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Electro-polymerization of pyrrole on graphite electrode: Enhancement of electron transfer in bio-anode of Microbial Fuel Cell --Manuscript Draft--

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Abstract:	The enhancement of the power output of a Microbial Fuel Cell (MFC) relays on two important issues: the immobilisation of the catalyst microbial film on the bio-anode where oxidation occurs and the electron transfer between them. In the present work, a graphite rod was used as anode and modified by electro-polymerisation using the conducting polymer (pyrrole). It was resulted an improvement of the electronic conduction and therefore an increase of the power density of the cell (i.e. from 7 to 25 mW/m2). The electroactive biofilm was produced from compost leachate garden, deposited naturally on the anode without prior polarisation. The efficiency of this modification was investigated to determine the supply of pyrrole in term of electricity generation. The results show enormous power density supply of the MFC using bio-anode modified with pyrrole. Besides, since the energy produced by a MFC is too small, it would be interesting to recover the maximum of it by selecting the appropriate materials which fulfil the two criteria: better electron transfer and longer bacteria life.		
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	the electro-polymerization of pyrrole on carbon graphite to be used as a bio-anode in a Microbial Fuel Cell. Yours Sincerely, M. KAMECHE (Corresponding author)
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Electro-polymerization of pyrrole on graphite electrode:

Enhancement of electron transfer in bio-anode of Microbial Fuel Cell

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Abstract

The enhancement of the power output of a Microbial Fuel Cell (MFC) relays on two important issues: the immobilisation of the catalyst microbial film on the bio-anode where oxidation occurs and the electron transfer between them. In the present work, a graphite rod was used as anode and modified by electro-polymerisation using the conducting polymer (pyrrole). It was resulted an improvement of the electronic conduction and therefore an increase of the power density of the cell (i.e. from 7 to 25 mW/m²). The electroactive biofilm was produced from compost leachate garden, deposited naturally on the anode without prior polarisation. The efficiency of this modification was investigated to determine the supply of the MFC using bio-anode modified with pyrrole.

Besides, since the energy produced by a MFC is too small, it would be interesting to recover the maximum of it by selecting the appropriate materials which fulfil the two criteria: better electron transfer and longer bacteria life.

Key Words: Microbial Fuel Cell; Leachate garden soil; Bio-anode; Conducting polymer.

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1. Introduction

Fuel cells are alternative energy sources that convert directly the stored chemical energy into renewable electrical energy. The conversion takes place via an electrochemical process and not combustion; a process not polluting and three times efficient than fuel burning.

Owing to environmental preservation, new but weak bacterial energy sources were investigated to degrade organic matter and therefore to reduce pollution [1]. Microbial Fuel Cells (MFCs) are good candidates for this purpose. They are electrochemical devices which generate electricity from oxidation and reduction processes taking place in micro-organisms [2]. In a MFC, the anodic chamber is usually separated from the cathodic chamber by a proton exchange membrane. In the presence of the electroactive biofilm adhered on the anode, the fuel (organic matter) oxidizes, by releasing electrons and protons [1, 3]. The basic operating principle of an MFC can be explained using the classical dual-chamber MFC. Under biocatalysis, organic carbons are oxidized by the biofilm covering the anode in the anodic chamber under anaerobic condition. Reaction (1) shows the half-reaction using acetate as an example organic carbon. The oxidation occurs inside the cytoplasm of the sessile cells (i.e. biofilm cells). The electrons released by oxidation are transferred by the sessile cells in the anodic biofilm to the anode surface. These electrons flow through an external circuit to reach the cathode in the cathodic chamber where they are used for reduction of oxygen. To maintain electro-neutrality, protons migrate from the anodic chamber to the cathodic chamber to participate in reaction (2) [4].

Anode:
$$CH_3COO^- + 4H_2O \rightarrow 2HCO^-_3 + 9H^+ + 8e^-$$
 (Eq.1)

Cathode:
$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$
 (Eq.2)

The materials such as Carbon Graphite (CG) and Carbon Felt (CF) are usually suitable as anodes in MFCs, due to their chemical stability and high electric conductivity [5].

Characteristics of bio-anode are also considered to be significant as it directly affects the bacterial interaction, electron transfer, and substrate oxidation [6, 7].

