Performance of metal-doped carbonaceous anodes in air-breathing microbial fuel cells

Sara Mateo, Pablo Cañizares, Manuel Andrés Rodrigo, Francisco Jesus Fernandez-Morales*

University of Castilla-La Mancha, ITQUIMA, Chemical Engineering Department, Avenida Camilo José Cela S/N. 13071 Ciudad Real, Spain.

* Corresponding author: Francisco Jesús Fernández Morales

University of Castilla-La Mancha, ITQUIMA, Chemical Engineering Dept., Avda. Camilo José Cela S/N 13071, Ciudad Real, Spain.

Tel: 0034 926 295300 (ext. 6350), Fax: 0034 926 295242.

E-mail: fcojesus.fmorales@uclm.es

Orcid iD: 0000-0003-0389-6247

Abstract

A comparison between different metal-doped carbonaceous anodes for air-breathing microbial fuel cells (MFCs) has been carried out in this work. In order to do that, the surface of carbon paper anodes were modified with Pt, Au and Ni. The current generated was higher when using these metal-doped anodes, exerting up to 7.4 A m^{-2} more than when using non-doped ones. Polarization curves results in a great performance of the Ni reaching 2.92 W m^{-2} at the steady state, followed by 0.99 W m^{-2} of the Au and 0.52 W m^{-2} of the Pt. Additionally, from the mathematical fitting of modelling results to a polarization curve model, it was observed that the mechanism that explain the better performance of the metal doped anodes was the reduction of the mass transfer limitations. In this sense, the addition of metal on the anodes increase the threshold current density causing mass transfer limitations, reducing also the significance of the mass transfer limitations when the cells are operated under conditions in which the process is diffusion controlled.

Keywords: Metal-doped anodes; microbial fuel cell; air-breathing

1. Introduction

The organic matter contained in wastewater could produce electricity through the use of Microbial Fuel Cells (MFC) [1]. This type of bioelectrochemical devices employ electrogenic microorganisms to transform chemical energy into electricity by means of a combination of microbial metabolic and electrochemical reactions [2]. In other words, when electrogenic bacteria are placed next to the anode of an electrochemical cell, they can use it as an electron sink. Therefore, by using this technology, the electrons exchanged in the microbial respiration can be easily recovered, taking a great advantage of the metabolic abilities of the electrogenic microorganisms [3,4].

Despite of being a promising sustainable energy technology, nowadays MFCs are not able to reach the expected efficiencies or productivities for its implementation. This lack of advance is becoming in a very important drawback, which is reducing the interest raised in the two last decades. Nevertheless, in the literature it has been described that new architectures of these devices may enhance their performance by reducing dimensions of the cells and, in particular, the inter-electrode gap (looking for a reduction in the internal resistance). In fact, new trends in the development of this technology focuses on the miniaturization, leading to minimal ohmic losses, reducing drastically mass transport problems and optimizing the formation of the biofilm on the anode. The pivotal role of the anodes makes them to meet many special requirements focused on the biofilm formation, electrons transfer and durability [1]. Usually, sp^2 -carbon materials are used as anodes in MFCs due to their very good properties and low cost [4,5]. These carbonaceous materials could be improved by different treatments which aims to modify their surface functional groups (trying to influence on the initial adhesion of biomass and on the electron transfer mechanisms) or to increase electric conductivity. In this context, pre-treatments such as acetone cleaning, heating, formic acid

washing have shown to be able to increase the performance of MFCs [6] and the deposition of metals [7,8]. In particular, doping metals in the anodic electrode is attracting great interest in the search of favouring the flow of electrons on the microbial-anode interface [9]. The variety and amount of metals that can be added is so great that it is difficult to compare their performance in the same conditions and reactors and not all metals seem to have a positive effect on the performance. Thus, Ag and Cu are considered as antimicrobial materials [10] and Co and Ti do not favour electrogenic activity [11] as well. Opposite, Mn (IV) and Fe (III) have been found to yield good results [12,13] and Au is known to enhance the anode performance due to its high conductivity and stability [14] as well as low passivity risk [15]. Thus, the performance of Au doped electrodes has been compared with clean electrodes, yielding the doped ones current densities up to 20 times higher [16]. In the literature, it has been also stated that composite electrode of carbon paper-Au shows better electrochemical performance than raw carbon paper [14]. The better performance has been explained in terms of a better bacteria attachment [17] and electron transfer [14]. Likewise, Pt coating on a graphite electrode increased 18 fold the current density [18] and polyaniline-Pt composites have also shown an improvement in the ion generation through the microbial metabolites direct oxidation [19,20].

