



# Performances of Metallic (sole, composite) and Non-Metallic Anodes to Harness Power in Sediment Microbial Fuel Cells

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## ABSTRACT

One chambered sediment microbial fuel cell (SMFC) was equipped with Fe, brass (Cu/Zn), Fe/Zn, Cu, Cu/carbon cloth and graphite felt anode. Graphite felt was used as common cathode. The SMFC was membrane-less and mediator-less as well. Order of anodic performance on the basis of power density was Fe/Zn ( $6.90 \text{ Wm}^{-2}$ ) > Fe ( $6.03 \text{ Wm}^{-2}$ ) > Cu/carbon cloth ( $2.13 \text{ Wm}^{-2}$ ) > Cu ( $1.13 \text{ Wm}^{-2}$ ) > brass (Cu/Zn= $0.24 \text{ Wm}^{-2}$ ) > graphite felt ( $0.10 \text{ Wm}^{-2}$ ). Fe/Zn composite anode have twisted 6.73% more power than Fe alone, Cu/carbon cloth boosted power production by 65%, and brass (Cu/Zn) produced 65% less power than Cu alone. Graphite felt have shown the lowest electricity generation because of its poor galvanic potential. The estuarine sediment served as supplier of oxidants or electron producing microbial flora, which evoked electrons via a complicated direct microbial electron transfer mechanism or making biofilm, respectively. Oxidation reduction was kept to be stationary over time except at the very initial period (mostly for sediment positioning) at anodes. Based on these findings, cost effective and efficient anodic material can be suggested for better SMFC configurations and stimulate towards practical value and application.

**Keywords:** Bioelectricity, Biofilm, Composite anode, Microbial corrosion, Oxidation reduction potential, Sediment microbial fuel cell (SMFC)

## 1. Introduction

Energy production with the help of microorganism by means of bio-electro chemical conversion has rapidly gained increasing research attention since the discovery of mediator-less microbial electron transfer to electrodes [1]. Two kinds of technologies are currently being studied: (i) microbial fuel cells (MFCs) for electricity production [2], and (ii) bio-catalyzed electrolysis for hydrogen production [3]. MFCs were first used to harvest power from the electrical current engendered by bacteria, but there has been an improvement in this systems resulting in application for other purposes. Additional voltage was added to the potential generated by the bacteria, permitting for various products to be generated at the cathode, such as hydrogen, methane, and hydrogen peroxide [4]. Many different strains of bacteria are known to be capable of exogenous electron transfer. These bacteria are known as exoelectrogens, including iron reducing bacteria such as *Shewanella putrefaciens* [5] and several *Geobacteraceae* strains [6], but also clostridia such as *Clostridium butyricum* and *Pseudomonas* [7]. Studies with *Desulfuromonas acetoxidans*, a marine representative of the *Geobacteraceae*, demonstrated that suspensions of this organism

could oxidize in a two-electrode fuel cell that simulated the marine sediment fuel cells, with no added mediator compounds [8]. Several steps have been as the controlling steps in a mediator-less MFC. They are (1) fuel oxidation at the anode, (2) electron transfer from microbial cells to anode, (3) resistance of the circuit, (4) proton conduction through the membrane, and (5) oxygen reduction at the cathode [9].

A fuel cell consisting of an anode embedded in marine sediment and a cathode in overlying seawater were used successfully to generate electricity. The anode embedded in the sediment was enriched with bacteria belonging to the family *Geobacteraceae*. However, power was increased to  $1,540 \text{ mWm}^{-2}$  by providing flow through a porous carbon cloth anode with additional electrode spacing [10]. Power production by MFCs has been increased by binding different materials to the anode. In many cases, materials have been chosen based on their ability to transfer electrons. Ostuni et al. [11] have been shown how different self-assembled monolayers of chemicals can affect electron transfer from cytochrome c to gold electrodes. Carbon cloth is an excellent substrate for anodic biofilms in MFCs, but fuel cell grade materials can be expensive. Carbon felt is another material that is often used in MFCs [12]. Various materials have been used in the labo



