Improvement of the Performance of Microbial Fuel Cell with Modification of Electrode using Copper Nanoparticles

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Microbial fuel cell (MFC) is one of the new methods to generate electricity. Design of microbial fuel cell to improve the performance of this system has been considered by many researchers. The internal resistance of the system is a factor that affects the performance and efficiency of MFC. In this study, the copper nanoparticles were used to reduce the internal resistance and increase the efficiency of MFC. First, performance of MFC was investigated with electrodes made of graphite. Then, electrode modification was done with copper nanoparticles using hydrolysis method and Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were used for verifying the existence of copper nanoparticles and determining their size. Finally, the fuel cell performance was investigated in the presence of the modified electrode. Our data showed that copper nanoparticles, with an average size of 89 nm and with spherical morphology, improve the performance and efficiency of microbial fuel cell. In the presence of copper nanoparticles the maximum voltage reached 930 mV while the maximum voltage of 720 mv was recorded with pure electrodes. The use of copper nanoparticles in the modification of electrode increases the power density and decreases the internal resistance of the system. The results showed that the maximum power density in the modified electrode state and the pure electrode was 1700 mW/m^2 and 900 mW/m^2 respectively. The maximum current density with the modified electrode was 1300 mA/m^3 and the maximum current density with the pure electrode was 900 mA/m^3. Copper nanoparticles reduced internal resistance and increased the efficiency of MFC.

Keywords: Microbial fuel cell, modified electrode, copper nanoparticles.

Humans have always tried to replace non-renewable energy with renewable energy. The microbial fuel cell (MFC) technology is one of the latest achievements to produce electricity. Within the microbial fuel, exogenous microorganisms oxidize organic matter to produce electrons and energy in form of ATP[1]. Figure 1 schematically shows a MFC system. The system is composed of two chambers. There is anode chamber, in which the exogenous microorganisms, in anaerobic conditions, oxidize the organic matter and produce electrons by forming a biofilm on the anode electrode. Finally, by passing through an external circuit, electrons reach the final electron recipient in the cathode chamber and are reduced. The two chambers are separated by a proton membrane

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made of Nafion. The protons reach cathode by passing through the anode chamber and produce water there, during a three-step reaction[2-4]. With the emergence of this technology researchers have faced different challenges to improve the performance of microbial fuel cell systems and they have been looking for new ways to increase the efficiency of microbial fuel cells. One of the challenges is internal resistance of the system that reduces the performance of the microbial fuel cell. Polarization resistance of the anode and cathode electrodes is one of the main factors in MFC internal resistance[5, 6]. To overcome this resistance, researchers initially tried to increase the efficiency of microbial fuel cell by changing the electrode material and using materials such as graphite plate, graphite sheet, graphite fiber, graphite brush, carbon coating, carbon paper, foams, graphite glassy carbon and other materials[7]. In recent efforts, the use of different catalysts on the surface of the electrode reduces the polarization resistance and results in high efficiency of MFC system. Materials that can be used as a catalyst on the electrode surface and have attracted the attention of many researchers are nanoparticles and nanotubes and carbon nanotubes[8]. Nanoparticles, in comparison with conventional materials, possess very large surface and have more potentiality for interaction with different chemical groups[9]. Many studies have proved the increase in efficiency of the biofuel cell with the modification of electrodes by nanoparticles. In one study Liu and Vipulan found the improvement of the microbial fuel cell with the modification of cathode electrode with nickel nanoparticles. Their results showed that MFC density power was increased from 0.07 mW/m^2 to 0.35 mW/m^2 [10]. Among nanoparticles, copper is widely used in industry due to its unique properties such as high chemical reactivity, low cost and conductivity. The application of these nanoparticles in solar cells increases the efficiency of a special type of solar cells. Also the use of these nanoparticles as an active anode ingredient in solid oxide fuel cells results in the increase of the thermal conductivity of the fluid[11, 12]. Considering the physicochemical properties of copper nanoparticles, these nanoparticles have been used in this study to modify anode electrode to improve the performance of the MFC.