Various non-noble metals also attains a positive effect on the performance of MFCs. Thus, nickel appears to achieve the highest performance, followed by stainless steel [11] and Ni- Fe and Ni-Fe-P nanostructures on carbon felt resulted in an increase of the MFC output in comparison with the values obtained without non-doped carbon felt. This behaviour was explained because of the metal electrocatalytic effects [21].

As stated above, metals may play a significant role, either as a catalyst or by affinity with bacteria, in both the direct and the mediated processes as well as in other electrochemical and

bioelectrochemical phenomena. For this reason, this work is focused on elucidate the mechanisms explaining the performance of carbon paper anodes doped with different metals. To do this, four MFCs life-tests were run simultaneously and under exactly the same operation conditions changing only the anode material used in each of the eight cells (each test was duplicated): clean carbon paper (CP) and carbon paper with a layer of Au (CP-Au), Ni (CP-Ni) and Pt (CP-Pt). Additionally, modelling tools were used to identify the driving forces of the best performances when operating with metal doped anodes.

2. Materials and Methods

2.1 Experimental set-up

In order to avoid external factors influencing the comparison of the results, all the experimental sets carried out in this work were started up at the same time, inoculated with the same sludge and operated at the same operational conditions. The experimental set-up consisted of eight different air-breathing MFCs made of methacrylate, being the cathode exposed to the atmosphere for the operational simplicity and cost-effectiveness. Anode and cathode were separated by a Nafion[®] exchange proton membrane (DuPontTM Nafion PFSA Membrane). The cathodic electrode was carbon paper (C2 Freudenberg, Fuel Cell Store, USA) on whose surface it was deposited a layer of 0.5 mg Pt cm⁻² [22] to favour the kinetics of the oxygen reduction into water. With regard to the anodic electrode, it was made of Toray carbon paper with a 10% of Teflon content (BASF, Germany). The surface of the anodic electrode was modified with metallic components. Regarding to these metallic compounds, the effect of loads of Pt (CP-Pt), Ni (CP-Ni) and Au (CP-Au) were studied and compared against a non-doped MFC. The metal deposition technique used in the anodes is described in section 2.4. At this point, it is important to highlight that clean brand new anodic and

cathodic electrodes, with an active area of 0.866 cm^2 , were used. The electrical circuit electrodes were treaded with tin wire for electrical contact through an external resistance of 120Ω . The anodic chamber had a volume of 0.364 cm^3 and was connected to an auxiliary tank of 115 cm^3 . In order to reduce as much as possible the internal resistance, the cathodic electrode and the membrane were assembled by a hot-pressure process and anodic electrode was placed as close as possible to the membrane [23] as the assembly process could damage the modified surface of the anode. For the sake of reproducibility all the experiments including the blank tests were carried out in duplicate.

A scheme of the MFC used is presented in Figure 1.

Figure 1. Schematic view of the MFC used in this work.

2.2 Inoculation and operational conditions

MFCs were inoculated with activated sludge from the aerobic reactor of the Wastewater Treatment Plant of Ciudad Real (Spain), more information about this facility can be found

elsewhere [24]. In order to colonize the electrode, the inoculation process was carried out following the procedure described in literature [25]. The auxiliary tank was filled with 100% of aerobic sludge, which was recirculated to the anodic chamber of the MFC during the first day. The second and third days, a 50% of the auxiliary tank volume was replaced by new inoculum and was left in recirculation mode during another day. Then, the system was operated under a sludge age of 7.5 days as described in the literature (REFERENCIA). To do that, 15 mL of the auxiliary tank volume was removed and replaced by fresh wastewater in a daily basis. MFCs were operated at room temperature and wastewater was pumped into the anodic chamber at a flow rate of 3 mL min^{-1} by a multichannel Heidolph (PD-5206 Peristaltic Dosing Dispensing Pump Drive).