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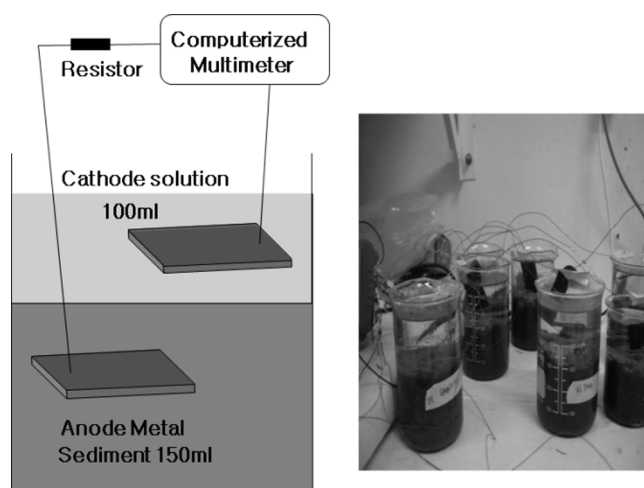
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**Fig. 1.** Sediment Microbial fuel cell set-up: Fe, Brass (Cu/Zn), Graphite felt, Fe/Zn, Cu, Cu/carbon cloth anode ( $0.004 \text{ m}^2$ ) uniquely placed in anaerobic sediment; graphite felt cathode placed in aerated seawater.

ratory as electrodes, but greater attention is now paid to electrodes that contain current collectors [13]. Current collectors have not been used with this material (carbon cloth, carbon felt, carbon mesh) and they must be selected with care to avoid corrosion. Copper is not suitable for high corrosion rate, toxicity to bacteria, and it will give the impression of high power densities due to galvanic corrosion. Many stainless steels also undergo corrosion, but careful selection of chrome content seemingly can produce material which keeps stable even in sea water [14].

Application of MFCs for wastewater treatment is very attractive due to energy recovery from waste as well as reducing production of excess sludge, disposal of which is very costly. The only immediate use of microbial fuel cells appears to be sediment microbial fuel cells that can power electronic monitoring devices with electricity extracted from marine sediment [15]. MFCs have been prepared for environmental biosensors or medical applications [16]. The cost of the electrode materials must be reduced, precious metals cannot be used, and current densities must be maximized. The challenges for bringing MFC technologies out of the lab, that is for practical applications, rest on a number of factors. The focus here is on selection of anodic materials by observing composite electrode materials performance, and on the significance of current collectors for improving power production of MFC systems.

## 2. Materials and Methods

### 2.1. Sediment

Sediment was collected from approximately 10 cm down from the sediment water interface of Lake SapKyo (N  $36^{\circ}52'9.3''$ , E  $126^{\circ}50'29.12''$ ) in a southern province in South Korea. The sampling was performed using a Ponar type grab sampler (2.4 L volume). All samples including surface water placed into clean polycarbonate jars (Nalgene; Thermo Fisher Scientific Inc., USA) with no headspace gas (i.e., air) and transported to the laboratory in

a cooler box with ice packs. All sediment were passed through a 2-mm size porous sieve to remove plant debris, macro fauna, and other large terrestrial leaves and then homogenized by mixing with a stainless steel spatula prior to use.

### 2.2. Anode Preparation

Iron, copper, graphite felt was used as sole and brass (Cu/Zn), Fe/Zn, Cu/carbon cloth were used as composite anode in sediment MFC. Composite anodic materials were alloy and collected from local marketplace. These electrodes were rinsed with copious amounts of deionized water (DIW), before used. The cathode was bare graphite felt and placed parallel to the anode and 4 cm above the sediment water interface. Both anode and cathode were connected by a platinum wire (internal resistance  $20 \Omega$ ) and an insulated copper wire to an external load. Dimension of each electrode is  $5 \times 4 \text{ cm}^2$ , i.e.,  $0.002 \text{ m}^2$ . Considering both sides and neglecting the thickness, we have  $0.004 \text{ m}^2$  of projected surface area.