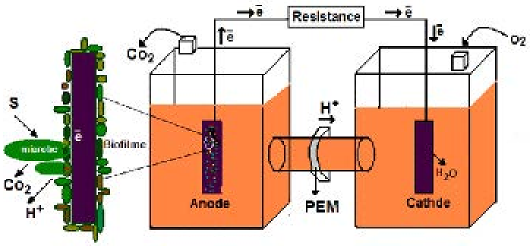

Fig. 1. Schematic of microbial fuel cell system

MATERIALS AND METHODS

The chemicals used in the modification of the electrode such as copper sulfate 5-hydrate, ethylene diamine tetra acetic acid, hydrochloric acid 37%, tin chloride, sodium hydroxide, Palladium (ÉÉ) chloride, formaldehyde 36% and all materials used in making the medium needed to growth microorganisms were obtained from Merck , Germany.

The electrode modification using copper nanoparticles

The electrode used in this experiment is of graphite plate material with dimensions of 5 cm to 5 cm and a thickness of 150 micrometer which were prepared from Arvin Danesh Arian Company. Table 1 shows the characteristics of this electrode. Electrode modification in this experiment was carried out using hydrolysis method. To do this, first graphite plate was washed. For absorbent surfaces on the electrode, the electrode was put in 15 g/l sodium hydroxide solution at 70 ° C for 20 min. To activate the electrode surface, first, a solution of 10 g/l tin chloride and then hydrochloric acid solution were used for 20 minutes. Palladium chloride bath was used to activate copper nanoparticles and to absorb them on the electrode surface. After activation of the electrode surface, the electroless bath was used for the modification of the electrode with copper nanoparticles. This bath contains copper sulfate 5-hydrate, ethylene diamine tetra acetic acid, sodium hydroxide, and formaldehyde 36%. In all moments of the modification of the electrode, bath temperature was maintained at 80 ° C and PH was maintained at about 12. After this step, the modified electrode was washed with deionized water and was used for the next step of the test[13]. Table 2 shows the condition and amount of electroless bath**.** Scanning Electron Microscope (SEM) and

Energy-dispersive X-ray spectroscopy (EDS) were used for verifying the existence of copper nanoparticles and modification of the electrode using these nanoparticles. For this purpose, the electrode used in this study was explored before and after coating with copper nanoparticles, using SEM and EDS.

Table 1. The characteristics of the graphite plate

Description	Unit	POCO3
Average grain size	Mm	<5
Specific Resistance	mWm	14
Specific Gravity	-	1.81

Table 2. The condition and amount of electroless bath

Materials and conditions	Amount(g/l)
Ethylene diamine tetra acetic acid	5.1
sodium hydroxide	3.5
Formaldehyde 36%.	0.2
Copper sulfate 5-hydrate	2.5
PH	12

Production and regulation of MFC

MFC used in this study consists of two chambers: anode chamber and cathode chamber. The volume of each of them is 2 Liters. The two chambers are separated from each other by a proton membrane of Nafion 117 (DuPont Co USA) with an average size of 100 cm, thickness of 183 µm and proton conductivity of 85 mS/cm. Before beginning the experiment, the membrane was washed with 3% hydrogen peroxide solution. Then rinsed with 0.5 M sulfuric acid and deionized water. The membrane only permits proton ions which are produced in the anode chamber to pass through the cathode chamber and react with the existing oxygen. Electrodes used in this study were made of the graphite plate and were coated with copper nanoparticles in order to improve the performance of the fuel cell. Anode and cathode electrodes were connected to each other using a copper wire. Since the production and transportation of electrons in the presence of oxygen will face problem, the system is designed so that the anode compartment is completely anaerobic and the cathode chamber is continuously ventilated to supply needed oxygen[14, 15].

Selection of bacterial strain and regulation of the environment for the growth and formation of bacterial biofilm

The strain used in this study was *Saccharomyces cerevisiae* (PTCC 5269) which was obtained from the Centre for Scientific and Industrial Research of Iran. Since the conditions required for the growth of microorganisms should be anaerobic, Co_2 gas was regularly injected into the anode compartment. 500 mg/l of glucose was used as the carbon source in this study. In addition to glucose, substances such as $NaH_2PO_4.H_2O$, $MnSO_4$, NH_4Cl and $MgSO_4$ with concentrations of 7400, 50, 20 and 130 mg/ml and 10 ml of yeast extract were used in the anode compartment. 50 mM of phosphate buffer was used in the cathode compartment for electron recipient[16, 17].