2.3 Materials

All chemicals were of analytical grade from PANREAC and Sigma-Aldrich and both aqueous solution and wastewater were prepared with Mili-Q water. The synthetic wastewater used as feedstock consist of 16.10 g L^{-1} of sodium acetate as the sole carbon source and a trace mineral solution. This solution contained 2.77 g L^{-1} of sodium carbonate, 1.85 g L^{-1} of ammonium sulphate, 1.11 g L^{-1} of potassium dihydrogen phosphate, 0.92 g L^{-1} of hexahydrate magnesium chloride, 1.25 g L^{-1} of calcium chloride and 0.07 g L^{-1} of ferric ammonium sulphate. In this work, a very high influent COD has been used with the aim to enhance as much as possible the electricity generation by the MFC. The use of high strength wastewaters provides an opportunity to convert a great percentage of organic matter into electricity [26,27]. In the literature it has been stated that high loaded wastewaters produced 1.8 times greater maximum power densities than domestic wastewaters [28].

2.4. Deposition of metals

The deposition of Ni was carried out under an electrodeposition process using a nickel sulfamate bath following the procedure described in literature [29]. The composition of this bath was 300 g L⁻¹ of nickel sulfamate, 6 g L⁻¹ of nickel chloride and 30 g L⁻¹ of boric acid. Triton X-100 was added to the bath to act as a template for the electrodeposition of nickel [30]. A sulfurized nickel bar was used as anode while the carbon paper was used in the cathode submerged in the bath. A constant current density of 10 mA cm⁻² was applied for an hour. Then, the electrode was washed to remove the template molecules.

The deposition of Au in the carbon paper was carried out using a layer-by-layer assembly procedure [31]. First of all, the Au solution of gold colloids with a 20 nm diameter were prepared according to literature [32][33]. To do that, 50 mL of HAuCl₄ solution was heated and stirred simultaneously. Once the solution was boiling, 0.95 mL of trisodium citrate solution was added very quickly and maintained boiling for 10 minutes. Then, it was cooled, stored at 4° C and ready to use. It is important to mention that this Au solution is negatively charged due to the citrate ion. The second step consists in the deposition process. The carbon paper electrode was immersed in a concentrated solution 3:1 v:v H₂SO₄-HNO₃ for one hour. This pre-treatment is carried out to introduce carboxylic groups on the electrodic surface and became it negatively and hydrophilic charged [34]. Then, the carbon paper electrode was immersed in a 10 mg mL⁻¹ polyethylenimine aqueous solution (PEI) to charge it positively and after 20 minutes it was immersed in the Au solution prepared for the same time. These two last steps were repeated several times until observe the electrodic surface covered by gold and between immersions the electrode was washed with MilliQ water and hot air drying.

Regarding to the deposition of Pt, it was carried out through airbrush technique. First of all, the ink was prepared sonicating the metal (40% w/w of platinum on carbon black Vulcan

XC-72) and N,N-dimethylacetamide as solvent for 45 minutes. Then, polybenzimidazole (PBI) solution (20 times less than the amount of coal existing in the metal) was added and N,N-dimethylacetamide to favours the correct dissolution. It was sonicated for 45 minutes. The ink was deposited on the electrode with an airbrush while the electrode is placed in a steel plate at 130°C until to reach a weight that corresponds with a layer of 0.5 mg Pt cm⁻².

Once finished the deposition procedure, the electrodes were dried at 190°C for 2 hours favouring the solvent evaporation. Finally, and in order to provide them with conductivity, 10 % w/w phosphoric acid was added.

The deposition of Au and Ni was made on carbon paper Toray with a 10 % of Teflon (BASF, Germany) while Pt was deposited on carbon paper Freudenberg C2 with a 10 % of Teflon (Fuel Cell Store, USA) and provided with a microporous layer for an easier Pt deposition.

