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Short Communication

Effect of various carbon-based cathode electrodes on the performance of microbial fuel cell

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HIGHLIGHTS

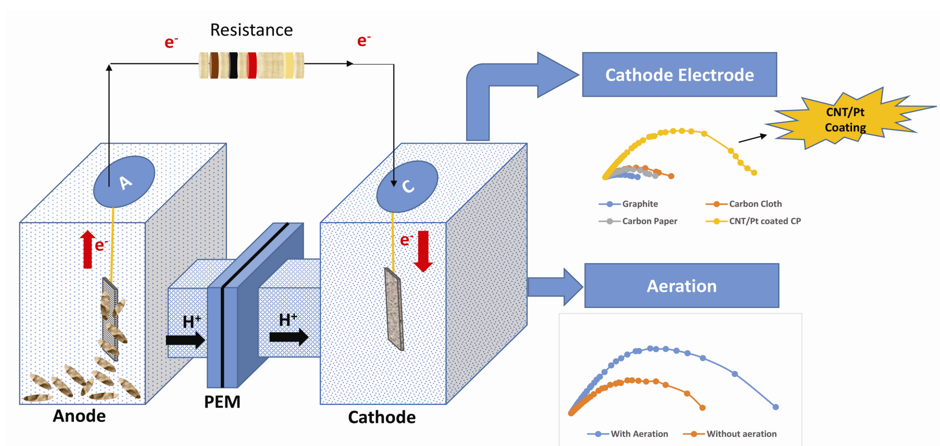
➢ The performance of different carbon-based cathodes was compared in a dual-chambered microbial fuel cell.

➢ A novel CNT/Pt-coated carbon paper was fabricated.

➢ The maximum current and power generated were 82.38 mA/m^2 and 16.26 mW/m^2, respectively.

➢ Aeration in the cathode compartment was found effective on power generation in MFCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cell (MFC) is a prospective technology capable of purifying different types of wastewater while converting its chemical energy into electrical energy using bacteria as active biocatalysts. Electrode materials play an important role in the MFC system. In the present work, different carbon-based materials were studied as electrode and the effect of dissolved oxygen (aeration) in the cathode compartment using actual wastewater was also investigated. More specifically, the effect of different electrode materials such as graphite, carbon cloth, carbon paper (CP), and carbon nanotube platinum (CNT/Pt)-coated CP on the performance of a dual-chambered MFC was studied. Based on the results obtained, the CNT/Pt-coated CP was revealed as the best cathode electrode capable of producing the highest current density (82.38 mA/m^2) and maximum power density (16.26 mW/m^2) in the investigated MFC system. Moreover, aeration was found effective by increasing power density by two folds from 0.93 to 1.84 mW/m^2 using graphite as the model cathode electrode.

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1. Introduction

The world faces energy crises as the traditional energy sources like coal, gas, and petroleum are running out (Scott, 2005). This has turned looking for new energy supplies into an important requirement for life. Among the most promising renewable energy supplies with minimal environmental impacts are wind energy, solar energy, and microbial fuel cells (MFCs). The first and second categories have been developed as there are many giant wind turbines and solar power plants all over the world while MFCs are still to be further investigated before used commercially (Rahimnejad et al., 2014; Beurskens and Brand, 2015; Chaudhari and Deshmukh, 2015; Green et al., 2015).

The MFC technology is a promising method of transforming bacterial metabolic energy into electricity (Chae et al., 2009). Traditional MFCs consist of two chambers in which electrodes are placed while a membrane separates the chambers from each other (Rahimnejad et al., 2012). Microorganisms in the anode chamber consume the substrate and produce electrons and protons. The produced electron is transferred by an external circuit to the cathode compartment and the generated protons are transferred by the proton exchange membrane to the cathode chamber (Du et al., 2007).

Therefore, electrodes play a very important role in the efficiency of an MFC (Ghoreishi et al., 2014). In fact, the electrons produced by bacteria are transferred on the anode's surface while on the cathode's surface an electrochemical reduction reaction takes place (Du et al., 2007; Freguia et al., 2007). Hence, the surface of the electrodes is of significant importance in the overall performance of an MFC. More specifically, the higher electrode surface area leads to an enhanced MFC performance. Traditional electrode materials commonly used as anode and cathode include graphite, carbon cloth, and carbon paper (Ghasemi et al., 2013). Many studies are underway with a focus on the fabrication of novel electrode materials in order to improve MFCs' system performance (Guo et al., 2015; Kim et al., 2015).