Data Analysis

In this study the performance of MFC was evaluated in the absence and presence of copper nanoparticles in a period of 200 hours during 5 stages of loading and in the laboratory temperature. Digital multimeter (DM3051) was used to record the voltage produced at each stage of loading. The current produced in this study was calculated and recorded by the equation 1 and system power was calculated by the equation 2. Through dividing the values of power density and current density by the electrode surface, the values of these two factors were calculated and recorded. The data obtained in this stage were used for plotting the polarization curve and the diagram of voltage change in each loading cycle. Furthermore, was used of 10Ù, 100 Ù, 1000 Ù, 10000 Ù and 100000Ù resistances for indicating the relation between power density and resistance in modified electrode state and basic electrode state.

$$I=V/R \quad ...(1)$$

$$P=V\times I \quad ...(2)$$

RESULTS AND DISCUSSION

As a set of microorganisms are able to grow anaerobically, *S. cerevisiae* was used in the study, due to its rapid growth and good ability for glucose substrate use. First, electricity production using MFC with electrodes made of graphite was investigated. Then, the electrode was coated with copper nanoparticles using chemical hydrolysis and microbial fuel cell performance was investigated in this state. Chemical hydrolysis is one of the most common methods for coating surfaces by a layer of metal and this is done using an aqueous solution of metal and without the use of electrical current. Because of the lack of use of electricity in this approach the metal layer covers all the pores of the surface and the density of the layer is the same in every part of the surface[13]. Figure 2 Shows the electron microscope image of the graphite plate in the case of pure graphite (Figure 2a) and the electrode modified with copper nanoparticles (Figure 2b) for using as electrode. As it is evident in this figure, after copper nanoparticle coating by chemical hydrolysis, copper nanoparticles with an average size of 89 nm and spherical morphology were observed on the basic electrode.

Figure 3 shows the EDS spectrum of the stages for modification of electrode made of graphite. Figure 3a shows the EDS spectrum of the basic electrode and Figure 3b shows the EDS spectrum of the electrode modified with copper nanoparticles. The results of this spectroscopy confirmed electron microscopy data and also verified the modification of anode electrode with copper nanoparticles.

Figure 4 shows the voltage variation over time in the two states. As shown in the figure, in

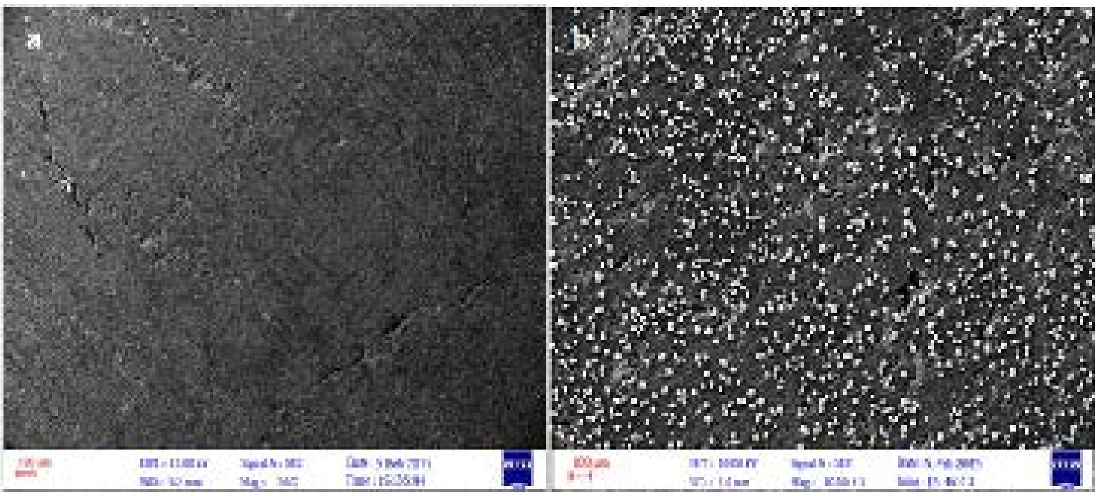

Fig. 2. Image of electron microscope. (a) Basic electrode (graphite plate). (b) Electrode modified with copper nanoparticles

