Examination of Zinc Electrode Performance in Microbial Fuel Cells

Nurettin ÇEK¹*,
¹Fırat University, Engineering Faculty, Metallurgical and Materials Engineering, 23119, Elazığ, Turkey

Abstract
Microbial fuel cells are one of the systems of renewable and clean energy generating. One of the most important things in microbial fuel cells is bacterial growth. Composts rich in organic substances are commonly used in microbial fuel cells because they positively affect bacterial growth. In addition, in recent years, studies on the use of non-inert (metal etc.) electrodes have increased; while inert (usually carbon based etc.) electrodes are generally used in microbial fuel cells. The objective of this study is to evaluate zinc anode performance by using microbial fuel cells mixed with compost. Experiments were carried out in microbial fuel cell equipped with zinc anode electrode and graphite cathode electrode. According to experiments, zinc is a suitable anode electrode of that utilizes electrochemical and biochemical reactions and therefore the microbial fuel cell produces high power density (5.33 W/m²). Zinc, which has a good electrochemical and biochemical performance, undergoes corrosion. But, according to measurements and calculations made on the basis of literature the anode zinc electrode used in this study is located in the category of corrosion-resistant material. The zinc anode for microbial fuel cells is the promising electrode technology. The experiments; the microbial fuel cell in this study, electrolyte, electrode, biofuel source, biocatalyst, etc. shows that the parameters work in harmony.

1. INTRODUCTION
Fuel cells are a developing electrical energy generation technology, which offers great advantages and the difference of applications for mobile, moving and still systems [1]. Microbial fuel cells are that converts the energy stored in chemical structures in organic materials to electrical energy through the catalyst reactions by the electrochemically active bacteria (biocatalysis). The performances of microbial fuel cells are strongly controlled by the electrochemically active microorganisms. Microbial fuel cells are often used in electrical energy generation and in the cleaned of aqueous waste. Microbial fuel cells are the clean and renewable energy production system and they are the signs of the development of technology. Microbial fuel cells are a type of biofuel cells and they are basically composed of electrolytes, electrodes, biofuels, biocatalysis, etc. components. In addition, proton exchange membranes are used in many microbial fuel cells, while proton exchange membranes are not used in some microbial fuel cells. In microbial fuel cells, inert electrodes such as graphite, carbon derivatives, and platinum are commonly used [2]-[7].

In recent years, non-inert metallic electrodes have also been used in microbial fuel cells. One example as of which is the use of zinc (Zn) electrodes in microbial fuel cells [3], [5]. Das (2015), in his work on algae microbial fuel cells, used zinc mesh anode electrodes and achieve good performance compared to other carbon derivative electrodes [5]. Çek (2016), in his work on moss microbial fuel cells, used, Zn anode electrodes and good performance obtained. Zn is an amphoteric metal that reacts both with acids and alkaline [3]. Therefore, it has the ability to work at every ambient. In addition, Zn has the good reduction potential (Zn²⁺ + 2e → Zn (E⁰ = -0.763 V)) [8]. Due to of all these properties, the ability to use zinc’s as an
electrode in microbial fuel cells should be investigated, more scientific research should be done, advantages and disadvantages should be identified. The organic materials support provided by compost gives a positive additional contribution to generate bioelectrical power in the microbial fuel cell. The compost provides additional organic nutrient materials to the bacteria living in the soil [7].

For these purposes, in this study, zinc as the anode electrode, graphite as the cathode electrode, organic compost soil material as biofuels source, bacteria as biocatalysis was used and microbial fuel cell was manufactured. Electrochemical performances of microbial fuel cell were observed and the advantages and disadvantages of using zinc used as the electrode in microbial fuel cells were determined.

2. MATERIALS AND METHOD

2.1. Materials

Materials and apparatus properties were as follows.

Zinc (Zn) plate electrodes; 99.9% purity, 3.060 grams, each electrode has 4 cm length and 4.5 cm wide. Graphite cylinder rod electrodes; 99.9% purity, 5.450 grams, 8 cm length, 0.75 cm diameter. Digital multimeter (UNI-T: UT61C) was used to make for direct current and voltage measurements. Resistance, 980 ohm (Ω). Digital pH meter (616.0.001, ISOLAB). Sensitive Scale (PKS 360-3, KERN). Plastic box shaped like a cube (5 cm x 5 cm x 5 cm) and the empty volume of the plastic box chamber was 125 cm$^3$ (125 milliliter (mL)). Microscope (BK5000-TR/L, SOIF). Plant, waste, animal waste etc. containing organic waste materials compost soil was used. Water is pH value about at 7.65 and electrical conductivity 260±20 µS/cm, it content includes sodium (Na), potassium (K), magnesium (Mg), calcium (Ca) cations and fluorine (F), chlorine (Cl), sulphate (SO$_4^-$) anion.