It is worth quoting that among the reasons given for the very poor performance of the currently-available MFCs for large-scale application is the low efficiency of electricity generation caused by the limited surface of electrodes (Qiao et al., 2007). Progresses in nanotechnology and nanomaterial sciences have brought about evolutionary developments in the MFC technology. This is ascribed to the fact that materials at nano-scale exhibit different and unique properties in comparison with their macro-scale forms (Klabunde and Richards, 2009). Accordingly, many researchers have tried to apply nanomaterials in the fabrication of electrodes (Qiao et al., 2007; Xie et al., 2010; Xie et al., 2012; Wang et al., 2015). In fact, the problems associated with the low surface area of electrodes could be overcome by the application of nanomaterials owing to their extensive active surface area. The low performance of MFCs is also attributed to the low conductivity and insufficient velocity of the electron transfer process caused by the high electrical resistance of conventional electrode materials (Ghasemi et al., 2013; Rahimnejad et al., 2015). Various microorganisms are used in the anode chamber of MFCs including pure or mixed cultures (Logan, 2009). The latter is however preferred as resembles the practical conditions more (Izadi and Rahimnejad, 2014).

In the present study, a two-chamber MFC was inoculated by using a mixed culture, i.e., anaerobic sludge as biocatalyst in the anode chamber. Several conventional carbon-based electrodes including graphite, carbon cloth, carbon paper (CP), as well as a novel electrode, i.e., carbon nanotube platinum (CNT/Pt)-coated CP were investigated as cathodes. More specifically, CNT and Pt were used to simultaneously achieve both high active surface and high conductivity, respectively. Generated power and current in the presence of these cathodes were evaluated to determine the best carbon-based electrode. Moreover, the effect of aeration in the cathode chamber was also taken into account. The biofilm formed on the anode's surface was also electrochemically investigated.

2. Materials and methods

2.1. MFC construction and operation

Two cubic and H-shaped chambers with a working volume of 760 ml each were constructed using Plexiglas material and were separated by a Nafion 117, acting as the proton exchange membrane (PEM). Both the cathode and the anode surface areas were 8 cm^2 and the MFC was operated at the ambient temperature and neutral pH (6.5-7) at the anode compartment. (Kim et al., 2002; Zhao et al., 2005). The pH was adjusted by the phosphate buffer solution. Graphite was used as the anode and cathodes were graphite, CP, carbon cloth, and CP coated by CNT/Pt (0.1 mg/cm^2). The MFC used is schematically shown in **Figure 1**.

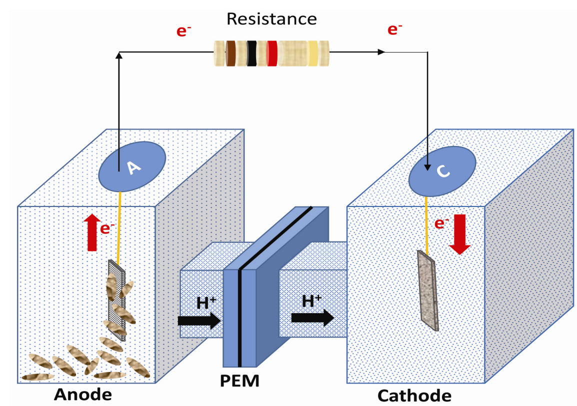

Fig.1. Schematic image of the fabricated MFC.

2.2. Microorganisms

Anaerobic sludge collected from the anaerobic process tank of the Ghaemshahr wastewater treatment center (Mazandaran, Iran) was used as inoculums. The media used contained (g/L): glucose (20), yeast extract (3), and peptone (1 g).