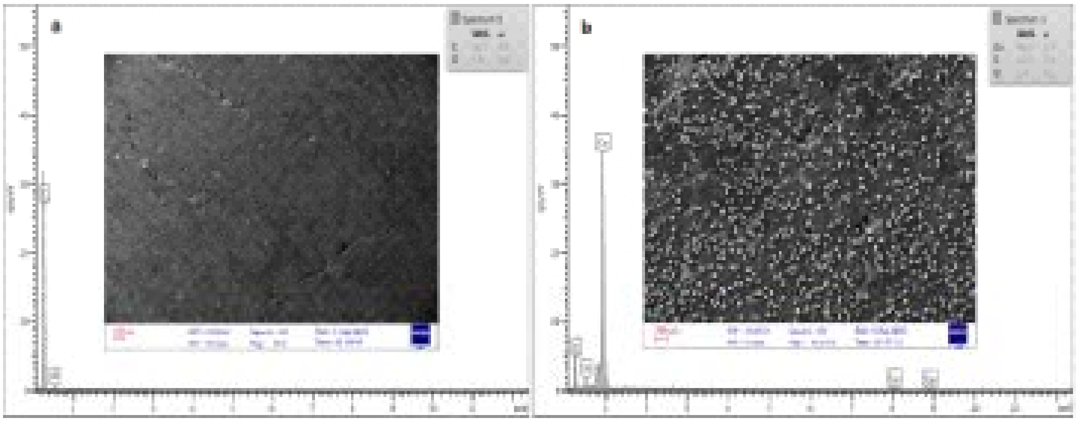

Fig. 3. EDS spectrum. (a) Basic electrode. (b) Electrode modified with copper nanoparticles

the presence of copper nanoparticles, the maximum voltage is 930 mV. However, in the absence of copper nanoparticles, produced maximum voltage was recorded 720 mV. The use of nanoparticles in improving the performance of microbial fuel cells and chemical fuel cell has been topic for many researches. The results of other studies clearly suggest that nanoparticles in a MFC act as a catalyst and result in rapid transfer of electrons. In a study conducted by Wang et al the maximum voltage produced in the presence and absence of Fe (co_5) was explored. The data of the aforementioned study showed that the maximum voltage in the presence of the materials was 580 mV. However, in the case absence of the aforementioned materials, the maximum voltage was 420 mV for the MFC. Nickel nanoparticles are among the nanoparticles that have been used by many researchers for exploring the improvement of MFC. In one study, Liu and Vipulanandan coated cathode electrode with nickel nanoparticles. Their data showed that the maximum voltage produced was equivalent to 450 mV. In comparison to this study, our data show that the maximum voltage produced at the presence of modified anode electrode is 930 mV [10].This difference may be due to the type of the used modified electrode.

Figure 5 shows the polarization curve. In this figure the changes in the power density and voltage density to current density changes can be seen. It is evident in the image that power density increases with current density changes. This increase reaches to its maximum value at the point where the internal resistance and external resistance become equal. The data of this study show that in the presence of copper nanoparticles power density has increased in a way that the maximum power density in the presence of copper nanoparticles is 1700 mW / m². However, in the absence of nanoparticles, the maximum power density of 900 mW / m² was recorded. At the point where the maximum power has occurred ohmic resistance and electrode potential have reached their maximum size and due to this, after this stage, power density is reduced.

Internal resistance of the system is among the factors that have an impact on the performance of microbial fuel cell. High internal resistance