2.2. Method

Weight (gram (g)) measurements are made with the precision weighing instrument (Sensitive Scale). Weight measurements were made before and after use of the electrodes and compost soil.

The surface area (125 cm$^3$) of the plastic box has about at 125 mL water intake capacity. Organic compost sludge was manufactured by mixing 50 grams of compost soil with 50 milliliters of water. After, zinc as anode electrode and graphite cathode as electrode was used in the microbial fuel cell. Both microbial cells were subjected to daily electrical measurements according to resistance-dependent and non-resistance-related conditions.

In addition, bacteria in manufactured microbial fuel cells, the time-dependent states of the anode and cathode electrodes, biofilm etc. factors have been detected. Discussions were held in regard to the formation, development and effects of these factors on the system.

3. RESULTS AND DISCUSSION

3.1. Electrical analysis

As the zinc plate (-) load electrode and as the graphite cylinder rod (+) load electrode the worked. This situation was detected by the multimeter. Without external load (resistance) on microbial fuel cells are open-circuit voltage (V$_{OC}$) and short-circuit current (I$_{SC}$) values measured by the multimeter. Volt (V$_R$) and current (I$_R$) values were measured by multimeter while the microbial fuel cells were connected to the external load (resistance).

Voltage values are with a ±0.5% error margin and current values are with a ±1% error margin measured. Taking into account the margin of error, the time-dependent electricity production values of the microbial cells are shown in Table 1.
Table 1. Electrical measurements by time of in this study

<table>
<thead>
<tr>
<th>Day</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (µA)</th>
<th>$V_R$ (V)</th>
<th>$I_R$ (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>14</td>
<td>0.009</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>42</td>
<td>0.032</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>0.48</td>
<td>36</td>
<td>0.032</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>0.48</td>
<td>75</td>
<td>0.060</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>0.48</td>
<td>86</td>
<td>0.068</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>0.49</td>
<td>100</td>
<td>0.075</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>0.44</td>
<td>137</td>
<td>0.098</td>
<td>98</td>
</tr>
<tr>
<td>8</td>
<td>0.44</td>
<td>75</td>
<td>0.045</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>0.48</td>
<td>120</td>
<td>0.045</td>
<td>45</td>
</tr>
<tr>
<td>10</td>
<td>0.44</td>
<td>72</td>
<td>0.033</td>
<td>37</td>
</tr>
</tbody>
</table>

One of the most important factors in a microbial fuel cell is the power (P) value it produces [2]-[4], [7]. Therefore, from the data in Table 1, the power (P) calculation is made according to the formula in equation (1).

$$P = V_R \times I_R$$  

(1)

Where P is power (Watt), $V_R$ is the voltage across the external resistance and $I_R$ is the ampere across the external resistance. When the current output of the microbial fuel cell arrived a constant value (on 8th-9th day according to the Table 1), the polarization status was analyzed by regulating the external resistance from 10 Ω to 220000 Ω. In addition, the power (P) value is the point of maximum power identified in a voltage-current polarization curve. The graph of the polarization curve is given in Figure 1.

Figure 1. Polarization curve measurement of in this study

In the Figure 1, the polarization curve was plotted to determine the power generation at external resistance. The voltage change and current change in the resistance were recorded by a multimeter. The results showed that the highest power was valued 9.604 mW. As understood from the linear curve, the values obtained are not very far from what should be. This status is evidence that the margin of error in measurements is low.

If Equation (1) is applied to the data in Table 1, the power values graph in Figure 2 is obtained.
As seen in Figure 2, the electrical power reached the highest level (peak point (9.604 mW)) on the 7th day. In addition, in Figure 2, the time-dependent power drop graph between days 7th and 10th showed a similar pattern to that of other microbial fuel cells. This status is evidence that this study is consistent with the literature.