2.3. CNT/Pt composite electrode

A chemical reduction technique was used to fabricate the CNT/Pt. First, the CNT was ultrasonicated in nitric acid for approximately 3 h. Then, the sample was dried, washed with deionized water several times, and air-dried. The dried sample was then ultrasonicated again with acetone for 1 h and a 0.075 M H_2PtCl_6 solution was added slowly under stirring. After 24 h, the mixture was reduced using a 1 M NaOH and 0.1 M $NaBH_4$ solution. When the mixture was ready, it was washed by deionized water and dried at 80 ^oC for 6 h. The required amount of the CNT/Pt was added to a small amount of ethanol, dispersed properly, and then brushed onto the CP surface.

2.4. Analyses and calculations

The current and power produced by the system were calculated by using the following equations (**Eqs. 1** and **2**).

$$I=\frac{V}{R} \quad (1)$$

$$P=R\times I^2 \quad (2)$$

Where I is the current (ampere), V is the voltage (volt), R stands for the external resistance (ohm) and P denotes the power (watt) produced by the system.

The MFC's internal resistance was calculated by two methods:

A. Polarization slope method (V-I curve): the slope of the voltage-current curve represents the internal resistance.
B. Power density peak method: the external resistance at which the MFC power output reaches maximum amount is considered as the internal resistance of system (Logan, 2008).

An IVUM package (Ivium Technology, Netherland) was used to analyze cyclic voltammetry (CV). The CV test was performed to identify the oxidation and reduction potential of the substrate. Potentials ranging from -400 mV to 1000 mV at a scan rate of 50 mV/s were applied to

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conduct the CV experiments. In order to measure the oxidation and reduction peaks, the CP (NARA, Guro-GU, Seoul, Korea) was used as the working electrode and Platinum (Platinum, gauze, 100 mesh, 99.9% meta basis, Sigma Aldrich) was used as the counter electrode. Moreover, Ag/AgCl electrode (Ag/AgCl, sat KCl, Sensortechnik Meinsberg, Germany) was utilized as the reference electrode.

All the chemicals and reagents used for the experiments were of analytical grades and were supplied by Merck (Germany). A HANA 211 pH meter (Romania) was employed for measuring the pH values. The initial pH of the working solutions was adjusted by the addition of diluted HNO_3 or 0.1 M NaOH solutions.

3. Results and discussion

As mentioned earlier, microorganisms play a very effective role in the performance of MFCs. A mixed culture of microorganisms was used as the electron generator in this study. Prior to the MFC experiment and in order to evaluate the required time to create a steady state by the mixed culture, the growth kinetics were surveyed using glucose as the only carbon source. After the inoculation, sampling was performed every 2 or 4 h and the light absorption of the samples at 620 nm was determined. Figure 2 presents the growth curve of the active biocatalyst used. As can be seen in the figure, the microorganisms used were capable of efficiently growing under anaerobic conditions. More specifically, the microbial growth initiated with a lag phase followed by a rapid and sharp tangent entry into the logarithmic phase. Then, after 26 h, the mixed culture reached the stationary phase (Fig. 2).

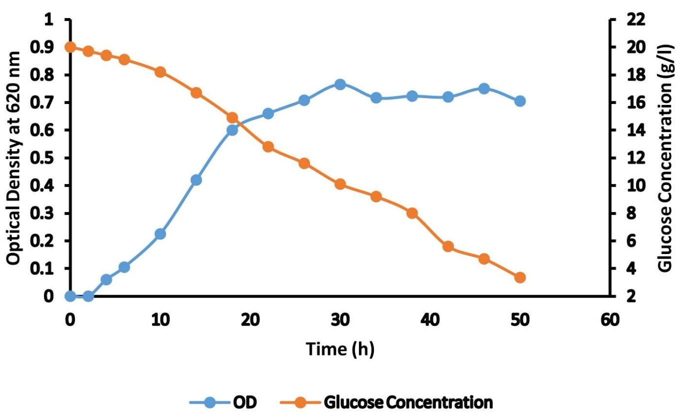

Fig.2. Growth curve of the used microorganisms under anaerobic conditions.