Anode for MFC, as the bacteria carrier, can influence not only the bacteria adhesion but also the electrons transfer process from the microorganisms to the anode. So an excellent anode should prompt the electrons transfer process described above and suitable for microbial growth. Various strategies have been developed to improve MFC anode, such as metal and nonmetal materials modified [8.9].

Conductive polymer materials, which have both strong conductivity and the properties of polymers, are widely used in electronics and biosensors [10]. Recently, they have earned more attention to improve MFC performance by modifying its anode.

In this study, pyrrole was used to modify electrode material, owing to its stable redox reaction and its outstanding electrical conductivity [11]. However, conductive polymers, due to the special characteristics, are likely to affect the bacteria attachment on anode and the process of electrons transfer from bacteria to anode, which can change the biofilm and further affect the MFC power generation. Even the power density can also affect microbial diversity of anode biofilm, in return [12].

Pyrrole was electro-polymerized on the CG, to enhance the electron transfer between the biofilm and the anode. The influence of modification of bioanode has been investigated by performance of the MFC measurement.

2. Experimental Sections

2.1. Materials

Garden compost was purchased from Neuhaus (France). The reagents hydrochloric acid, potassium chloride and sodium acetate were of analytical grade. The Nafion 115 membrane from DuPont de Nemours (USA) was used as a separator in the MFC. The materials used for the electrodes were: CG or CF as bio-anode and the alloy titan-platinum or stainless steel sheets as cathode. The multi-meters Fluck 175, pH meter Hanna and conductimeter Hanna were also used. Solutions were prepared using reverse osmosis demineralized water. The TOC instrument for to measure the degradation organic carbon. The potentiostat-galvanostat Voltalab PGZ301 was also used for the modification of the bio-anode and its electrochemical characterization using chrono-amperometry and voltammetry techniques.

2.2. Methods

2.2.1. Preparation of compost leachate

The microbial flora was extracted by lixiviation, from the mixture of 500g of the Neuhaus garden soil and 1 L of aqueous potassium chloride solution 60 mM. The mixture was placed in an Erlenmeyer and stirred with a magnetic agitator during 72 hours. Then, it was filtered using a paper filter to yield the leachate compost having an ionic conductivity of 4 mS/cm at pH 6.5.

2.2.2. Elaboration of bio-anode

A CG bar having the dimensions $(0.5 \times 0.5 \times 5.0 \text{ cm})$ was immersed into the compost leachate where it was stored. Then, it was removed from the conditioning solution and dipped again into a new leachate solution, to be used as a bio-anode inside the MFC.

2.2.3. Modifications of bio-anode

In order to improve its electronic conduction, the CG anode was modified by electropolymerisation of Pyrrole (Sigma Aldrich) known as a high conducting polymer. According to the literature the electrical conductivity of Polypyrrole (PPy) ranges between 2.0 - 2.5 S.cm⁻¹ in LiBF₄ aqueous solution [13] and that of graphite carbon is about 10⁻² S.cm⁻¹ [14]. In effect, the aqueous solution of lithium tetrafluoroborate (Aldrich) was used as a support electrolyte, in the conventional three-electrode electrolysis cell. It consists of the graphite working electrode, Ag/AgCl reference electrode and platinum counter-electrode. PPy films were electro-generated and electro-deposited at room temperature by cyclic voltammetry in the potential range (0-0.9 V). Cyclic voltamograms (Fig.1) shows the formation of dimers (pyrrole oxidation) from 0 to 400 mV. More than 400 mV the synthesis of PPy is started (the combination of dimers).

The polymerization of pyrrole is well described elsewhere [15,16]. The electrochemical synthesis mechanism is due to the partly conjugated PPy.

