved that it is possible to develop the reduction reactions with lower thickness of TLG.

4.4. TGL as Cathode in the MFC

The TLG of 225 nm thickness treated with the ITT of 300 ºC was employed as a cathode in an air-cathode MFC. The open circuit voltage (V_{oc}) and the short circuit current (I_{sc}) were measured.

The best results obtained were a V_{oc} of 541 mV and I_{sc} of 1.44 x 10^{-2} mA. There was observed an increase of the I_{sc} to 2 x 10^{-2} mA when the area of the anode was increased to two times the original area and the highest I_{sc} of 10 x 10^{-2} mA when the area of the anode increased three times. The V_{oc} was 431 mV and 452 mV respectively. Then, the performance of the TLG as cathode was proved to be available with a maximum power density of 7.38 mW cm^{-2}. The polarization curve of the cell is shown in figure 4.

Table 1. Kinetic parameters for the reduction reaction in the TGL with different thicknesses

Thickness of the TGL (nm)	Temperaures of ITT (C)	Slope (mV / dec)	α	J_0 (mA / cm^2)
350	300	132	0.11	$6.84x10^{-4}$
225	300	221	0.07	$1.32x10^{-3}$
225	250	240	0.07	$8.70x10^{-4}$

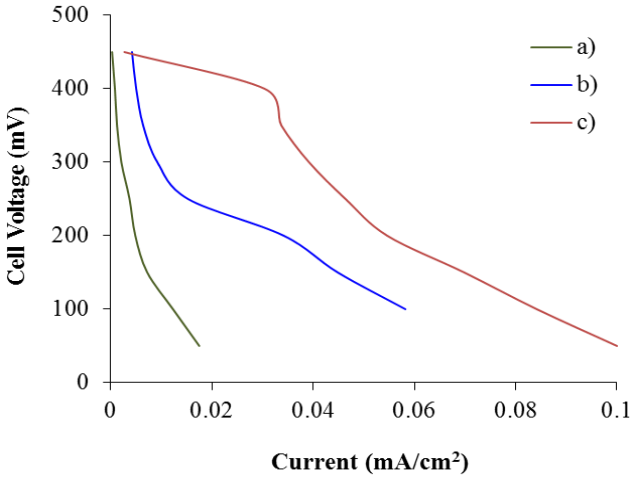

Figure 4. Polarization curve of the CEM with a TLG of 225 nm and ITT of 300 ºC and different geometric areas of the anode. a) 1 cm^2 b) 2 cm^2 c) 3 cm^2

The maximum power density of 369 ±8 mW m^{-2} was reported by Cheng et al [13]. This result was obtained with a similar air-cathode MFC and transition metal carbon cathodes catalyzed with cobalt tetramethoxyphenylporphyrin CoTMPP. This result was reported to be only 12 % lower than that with 0.5 mg Pt cm^{-2} [1]. This work presents higher V_{oc} and I_{sc} responses compared to the similar MFC with electrodes catalyzed with CoTMPP.

The TLG developed in this work is the electrode and the catalyst itself. This layer eliminates the need of an extra material as electrode or as support of the catalyst which is an advantage compared to other electrodes. Besides, this layer could be formed on different cell designs. Conventional fuel cell electrodes are generally fabricated by mixing powders of active materials with conducting materials (e.g., carbon black) and polymer binders (e.g., polytetrafluoroethylene) to form pastes and then apply the pastes to current collectors and usually those electrodes suffer from drawbacks of low active material utilization because some catalysts are unable to contact with current collector and/or electrolyte [17] then the TLG presented in this work can simplify the processes of the cathodes fabrication.

5. CONCLUSIONS

This work demonstrated that a simple ITT can solve the detachment of the Au from a glass surface. This method could be used for several applications as MFC. The TLG presented good kinetic characteristics for applying it as cathode. The technique to obtain the TLG described here allows enlarging the options of the cell and the electrodes designs as well. The process described in this work to obtain TLGs can be very useful for scaling up of the devices. The ITT is related to the crystal size of the TLG and this may be the reason for the differences in the adherence to the glass surface. There is also a relation between the TLG thickness and the ITT that

allows getting the best kinetic performance. In this work it was proved that the TLG supported on glass had a good performance as cathode in a MFC.

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