After the deposition, the electrodes were checked with EDAX technique. Figure 2 shows the EDAX photographs, where the presence of Ni and Au can be observed in blue while the Pt can be observed in yellow.

Figure 2. EDAX images of the electrodes CP-Ni, CP-Au and CP-Pt.

The EDAX analyses pointed out a percentage of Ni on the surface of 88.89 % w/w, Au content was 36.08 % and in the case of the Pt, the content was 25.66 %.

2.5 Analytical and electrochemical measurements

Conductivity and pH were measured using a GLP22 Crison pH-meter. The COD removal was measured according to Standard Methods [35]. Regarding the electrical measurements, the output current density was followed by continuously registering the voltage exerted with a Multimeter Keithley 2000 and the electrochemical characterization was carried out periodically by an AUTOLAB PGSTAT30. The Coulombic Efficiency (CE) was determined by integration of the current over the time in fed-batch mode following the Equation 1 [36], where M corresponds with the molecular weight of oxygen (32), F is Faraday's constant, b is related to the number of electrons exchanged per mole of oxygen (4), v_{An} is the volume of liquid in the anode compartment and ΔCOD is the change in COD over time t_b .

$$CE_{Fed-batch}(\%) = \frac{M \int_0^{t_b} I dt}{F b v_{An} \Delta COD} \quad (1)$$

3. Results and discussion

3.1 Microbial fuel cell performance

Figure 3 shows the evolution of the exerted current density (part A) and the COD removal (part B) rates, when various carbon paper electrodes, doped with different metals (Ni, Au and Pt), were used as anodes of air-breathing mini-MFCs.

A)

B)

Figure 3. A) Evolution of the current density produced and B) COD removed by the MFCs with the time. Electrodes of carbon paper with metallic compounds deposited: ($\blacktriangle$) MFC-Pt; ($\bullet$) MFC-Ni; ($\square$) MFC-Au; ($\diamond$) MFC-CP.

As can be seen in Part a, in all the cases, lag, the characteristic exponential growth and steady state phases can be discerned in the current density exerted. The length of the tests was long enough to ensure steady-state and, therefore, to fully characterize the influence of the different anodes on the different stages. Initially, the exerted current densities were almost negligible in all the cases. However, once the biofilm formation started, it drastically increased in the MFCs equipped with metal-doped anodes. Thus, the best enhancement in the production of current was obtained when using CP-Ni anodes (7.5 A m^{-2}), followed by CP-Au (4.2 A m^{-2}) and finally CP-Pt (2.0 A m^{-2}). It is also important to remark that, according to the exerted current, after the lag phase, CP-Ni and CP-Au leads to a more intense exponential growth than the observed with CP-Pt, which in fact, seems to be divided into two shorter stages with an intermediate steady-state phase. These different behaviours suggest the combination of very complex processes, in which the metal doping the anode clearly influences on the performance of the bioelectrogenic culture.

At this point, it is important to highlight that effects of the metals on the suspended culture are not expected to be important, because no metal is released to solution during the tests, at least in measurable concentrations. Hence, the differences should be explained in terms of the influence over the biofilm attached to the anode, which are favoured in the sequence CP-Pt < CP-Au < CP-Ni.

Regarding to the COD removal rate, it must be pointed out the similar changes in the COD consumption rates in the four cases evaluated. This response is in agreement with the

expected behaviour of biological reactors, because they are operated with the same sludge age and they are fed with the same substrate (ref Sara). COD consumption is higher at the beginning of the tests and this fact can be explained in terms of the higher population of microorganisms in that moment. Thus, initially a very high concentration of microorganisms was seeded into the cell and during acclimation, this population decreased while, at the same time, it was adapting to the new conditions. The lower population stands for the lower COD consumption. In the steady-state, the MFC-CP presented the best COD removal (about 1100 mg COD/L/d) whereas the MCF doped with metals removed only about 700 mg COD/L/d, indicating a partial inhibition in the COD consumption in these three cases, which did not depend on the nature of the metals but just on its presence on the anode surface.