Fig.1

SEM images

The magnified SEM images (Fig2) allow for clear perception of the fine structure details. They show the electrode surface before and after modification with PPy. In effect, in the absence of the polymer, it can be observed thin wafers of carbon graphite, separated by empty spaces. In contrast, in the in presence of PPy, the wafers are tightly joined to each other by reducing spaces between them. Moreover, the roughness of the modified electrode becomes higher unlike to smooth electrode without PPy. This modification may provide a better adhesion of the biofilm onto the electrode and therefore a better electron transfer. Besides, on a fundamental scale, the displacement of the electron is relatively higher, because the band gap in carbon is reduced by PPy allowing mean free path of the electron inside the material. For all these reasons, the electron density produced by the MFC increases. As it is illustrated by the diagram given by Fig., the the electrical conductivity of PPy is highly greater than that of graphite carbon

Fig.2

2.2.4. Electroactive biofilm growth

The electroactive biofilm growth was carried out naturally without applying chronoamperometry as did previous researchers in the field [16, 17]. In Fig.3a, the solution of the compost leachate was dark brown in the beginning. After 20 days of mature, the leachate became almost transparent and a great deal of bio-film aggregated around the anode (Fig.3b). However, small amounts of aggregates flatted on the solution surface. During 10 days, Champavert *et al.* found an electromotive force almost equal to ours [17].

Fig.3a

Fig.3b

2.3. Microbial Fuell Cell design

As illustrated by Fig.4, the MFC consists of two half-cells made glass, connected to each other by the Nafion[®] membrane (cationic exchange perfluorinated membrane). The CG bioanode and the platinized titanium sheet (1 x 5 cm) are placed inside the anolyte and the catholyte respectively. The anolyte contains the leachate solution; whereas the catholyte contains hydrochloric acid solution 0.1 M. the solutions were stirred with magnetic bars. The top end of the anolyte was tightly sealed with paraffin film to avoid penetration of oxygen. The circuit of the cell was closed with an external resistance of 1 000 Ω . The cell voltage of the cell was measured with a multimeter placed in parallel. Owing to the fact of very values, the current density was deduced using Ohm's law. After 20 hours of functioning, both the level of the solution and the current density fell, as a result of the decrease of the contact surface of interface solution/bio-anode. So, the amount of leachate removed, was substituted

by the same amount of sodium acetate 20 mM. After 5 hours, as a result of acclimation, a significant increase of the current was observed (approximately twice higher than that obtained with just pure leachate) and continued to increase provided the fuel was added.

Moreover, from the higher current obtained, the power density was determined in terms of current density by varying the external resistance from 100 to 50 000 Ω . Generally, the value of the current stabilized within 3 minutes. However, the required time needed to reach the initial value, depended upon the value of the resistance. In effect, the smaller the value of the resistance, the higher the cell discharge.

Fig.4

2.4. Total Organic Carbon Analysis

The Total Organic Carbon (TOC) is the amount of carbon found in an organic compound. In our case, the amount of carbon contained in sodium acetate was measured with a TOC analyzer received recently by our laboratory. As it is illustrated by Fig.5, during the course of experiment, the quantity of carbon present initially in the solution was drastically reduced, showing the degradation of the fuel (acetate anion) by the bio-film. This yielded an amount of CO_2 which will be consumed by the bacteria. This finding is coherent with the oxidation reaction of acetate (Eq.1). In the cases of sodium acetate, for leachate and mixture (MFC before operating), it is clear that the content of carbon was relatively high. But, when the MFCs started working, the amount of carbon was reduced equally by 25%, whatever the type of the bioanode (unmodified or modified). This finding makes in evidence the degradation of the organic matter by biofilm, transforming the carbon into hydrocarbonate (HCO₃⁻).

$$CH_{3}COO^{-} + 4H_{2}O \xrightarrow{Biofilm}{2HCO_{3}^{-} + 9H^{+} + 8e^{-}}$$
(Eq.1)



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3. Results and Discussion

3.1. Evolution of ElectroMotive Force (EMF)

This work presents the novel bioanode electrode modified with PPy for use in the microbial fuel cell described above, with the aim to obtain the highest electrical energy. The generated EMFs of MFCs using both unmodified and modified bioanodes were represented in (Fig.6). During the course of the experiment, the EMF decreases a little bit and remains almost constant, for 24 h. However, their values are completely different (two times higher) right down from the beginning until the end of the experiment. Besides, the cell's EMF using the CG bioanode, compares well with that of Godwin et al. [16], although they have used more operating conditions (i.e. polarization and immobilized mediator).