### 2.3. Sediment MFC Inoculation and Operation

A one-chambered sediment cell was inoculated to analyze the performance of different electrodes. The body of the SMFC was a 500-mL Pyrex beaker. Aliquots of 150-mL wet sediment and 100-mL of sea-water were loaded into the lower and upper part of sediment MFC, respectively (Fig. 1). The SMFC were observed for 156 hours. During the runs, water loss due to evaporation was compensated daily by adding distilled water.

### 2.4. Analytical Measurements and Calculations

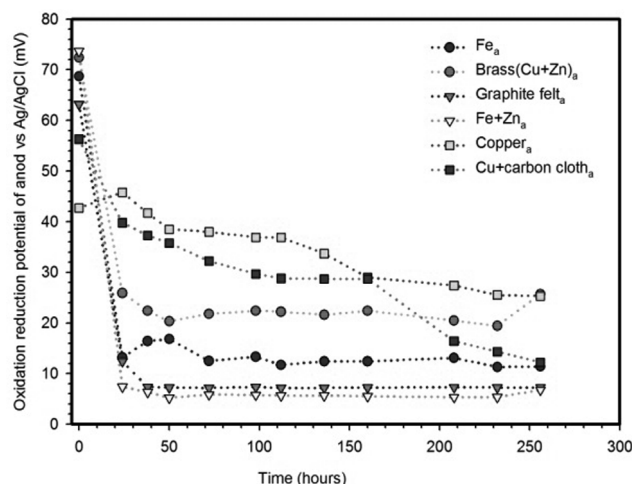
Redox potentials were measured using an Ag/AgCl reference electrode (9678BNWP; Thermo Orion, USA). The pH was measured using an automatic calibrated pH meter (Model pH 20; Hanna Instruments, USA). Cell voltage was recorded using a multi-meter and a data acquisition system (Model 2700; Keithley Instruments, USA). Current density,  $i$ , was calculated as  $i = I/A = V/(R.A)$ , where  $V$  (mV) is the voltage,  $I$  (mA) the current in electrochemical tests,  $R(\Omega)$  the external resistance, and  $A(\text{m}^2)$  the projected surface area of the studied electrode. Power was calculated according to  $P (\text{Wm}^{-2}) = iV$ , where all in MKS units. Current density was also calculated by dividing the current by the apparent surface area of anode.

## 3. Results and Discussion

### 3.1. Oxidation Reduction Potential (ORP) of Sediment MFC

Oxidation reduction potential (ORP) of sediment MFCs were measured with respect to Ag/AgCl reference electrode by changing anode. Different metals like Fe, Cu; non-metal graphite felt; and composite of them like brass (Cu/Zn), Fe/Zn, Cu/carbon cloth anode were examined in contrast to plain graphite felt cathode. ORP is the activity or strength of oxidizers and reducers in relation to their concentration and electrochemical level. Laboratory evaluations of ORP for six types' anodes were shown typical values. Decreasing trends of ORP observed for all anodes whereas cathodic ORP did not show substantial change (Fig. 2). The cathodic ORPs