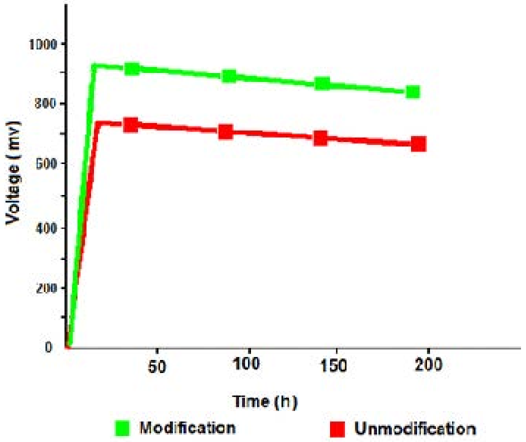

Fig. 4. The voltage changes over time

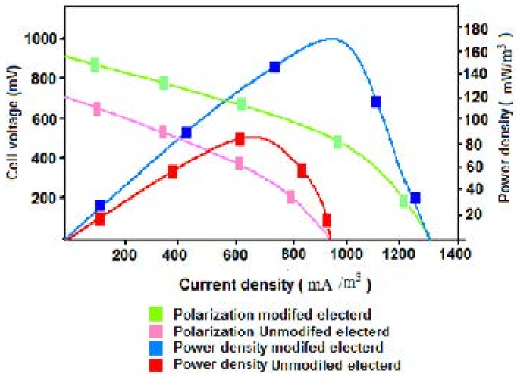

Fig. 5. Polarization curve

reduces the power production of the system. However, the maximum produced power by a microbial fuel cell is reached when the internal and external resistances of the system become equal. In this study, the maximum power produced by the microbial fuel cell in the presence and absence of copper nanoparticles was investigated to improve the performance of microbial fuel cell. Figures 6 and 7 show the maximum power produced by the system in all of the 5 levels in the presence and absence of copper nanoparticles. As it is evident in Figure 6, the maximum power density was recorded at external resistance of 10kÙ. But the maximum power density when the electrode was used without copper nanoparticles was recorded at a higher resistance. The data showed that copper nanoparticles, in addition to reducing the internal resistance of the system, increase the power density of the system. In a study Torabiyan et al. examined the performance of the MFC using platinum nanoelecterode and titanium nanowires and acetate substrate. Their results showed that the maximum output voltage is equal to 1425 mV. In comparison this study, our data indicate that the use of copper nanoparticles in modified electrode increases the production voltage from 730 mV to 920 mV. However, the difference in the produced voltage between the results of the present study and the results obtained by Torabiyan et al. may be due to the differences in the size of the nanoparticles. They showed that the maximum power density is 78mW/m^{-2}. However, our results showed that the maximum power density in the case of using copper nanoparticles is 1700 mW/m^{-2}, this difference may be due to the type of the substrate used[8].

In this study, the copper nanoparticles were coated on the electrode using hydrolysis method and without the use of electrical current.

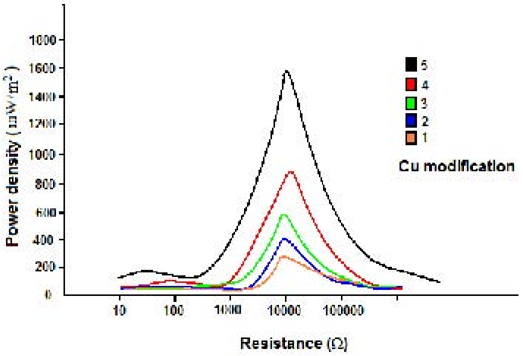

Fig. 6. The relationship between power density and resistance in the process of working with electrode modified with copper nanoparticles

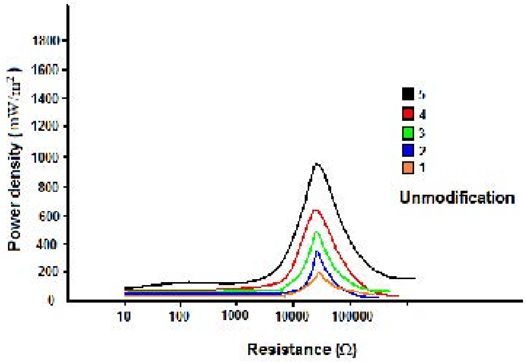

Fig. 7. The relationship between power density and resistance in the process of working with the electrode without nanoparticles

In this approach the coating occurs by degradation of coating soluble due to reduction and sediment of metal on the surface. This method results in the reduction of the metal ions in the presence of the reducing agent in an aqueous solution using chemical method. The density of the covering metal layer in the reduction method was higher than that of other methods and the uniformity of the layer is one of the advantages of this method. Therefore the methods used for the modification of the electrode and coating by nanoparticles can affect the performance of MFC. In the study which was conducted by Liu and Vipulanandan Nickel nanoparticles were synthesized using foam method and MFC performance was explored in the presence of these nanoparticles. Their results showed that the maximum voltage was 450 mV [10]. In the present study copper nanoparticles were produced using hydrolysis and better results were observed in comparison with the aforementioned study.

CONCLUSION

In this study nanotechnology was used to improve the performance of MFC. One of the characteristics of nanoparticles is increasing the ratio of surface to volume. The ratio of surface to volume increased by modifying electrode using copper nanoparticles, and therefore the internal resistance of the system was reduced and the efficiency of MFC was increased.

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