Fig.6

3.2. Electrochemical characteristics of MFC

After closing the anode compartment (anaerobic condition), the power density was stable in both MFCs. The characteristic curves of polarization and power were used to evaluate the electrical performance of the cell. The polarization was obtained using different values of the resistance ranging between 10 and 50 000 Ω . As shown in Fig.7, the polarization curve presents three regions: voltage drop of activation (low current), Ohmic drop in electrolyte (linear part) and voltage drop due to limiting phenomenon (high current). The power curve yields the maximum corresponding to the highest energy that can be delivered by the MFC.

These results obtained with similar compost-leachate, also indicate that MFCs even inoculated from the same source, can have different behaviors depending on the nature of the electrode. The polarization curves of Fig.7, i.e. the power density versus current density of the two MFCs (with and without modification), show a relatively large difference. Such observation can explain, the discrepancies reported in the literature about the effect of the polymer. It has often been observed that power density increased as the electrode was

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modified with conducting polymer. In effect, in the tests using PPy-methylene blue and PANI, the power densities of a similar MFC were respectively 7 mW/m² [16], and 27.3 mW/m² [18].

In our case, it can be clearly seen that PPy had an influence on the performance of the MFC. The lowest power density i.e. 7 mW/m^2 was observed in unmodified MFC, whereas the highest power density 25 mW/m^2 appeared in PPy modified MFC (corresponding to cell voltage of 200 mV and current density of 150 mA/m^2). These results are summarized in Table 1. The MFC using modified anode with PPy, had a relatively good performance for its maximum power. Thus, the PPy enhanced the power output of MFC by three times comparing with unmodified MFC. This relatively large difference is certainly due the enhancement of electron transfer using PPy as a conducting polymer.

Fig.8

Table 1

3.3. Electrochemical characteristics of bioanode

Bioanodes were characterized by cyclic voltammetry after the growth the biofilm. Indeed Fig (9) shows oxidation peaks at 0, 45 V. However, the peaks lying from 0-0,45 V, have small amplitudes which are perhaps adsorption of the electroactive species in the lixiviat solution. But Fig (10) shows voltamogram of the modified bioanode revealing larger current responses compared to the bioanode CG. The increase in the electron transfer is certainly attributed to the conductive proprieties of PPy.

Fig.9

Fig.10

4. Conclusions

- PPy regarded as conductive polymer, was used to modify the bioanode of MFC which yielded maximum power density supply (i.e. 25 mW/m²).
- 2- The bacterial species of leachate garden compost adhered well on anode and were not poisoned and influenced by the presence of PPy since the MFC gave an open circuit EMF of about 600 mV during 20 days. In effect, PPy provided a more stable biofilm on the anode and more allowance for the power the MFC.
- 3- Without using chronoamperometry for adhering biofilm on CG, a relatively high and stable value of EMF was obtained naturally by us.

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MFC	Bio-anode	Cathode	Separator	Power density (mW/m ²)		
Fuel Cell without bio-film	Carbon graphite (modified with PPy)	Platinum sheet	Nafion	~ 0		
MFC1-a	Carbon graphite	Platinum sheet	Nafion	6.5		
MFC-b	Carbon graphite (modified with PPy)	Platinum sheet	Nafion	25		
MFC-c [Ref.2012]	Stainless steel rod modified with PPy-MB)	Carbon graphite (modified with pyrrole)	Nafion	7		

Table 1: Power densities obtained with different MFCs

Captions to Figures:

Fig.1: Cyclic voltammograms during the electropolymerization of pyrrole . vs Ag/AgCl

Fig.2. SEM images of different anodes (A)- (B) Carbone graphite, (C)-(D) modified Carbone graphite

Fig.3a: Microbial Fuel Cell before the formation of bio-film

Fig.3b: Microbial Fuel Cell after the natural formation of bio-film

- Fig.4. Schematic representation of MFC
- Fig.5: Amount of carbon consumed in both MFCs

Fig.6: Evolution of open circuit MFC using different electrodes

Fig.7: Current-Voltage and power curves of MFC using CG anode (without polarization).

Fig.8: Power densities of MFCs

Fig.9: Cyclic voltammetry performed with bioanode CG after operating MFC

Fig.10: Cyclic voltammetry performed with PPy-modified bioanode after operating MFC.











Fig.3a



Fig.3b



Fig.4



Fig.5



Fig.6



Fig.7



Fig.8



Fig.9



Fig.10

Supplementary Material

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