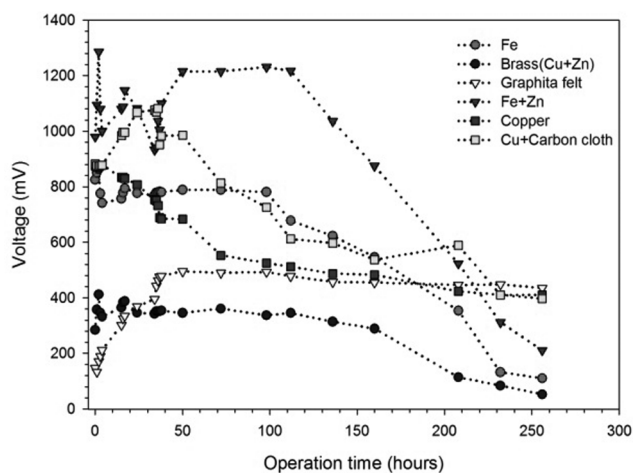
were apt to increase slightly in early times, and showed ups and downs for different material (not shown here). Overall, they developed a kind of stationary phase, i.e., overlapped within a narrow range. We have not certain grounds of the variations; probably attributed by small-scaled physicochemical and biochemical uncertainties in the cathodic compartment. Further investigation is need for this subject. Opening and termination (0 to 256 hr) ORP of Fe, Cu and graphite felt were 68.7 to 11.4, 42.7 to 25.3, and 53.2 to 7.25 mV respectively. Though ORP of all anodes were dropped drastically within 24 hours, as single anode graphite felt showing lowest value and then follow steadiness until end time. Opening and termination (0 to 256 hr) ORPs among the composite anode were for Cu/carbon cloth 56.3 to 8.4, for Cu/Zn 73.4 to 25.7, for Fe/Zn 73.7 to 6.76 mV and series of consistency rate were Cu/carbon cloth, Cu/Zn and Fe/Zn (Fig. 2). This suggests that microorganism of same sediment showing different electrochemical nature verities with anode materials. In that case electron-transfer reaction might be hampered by corrosion problem around the anode surroundings. It is important to note that the cases discussed here, where the same bacteria inhibit corrosion of a number of different metals, differ from the cases of corrosion inhibition by chemical compounds, where inhibition normally is observed only for very specific combinations of metal/compound/environment [17]. The open circuit potential (OCP) of the iron-containing anodes and manganese containing electrodes are different from each other from that of plain graphite anodes, indicating that different electron transfer reactions occurs at each of this anode types. ORP of sediment MFC was high at opening time. It might be for active part of anode was significantly high (till 24 hours). But metallic corrosion has shrunk this active part, resultantly ORP value follow uniformity after 24 hours until terminating time (256 hr). In the frame work of microbial corrosion, the concentration of supplied ingredient is one of the key parameter to be monitored. Ryckelinck et al. [18] have investigated the anodic mechanism associated with electricity generation, but the main focus on the role of reduced inorganic compounds (e.g., sulfide) in marine sediment.



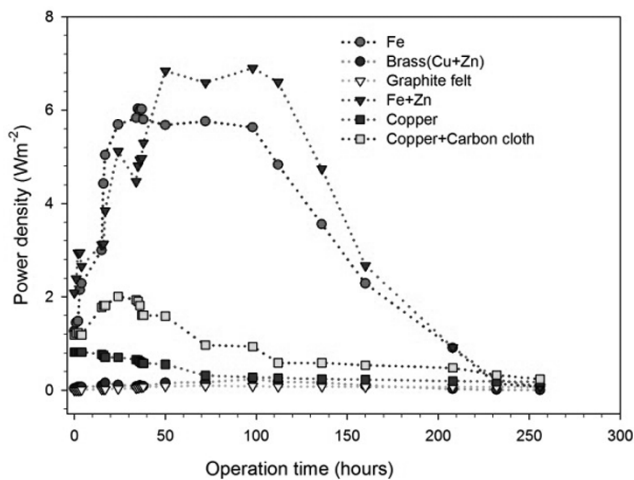
**Fig. 2.** Oxidation reduction potential (ORP) of sediment MFC (anodic chamber) at 256 hours operation time.