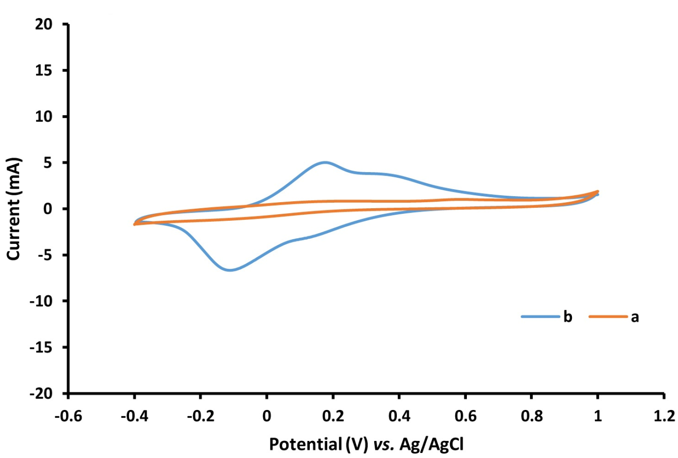

Fig.3. Investigation of the developed active biofilm on the anode's surface by electrochemical analysis at 0.05 V/s scanning rates, a) before, and b) after the development of the biofilm by the mixed culture used.

The capability of the mixed culture in producing biofilm on the surface of the anode electrode (graphite) was also examined by CV analysis and the results obtained are presented in Figure 3. As could be seen, no electrochemical activity was observed on the anode's surface before the development of an active biofilm. However, after the development of an active biofilm by the end of the process, electrochemical analysis revealed the existence of two oxuidation/reduction peaks confirming the suitability of the mixed culture used (Fig. 3).

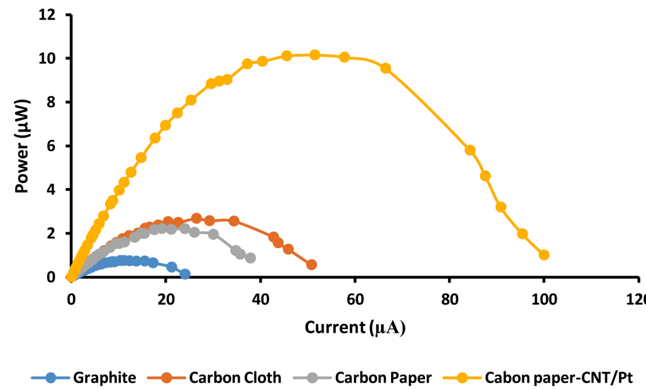

Fig.4. Polarization Curve of the graphite, carbon cloth, carbon paper (CP), and the CNT/Pt-coated CP electrodes without aeration.

In MFCs, electrodes are electron transferring sites and by selecting a suitable electrode, it is possible to maximize the output power of the system. In the present study, four carbon-based electrodes were used as cathode. Among the conventional electrodes used, the carbon cloth and the CP were respectively the most suitable cathode electrodes in terms of the generated power density (Fig. 4). More specifically, the maximum power density values obtained were 0.937, 2.76, and 3.35 mW/m^2 for the graphite, CP, and carbon cloth electrodes, respectively. It is worth quoting that the conductivity of the carbon cloth, the CP, and the graphite electrodes were approximately equal but the higher surface area of the carbon cloth and the CP electrodes compared with the graphite electrode led to higher efficiencies of the MFC system. The current density of the MFC using the graphite, CP, and carbon cloth electrodes was measured at 13.92, 23.9, and 33.07 mA/m^2, respectively.

The modification of the CP with the CNT/Pt coating resulted in significant changes. In more details, the power and current generated by the CNT/Pt-coated CP (16.26 mW/m^2 and 82.38 mA/m^2, respectively) increased by approximately six folds and three folds in comparison with the conventional CP (2.76 mW/m^2 and 23.9 mA/m^2, respectively). These improvements could be attributed to the high active surface area of the CNT and the high electrical conductivity of the Pt. In another words, the CNT and the Pt dispersed on the surface of the CP provided a desirable conductive porous surface for the electrons to rapidly react with oxygen. This could have consequently resulted in decreased proton accumulation and therefore, the pH of the anolyte and catholyte remained in an acceptable range for both metabolic activity of the microorganisms and the existence of a driving force for proton motion to the cathode chamber in which the reduction reaction occurred.