Power density (W/m²) was calculated using equation (2) \[3\], \[4\], \[7\].

\[
\text{Power density}=\frac{V \times I}{\text{anode surface area (m}\text{²})} \tag{2}
\]

The anode electrode surface area (4 cm x 4.5 cm) used in this study is 18 cm² (0.0018 m²). If Equation (2) is applied to the data in Figure 1, the maximum power density in equation (3).

\[
\text{Power density}=\frac{0.009604 \text{ W}}{0.0018 \text{ m}\text{²}}=5.3355 \text{ W/m}\text{²} \tag{3}
\]

3.2. Chemical analysis

In this study, the anion and cation ions in the water, the water-soluble ions of the compost soil have served as electrolytes. Organic materials in the compost soil form the source of biofuels. Bacteria in compost soils also serve as biocatalysts. *Bacillus* type bacteria and *coccus* type bacteria are commonly in composted soils \[9\], \[10\].

According to microscope studies in this study, *bacillus* type and *coccus* type bacteria were frequently seen in the composted soil. These findings are consistent with the literature. As mentioned in the literature, bacteria growth was positively affected by compost organic material, organic material was catalyzed by bacteria and therefore electrons and protons were revealed \[7\].

The electrons went to the anode electrode and then to the cathode electrode through the external circuit. Protons (H⁺ ions) went to the cathode electrode by the electrolyte and react there with oxygen to form water. Protons (H⁺ ions) go to the cathode electrode by the electrolyte and the react there with oxygen to form water. Therefore, the microbial fuel cell generates electrical power \[1\], \[2\], \[4\], \[6\], \[10\].

Microbial fuel cell operating schema is shown in Figure 3.
A biofilm layer is formed on the anode electrode surface due to bacteria. Biofilm provides electrons of transfer to the anode electrode. Therefore, biofilm formation and biofilm growth in the anode electrode increases the electrical power produced in microbial fuel cells [11]. These conditions are particularly valid for inert anode electrodes. In this study, zinc electrode surface used as an anode is covered with biofilm layer. As can be seen from the graph in Figure 2, the electrochemical properties of zinc due to biofilm deteriorate, resulting in an unhealthy transfer of electrons from the biofuel (organic materials) and therefore reducing the electrical power produced in a few days. According to by Zuo (2007), if a bacterial biofilm is formed on the metal surface, corrosion is either accelerated or impeded [12]. According to the literature, zinc easily affected by bacilli bacteria particularly and can be covered with biofilm. In addition, the binding of the bacteria (biofilm) to the zinc has brought the corrosion rate more regularly [13]. Researches have shown that Bacillus mycoides bacteria accelerate corrosion on zinc metal [14]. Coccus bacteria also have a corrosion effect on metals. For example; on the corroded rail sample has seen coccus bacteria [15]. According to the summary result from the literature is that some bacteria (especially bacillus types) biofilms have a corrosion effect on zinc. In this study, corrosion of the zinc anode electrode occurred. This information supports the literature. In this study, during this process; biofilm, rust and corrosion on the zinc have occurred. This corrosion rate (CR) is calculated by the formula in equation (4) [16], [17].

\[
CR = \frac{W}{A_{xt}}
\]  

(4)

Where, \( W \) is the difference between starting weight (\( W_{\text{start}} \)) and end weight (\( W_{\text{finish}} \)), \( A \) is the surface area of immersed anode metal and \( t \) is time (hours) of application. In this study; \( W_{\text{start}} \) is 3060 milligrams (mg), \( W_{\text{finish}} \) is 3051 milligrams (mg), \( A \) is 18 cm\(^2\), \( t \) is 240 hours (h). This study corrosion rate (CR) is calculated by the formula in equation (5).

\[
CR = \frac{3060-3051}{18 \times 240} = 0.0020 \text{ mg/cm}^2\text{h}
\]  

(5)

The annual corrosion rate is calculated using equation (6) [18].

\[
CR = \frac{\Delta m}{P_s \times S \times 3.65 \times 10^{-2}} \times \frac{3.65 \times 10^{-2}}{\Delta t}
\]  

(6)

Where; \( \Delta m \) is the zinc mass lost (mg), \( P_s \) is the volumetric mass density of zinc (g/cm\(^3\)), \( S \) is the surface area of the corroded zinc reinforcement (dm\(^2\)), \( \Delta t \) is the duration of the active corrosion period (days). This study; \( \Delta m \) is 9 mg, \( P_s \) is 7.14 g/cm\(^3\), \( S \) is 0.18 dm\(^2\), \( \Delta t \) is 10 days. The annual corrosion rate (CR) of in this study is calculated using equation (7).

\[
CR = \frac{9}{7.14 \times 0.18} \times \frac{3.65 \times 10^{-2}}{10} = 0.025 \text{ mm/year}
\]  

(7)
The appearance of the zinc anode undergoing corrosion was shown in Figure 4.