### 3.2. Power Density and Voltage of Sediment MFC

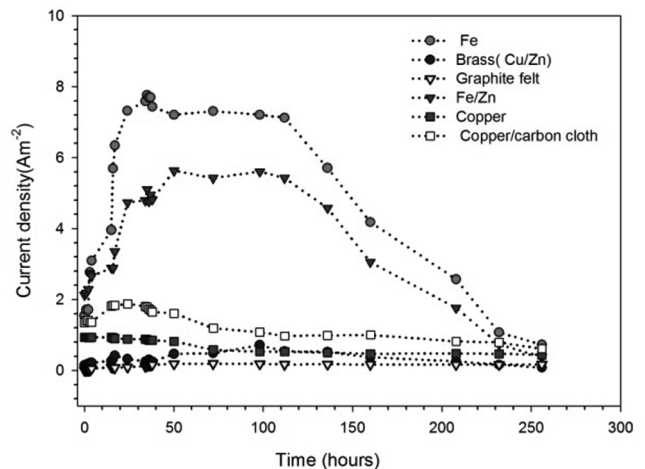
Voltage and power density were shown similarly for each anode. The maximum power density and voltage of Fe, Cu and graphite felt were shown 6.03, 1.13, 0.1  $\text{Wm}^{-2}$  and 864, 942, 595 mV respectively. Fe anode were achieved greater power density than Cu and graphite felt. Power density of iron anode is 5 times greater than Cu and 60 times greater than graphite felt. Brass (Cu/Zn), Fe/Zn and Cu/carbon cloth were used as composite electrode (Fig. 3). The maximum power density and voltages were 0.24, 6.90, 2.13  $\text{W/m}^2$  and 419, 1284, 1132 mV respectively. Fe/Zn anode achieved the highest value of power density and voltage among composite anodic materials (Fig. 4). Voltage of Fe/Zn anode had increased distinctly compared with other voltages that have showed in Fig. 5. These maximum outputs were achieved within first 100 hours for both of them (sole and composite anode). Traditionally it has been assumed that the interaction of bacteria and metal surfaces always results in increased corrosion activity. Results suggested that microbially induced metal corrosion might be the cause of variation with power generation. A fuel cell using a plain graphite anode could sustain maximum power of  $\sim 20\text{mW/m}^2$  ( $\sim 66\text{ mA/m}^2$ ) at 0.30 V [15]. When operated with anthraquinone-1,6-disulfonic acid(AQDS)- modified anode, the deployed fuel cell reached it maximum power density  $\sim 98\text{ mW/m}^2$  ( $\sim 560\text{ mA/m}^2$ ) at the cell voltage of 0.24 V. When utilizing the  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  anode, the deployed fuel cell achieved a maximum power density of  $\sim 105\text{ mW/m}^2$  ( $\sim 350\text{ mA/m}^2$ ) at 0.35 V. The current density for the fuel cell configured with both anodes decreased with square root of time, indicating mass transfer limited current density, and hence, diffusion limited kinetics [15]. However, corrosion inhibition due to the formation of biofilms has been observed for different materials exposed to corrosive environment in the presence of different bacteria [19, 20]. The concept of microbiologically influenced corrosion inhibition (MICI) have reported by F Mansfeld [17] for AL2024, mild steel and brass exposed to artificial seawater (AS). Power density of Cu anode was 65% less than Cu/carbon cloth anode but 65% higher than brass (Cu/Zn) anode. This result demonstrated that copper wrapped with carbon cloth produced



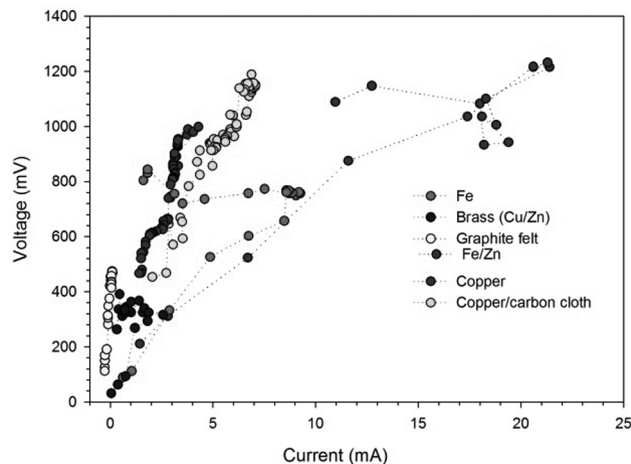
**Fig. 3.** Voltage of sediment MFCs obtaining for various anodes at 256 hours operation time.



**Fig. 4.** Power density for sediment MFCs with different anodes with respect to operation time.



**Fig. 6.** Current density in  $\text{Am}^{-2}$  vs. time duration for different anode of SMFC. Surface area was  $0.004 \text{ m}^{-2}$ .