This behaviour is rather different than that observed in the exerted current density, indicating the presence of microbial populations with and without electrogenic abilities. Anyhow, as the principal purpose of this work was to obtain high performance and high efficiency, the coulombic efficiency (CE) has been calculated for all the devices at the start-up and once the steady-state was reached. The average results obtained during the steady-state operation are presented in Figure 4.

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Figure 4. Coulombic efficiency of the MFC used in this study. Data presented correspond to an average of steady state operation during 15 d. The standard deviation was lower than 8 % in all the cases.

It can be observed an increasing CE when metals were added to the MFCs, corresponding the highest values to the MFC in which the anode was doped with Ni. These results ratify the better bioelectrogenic performance associated to the presence of the metal on the anode. Initially, it can be hypotheticized that this better performance can be explained because the metals should make easier the electron transfer from the microorganisms to the anode leading to an enhanced electrogenic performance.

With the aim to evaluate the biomass growth in the MFC used in the study, the nutrient consumption due to biomass growth and the medium characteristics, including biomass concentration measured as turbidity, were determined. The results obtained, presented in Table 1, indicated that similar biomass growth rates were obtained in all the MFC.

Table 1. Medium characteristics during the steady state.

Electrode	pH	Conductivity (ms cm ⁻¹)	Turbidity (FAU)	N removal (ppm)	P removal (ppm)
CP	8.14±0.14	12.62±1.42	736±353	36.56±2.95	10.51±2.14
CP-Pt	8.12±0.29	14.13±2.69	884±221	31.58±3.73	9.59±3.8
CP-Au	8.44±0.18	12.57±2.21	938±203	29.59±5.37	9.48±4.72
CP-Ni	8.36±0.32	12.93±1.38	958±533	27.78±3.15	8.15±5.43

As can be seen in Table 1, the pH and conductivity values were nearly the same in all the cases. Additionally, almost the same nitrogen and phosphorous removal rates were obtained in all the cases, ratifying the fact that similar biomass growth rates were obtained in the four cells. Similar nutrient consumption has been reported in the literature when operating with electrogenic microorganisms [25,38].

3.2 Polarization curves

The characterization of the MFCs requires additional electrochemical measurements. For this reason, polarization curves were carried out on a weekly basis. For the sake of clarity, only curves during the start-up (the 5th day) and the steady-state (the day 40) are shown in Figure 5.

Figure 5. Polarization and power curves A) at the start-up, B) during the steady state. (---) CP-Pt; (-.-) CP-Ni; (—) CP-Au. Inset corresponds to non-doped CP anode.

From the polarization and power curves, the main operational parameter of the MFCs were determined and these results are presented in Table 2.

Table 2. Main electrochemical parameters during the start-up and steady state operation.

OCV, $P_{\max}$ and $J_{\max}$ values are referred to those presented by the non-doped carbon paper anode.

MFC	Initial characterization			Steady state characterization		
	OCV (V)	$P_{\max}$ (W m^{-2})	$J_{\max}$ (A m^{-2})	OCV (V)	$P_{\max}$ (W m^{-2})	$J_{\max}$ (A m^{-2})
CP	0.061	0.001	0.073	0.088	0.002	0.089
CP-Pt	0.119	0.205	3.213	0.274	0.528	7.532
CP-Au	0.274	0.064	6.098	0.308	0.992	11.420
CP-Ni	0.304	0.559	6.735	0.436	2.925	33.930

The OCV is related to the reactions taking place at the anode and the cathode. In this work, the OCV evolved favourably in all cases, showing their best values once reached the steady-state. The obtained values reflected the benefits of incorporating metals to the anode surface, presenting the best performance the MFC doped with Ni. Thus, once reached the steady-state, it is interesting to emphasize that the best values of OCV corresponded to CP-Ni (0.436 V). All MFCs enhanced their performance along the experiment and the exerted current density was doubled when using Pt and Au, whereas when using Ni the exerted current intensity increased about five times. Regarding to the power exerted, the greatest power density of 2.92 W m⁻² was reached by the nickel deposited electrodes, much higher than the ones for CP-Au (0.99 W m⁻²) and CP-Pt (0.52 W m⁻²). A similar behaviour presented the maximum exerted current density, corresponding the highest value to the MFC-Ni, 33.9 A m⁻², followed by MFC-Au and MFC-Pt exerting 11.4 and 7.5 A m⁻² respectively. Both performance parameters, power and current density exerted, were significantly lower in the MFC equipped with the raw carbon paper.