![Figure 4. Corrosion of zinc anode of in this study](image)

Corrosion of the zinc is evidence of electrochemical reactions in the zinc. The graphite cathode electrode was to have not mass loss. Graphite cathode electrode has a strong ability to used oxygen but a weak ability to reduction potential. Graphite is an inert electrode material. Ionic conductivity in fuel cells is an important factor [19]. Ionic conductivity is reduced in corroded electrodes. This status increases the internal resistance of the microbial fuel cell over time and reduces its performance over time. Also, on the electrode surface is the increase in biofilm layer thickness, the increase in oxide layer thickness, and the accumulation of inert biomass reduce the performance of the microbial fuel cell [20]. Together with all these, the microbial fuel cell continues to perform better than the microbial fuel cells that use the inert electrodes.

Based on the literature, the anode zinc electrode used in this study is located in the category of corrosion-resistant material [21]. This status is an advantage and is an indication that the zinc anode electrode is a good electrode material for microbial fuel cells.

### 3.3. Comparison with the literature and summary

Electrochemical performances of zinc anode electrode in compost used microbial fuel cells were investigated and in this study has shown good electrical power generation performance compared to some the latest works in the literature (in Table 2).

<table>
<thead>
<tr>
<th>Biofuel (Energy) Source</th>
<th>Anode Electrode</th>
<th>Cathode Electrode</th>
<th>Max. Power (mW/m²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wastewater</td>
<td>Graphite</td>
<td>Graphite</td>
<td>0.0128</td>
<td>[4]</td>
</tr>
<tr>
<td>Compost</td>
<td>Carbon felt</td>
<td>MnO₂</td>
<td>5.29</td>
<td>[6]</td>
</tr>
<tr>
<td>Potato+Sludge</td>
<td>Carbon felt</td>
<td>Carbon felt</td>
<td>6.8</td>
<td>[23]</td>
</tr>
<tr>
<td>Organic matters</td>
<td>Carbon felt</td>
<td>Carbon felt</td>
<td>7.07</td>
<td>[7]</td>
</tr>
<tr>
<td>Moss</td>
<td>Zn</td>
<td>Cu</td>
<td>17.6</td>
<td>[3]</td>
</tr>
<tr>
<td>Moss</td>
<td>Zn</td>
<td>Cu</td>
<td>18.24</td>
<td>[3]</td>
</tr>
<tr>
<td>Plant+Compost</td>
<td>Carbon fiber</td>
<td>Carbon fiber</td>
<td>39.20</td>
<td>[7]</td>
</tr>
<tr>
<td>Composted soil</td>
<td>Zn</td>
<td>Graphite</td>
<td>5335.5</td>
<td>This study</td>
</tr>
</tbody>
</table>

According to Table 2, the microbial fuel cell produced in this study produced higher electrical energy than microbial fuel cell studies using carbon-based anode electrodes. When carbon-based electrodes are used, the biochemical reactions that occur through the bacteria act [2], [3], [4], [22], [23]. However, the main advantages of using zinc anode electrode are: It is corrosion resistant material, compatible with
bacteria, benefited from electrochemical reactions and benefited from biochemical reactions. Due to these advantages in this study, the microbial fuel cell was performing steadily. In addition, zinc anode electrode has made the positive contribution to the microbial fuel cell and according to carbon has as alternative electrode technology emerged.

4. CONCLUSION

In this study have developed alternative anode electrode material thanks to zinc in the microbial fuel cell system in which the electrical energy generation process. Thus, it can be seen that the “zinc anode” method provides a novel strategy for identifying electrical energy generation process of this microbial fuel cell and can also be extended to other microbial fuel cells that are inoculated with various bacteria. This study would provide a new approach to prepare anode electrode and it is beneficial to for promote the performance of microbial fuel cell. All of these are positive and promising developments for microbial fuel cell technology. The biofilm, oxide layer, corrosion, accumulation of inert material, etc. on the electrode of happening problems further studies are needed to solve the problems.

ACKNOWLEDGEMENTS

Koç Holding and Arçelik thanks for the experimental instruments. I thank Prof. Dr. Mustafa Aksoy and Assoc. Prof. Dr. Ahmet Erensoy for their scientific supports.

REFERENCES