**Fig. 5.** Voltage vs Current for sediment MFC with different anode (internal resistance was  $20\Omega$ ).

better electric performance than copper only, possibly because the cloth not only prevented the acceleration corrosion at the copper surface by some degrees but also helped growing electron emitting microbes on its surface. In other case Fe/Zn showed 6.73% higher electric performance than Fe anode. However, each of the compounds has different potential that possess in the oxidation reduction, and their differences result in differences in generated electricity. The difference in the chance of contact electron shuttles and anode electrodes can also cause the variation in electricity generation [6].

### 3.3. Current and Current Density of Sediment MFCs with Anodic Diversity

Maximum current density was achieved for Fe and Fe/Zn anode but copper, Cu/Zn, Cu/carbon cloth and graphite felt have shown lower current density (Fig. 6). Maximum current density were 7.76, 5.63, 1.93, 1.20, 0.72, 0.20 for Fe, Fe/Zn, Copper/carbon cloth,

copper, brass (Cu/Zn), and graphite felt, respectively. Fe and Fe/Zn showed better performance than Cu and brass (Cu/Zn). However, evaluation of wide diversity of materials has demonstrated that *G. sulfurreducens* is capable of transferring electrons to many conductive metals and polymers [21]. Current density was derived from the current produced through anodic materials. We have used same size of anode and cathode. Very little corrosion and microbial activity might be acted on graphite felt surface, which kept current density and power density not that high with respect to other values.

### 3.4. pH and Resistance of Sediment MFCs

The pH values of sediment MFC were measured and analyzed. Though pH does not significantly vary with time but pH has increased in both part of sediment MFC (anode and cathode). The pH value in anodic part of sediment MFCs changed 7.03 to 7.13, 7.08 to 7.20, 7.03 to 7.31 and simultaneously that in cathodic part of SMFC changed 8.09 to 8.34, 8.16 to 8.30, 8.13 to 8.33 at initial time and ending time for Fe, brass (Cu/Zn), Fe/Zn anode and graphite felt cathode, respectively. The changes in pH reflect some chemical changes in anode and cathode surroundings. Lower electricity generation and no use of mediator might be the cause of lower change of pH. The anode resistance depends on the size of the anode and the activity of the electricity-generating bacteria [22]. Total internal resistance of a sediment MFCs are dissected into anodic resistance, cathodic resistance, membrane resistance (if any), and electrolyte resistance, as well as limits the power output of an MFC [6]. Anodic resistance indicates mainly oxidation resistance ( $R_{ox}$ ) at anode surface. Here, we were measured oxidation resistance ( $R_{ox}$ ) and have observed that there were no sequence over time, when external resistance and assuming resistance were  $5.75\Omega$ ,  $20\Omega$ , respectively. Maximum and minimum value of oxidation resistance ( $R_{ox}$ ) were  $408.46 \Omega$  and  $51.65 \Omega$  for Fe,  $122.07 \Omega$  and  $22.81 \Omega$  for Fe/Zn,  $242.58 \Omega$  and  $242.58 \Omega$  and  $169.43 \Omega$  for Cu,  $538.63 \Omega$  and  $84.93 \Omega$  for brass (Cu/Zn),  $189.52 \Omega$  and  $80.79 \Omega$  for Cu/carbon cloth,  $14688.50 \Omega$  and  $1224.91 \Omega$  for graphite

felt anode. The change of oxidation resistance ( $R_{ox}$ ) has provided the comprehensive insights of the biofilm development and kinetics of anodic reaction.

## 4. Conclusions

Anodic part of sediment MFCs plays a key role to produce high energy by various dimensions because electron transfer process occurred at surface of anode and it depends on active area of anode surface which related with corrosion behavior of anode materials. Electricity generation of sediment MFCs could be increased by changing anodic element. This study has shown that Fe/Zn electrode is more efficient than Fe and Cu/carbon cloth electrode. Graphite felt anode did not show higher electricity generation because of its intrinsic bacterial function. This work suggests further investigation on the evaluation of alloys as anode of sediment MFCs.

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