Besides the above-mentioned parameters, the internal resistance of the MFC was also studied. The internal resistance calculated by means of the V-I curve is shown in Figure 5. The slope of the linear parts of the V-I curve represents the internal resistance of the MFC (Ghasemi et al., 2013). It was found that by applying the carbon cloth, CP, and the CNT/Pt-coated CP as cathode electrodes, the internal resistance could be decreased by 20-25% (from 5.2 to 3.9 kΩ) compared with the graphite electrode. In fact, the CNT/Pt coating did not change the internal resistance of the CP while it increased the voltage and current generation significantly. This finding could be attributed to the voltage losses due to the higher current as a result of the coating applied (Logan, 2008). Calculations of the internal resistance were also carried out by the Power density peak method and similar results were obtained (data not shown).

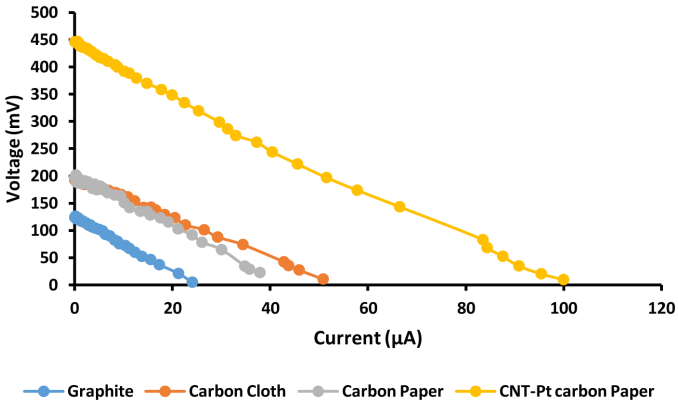

Fig.5. Voltage-current curves of the electrodes used as cathode.

Figure 6 demonstrates the effect of aeration on the performance of the MFC using the graphite electrode as cathode. The graphite electrode was selected to solely take into account the impact of aeration and not the electrode composition. The aeration in the cathode chamber increased the maximum voltage by more than 50% (from 124 to 190 mV). The power and current generation also increased significantly from 0.9 to 1.84 mW/m^2 and from 15 to 21 mA/m^2, respectively. In fact, the aeration in the cathode chamber was shown to result in a more complete and faster reduction reaction and minimal potential losses owing to limited electron acceptor concentration level in the catholyte. This finding was in line with those of Rabaey and Verstraete (2005).

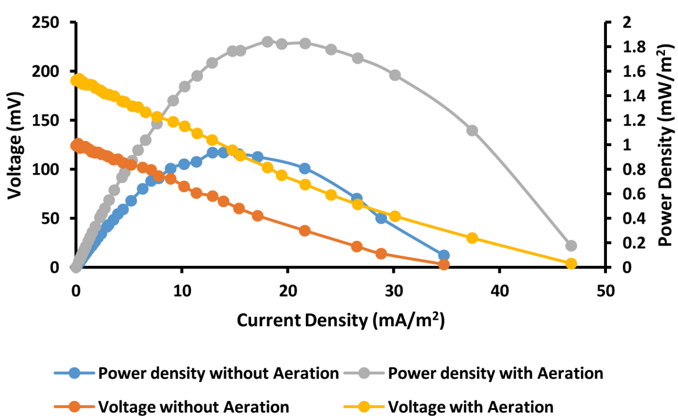

Fig.6. Polarization curve of the graphite electrode with and without aeration.

4. Conclusions

The performance of an MFC by using an active biocatalyst was investigated. The CV analysis demonstrated microbial biofilm production capabilities of the biocatalyst on the anode's surface. Different carbon-based materials as cathode electrode were also investigated. The best performance parameters were achieved by using the carbon paper electrode modified by CNT/Pt. This novel electrode led to significantly higher generated power (16.26 mW/m^2) and current (82.38 mA/m^2) compared to the other carbon-based cathode electrodes used, i.e., graphite, carbon cloth, and carbon paper. This was accomplished owing to the perfect electrical conductivity of the Pt and the high surface area of the CNT. It is worth mentioning that a separate experiment revealed that aeration in the cathode chamber led to a considerable increase in MFC performance (i.e., power density) by two folds.

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