With the aim to go deep inside on the behaviour of the electrochemical systems, the polarization curves were modelled by using an empirical polarization curve model developed by Kim et al [39] and presented in equation 1. In this model, the parameter E_0 can be described as shown in eq. 2, where the term E_0 is used in order to simplify the mathematical fitting procedure.

$$E_{cell} = E_0 - b \cdot \log(i) - Ri - m \cdot \exp(ni) \quad [1]$$

$$E_0 = E_{OCV} + b \cdot \log(i_0) \quad [2]$$

In the model, the term $-b \cdot \log(i)$ represents activation losses, $-Ri$ the ohmic losses, and $-m \cdot \exp(ni)$ is an empirical term that approximates mass transfer losses. The fitting of the

model involve fitting the current-voltage data over the entire range of current densities. Theoretically, a polarization curve should present three stages related with these three losses. However, when working with MFC usually a straight polarization curves are obtained (Referencia Logan), being really difficult to identify the controlling stage of the process.

In order to ensure an accurate identification of the main processes controlling the performance of the MFC used in this study, and accurate fitting of the model was required. For accurate fittings it is requires accurate initial approximations of the fitting parameters of the model. Because of that, the initial approximations of the E_0 were based on the OCV values measured in the polarization curves carried out. Due to the lack of low current data, the parameter b was supposed to be the same in all the cases, -0.005 V/decades. This value is in agreement with the typical values presented in the literature [40]. The initial approximations of the parameter R was taken from electrochemical impedance spectroscopy analyses. Finally, initial values for the m and n parameters were taken from the literature [Hao, 2016, An Improved Empirical Fuel Cell Polarization Curve Model Based on Review Analysis]. Once selected the initial approximations, all the parameters were simultaneously fitted to the experimental results presented in the polarization curves. The fitting values of all the parameters, as well as the obtained results, are presented in Table 3 and in Figure 6, where an accurate fitting can be observed.

Table 3. Fitting values of the parameters of the empirical model corresponding to the polarization curves.

	CP		CP-Ni		CP-Au		CP-Pt	
Parameter	Start-up	Steady-State	Start-up	Steady-State	Start-up	Steady-State	Start-up	Steady-State

E_0 (V)	1.865	2.271	0.592	3.000	0.329	0.436	0.196	1.111
b (V/decades)	-0.005	-0.005	-0.005	-0.005	-0.005	-0.005	-0.005	-0.005
R (Ω)	-32.20	-32.20	-6.22	-6.22	-3.40	-3.40	-11.83	-11.83
m (A)	-1.829	-2.206	-0.316	-2.60	-0.061	-0.156	-0.039	-0.846
n (A^{-1})	5000	5000	1150	53	3361	1148	6153	455

Figure 6. Modelling of the A) initial and B) steady-state polarization curves. (Δ) MFC-Pt; ($\circ$) MFC-Ni; ($\square$) MFC-Au; ($\diamond$) CP.

By analyzing the fitting results, it can be highlighted that the E_0 value was in the same order in all the cases, ranging from 0.4 to 3.0 V when operating under steady-state conditions. The similar E_0 values suggest that the E_{OCV} are very similar, being negligible the effect of the metal doping on the typology of the reactions taking place (there are no different reactions on the electrode surface). Likewise, the constant value of the term io may suggest a minor electrocatalytic contribution of the metal. Moreover, in all the cases the E_0 value increased with the time. The increase of the E_0 indicates that performance of the MFCs is enhanced as time goes by, which could be explained because of the development of a more active electrogenic biofilm on the surface of the electrode.

Regarding the parameter b , as it was stated below, there was a lack of low current data to attain a good fitting and it was found that the initial value proposed help to fit well all experimental results. The identical value of the b parameter in all the MFCs shows the negligible influence of the metals over this term of the model.

On the other hand, in the literature, R has been usually identified as the controlling stage of the processes taking place in MFCs. However, the modelling results indicates that the metal doping to the carbonaceous electrodes slightly modify the R values which ranged from 32.2 Ω to 3.4 Ω . This slight effect could be related to the better electrical conductivity of the metal doped anodes when compared with the raw ones. Table 4 presents a comparison of the electrical properties of the materials used in this work. In this Table, it can be seen that the electrical conductivity and resistivity of the metals were significantly higher and lower respectively as compared to the carbon paper. With regard to the R values it is also worth to mention that the values presented in each MFC remained completely stable with the time in all the cases. This behavior suggests that the addition of metals slightly modify the physical properties of the electrode but does not affect the subsequent bioelectrochemical processes.

Table 4. Electrical properties of the materials under study.

<i>Material</i>	<i>Electrical conductivity (S/m) at 20 °C</i>	<i>Specific electrical resistivity (Ω m)</i>
<i>Carbon paper</i>	2.0	8.0
<i>Au</i>	4.10^7	$2.3.10^{-8}$
<i>Pt</i>	$9.43.10^6$	$1.06.10^{-7}$
<i>Ni</i>	$1.43.10^7$	$7.1.10^{-8}$

Hence, because of the results obtained with the E_0 , b and R_i parameters, it can be said that the addition of the metal to the anodes does not modify the thermodynamics, electrocatalytic behavior nor the internal resistance of the process taking place in the anode. With regard to the

mass transfer, two parameters were fitted: m and n . The parameter n is inversely related to the smallest current density that causes the voltage to deviate from linearity, which is that the system experience mass transfer limitations. In this sense, the lower the n value the less sensitive the system to mass transfer limitations. In Table 3, it can be seen that when doping the carbon electrodes the value of n decreased by a factor of almost 100, shifting from 5000 A⁻¹ when using raw carbon paper to 53 A⁻¹ of the Ni doped anode. This behavior indicates that the addition of metal reduced the mass transfer limitation in the MFC. It is also important to highlight that the value of the parameter n remained constant when working with raw CP anode, whereas the value of n decreased when operating with metal doped ones. The value of n decreased by 3 times when using Au, 12 times when using Pt and 20 times when using Ni, being therefore even less sensitive to the mass transfer limitations. On the other hand, m coefficient is inversely related to the relevance of the mass transfer phenomenon occurring over the entire range of current densities, presenting in all the cases negative values. As can be seen in Table 3, the addition of the metal increased the m value leading to a better performance in all the cases but mainly when the threshold current density was overcome. It is also worth to mention that the m value decreased along the experiments, which could be explained because of metal catalyst fouling. In this sense, the evolution of the n and m values indicates that the threshold current density causing mass transfer limitations was increased when the anodes were doped with the metals. Moreover, the intensity of these mass transfer limitations was lower when metals were added to the anodes. Hence, from the modelling results, it must be said that the addition of metal on the anodes increase the threshold current density causing mass transfer limitations, reducing also the intensity of the mass transfer limitations when they took place.

4. Conclusions

From the results obtained in this work, it can be stated that the addition of metallic compounds to the surface of the carbonaceous anode enhanced the performance of the MFCs. Metals reduce the internal resistance and the mass transfer limitations favouring the development of an electrogenic culture and increasing the CE. The best results were obtained when using Ni as doping metal. The enhancement in the current densities obtained were 7.5 A m^{-2} when doping with Ni, 4.2 A m^{-2} when using Au and 2.0 A m^{-2} when using Pt, being the reference in all the cases the result obtained by the non-doped MFC. Regarding to the power density, when Ni was doped the power exerted was 2.92 W m^{-2} , which represents about 3 times that exerted by the MFC without metal addition. From the modelling results, it was observed that the primary mechanism that explain the better performance of the cells equipped with metal doped anodes was the reduction of the mass transfer limitations. In this sense, the addition of metal on the anodes increase the threshold current density causing mass transfer limitations, reducing also the strength of the mass transfer limitations when they took place.

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