

A REVIEW ON THE EFFECT OF CONDUCTIVITY ON THE PERFORMANCE OF MICROBIAL FUEL CELLS

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ABSTRACT

Currently, there is limited information about the factors that affect the power generation of microbial fuel cells (MFCs) using soil organic matter, sewage sludge, marine sediment, garden compost, industrial and domestic waste, and animal waste as fuel sources. However, a

number of scientists have worked on some factors with the view of knowing their effect on the microbial fuel generation from the aforementioned organic matters. This review provides an overview of the effect of conductivity on the performance of MFC and the different salt used in enhancing MFCs conductivity. Different sodium salts have been found to enhance the performance of MFC. Sodium chloride (NaCl) salt, which is readily available at cheap price can be used to improve the performance of different MFCs.

KEYWORDS: Microbial fuel cell, conductivity, salinity, sodium chloride, bioelectricity, sodium salts.

INTRODUCTION

The use of fossil fuels, especially oil and gas, for all human needs in recent years has accelerated and this triggers the global energy crisis. Renewable bioenergy is viewed as one of the ways to decrease the current global warming crisis. It is well known that fuels, such as ethanol, butanol, methane and hydrogen can be produced by microorganisms. But the electricity production using microbes, which is known as microbial fuel cells (MFCs), is recent development in energy biology and highly attracting area. Microbial fuel cells put

forward the possibility of harvesting electricity from organic waste and renewable biomass. MFCs are devices that convert chemical energy directly into electricity. In an MFC, electrogenic bacteria degrade organic compounds under anaerobic condition and transfer electrons to anode. The electrons then flow through a conducting wire to cathode where the electron acceptors are reduced. The electrical current can be generated during the process. Materials with a large population of microorganisms and high content of organic matter have been used to generate power in MFCs, including marine sediment (Bond *et al.*, 2002; Scott *et al.*, 2008), sewage sludge (Zhang *et al.*, 2012), garden compost (Parot *et al.*, 2008), industrial/domestic waste water (Rabaey and Verstraete, 2005) and animal waste (Yokoyama *et al.*, 2006).

Factors affecting the performance of MFC

There is limited information about the factors that affect the power generation of MFCs using soil organic matter as a fuel source, sewage sludge, marine sediment, garden compost, industrial and domestic waste and animal waste but a number of scientists have worked on some factors with the view of knowing their effect on the microbial fuel generation from the aforementioned organic matters. Many factors were investigated but in this review we study the effect of conductivity on the performance of microbial fuel cell and the different salt used in enhancing the conductivity.

List of abbreviations used:

AC	-	Activated Carbon
CE	-	Coulombic Efficiency
CEM	-	Cation Exchange Membrane
CD	-	Current Density
COD	-	Chemical Oxygen Demand
LSV	-	Linear Sweep Voltammetry
MFC	-	Microbial Fuel Cell
PD	-	Power Density
PEM	-	Proton Exchange Membrane
SMFC	-	Solid-phase Microbial Fuel Cell

Effect of conductivity on the performance of MFC

Huang *et al.*, 2010 reported the effect of ionic strength on the conductivity of MFC cell and it was observed in the study that increasing the ionic strength of the electrolyte in a MFC can

remarkably increase power output due to the reduction of internal resistance. However, only a few bacterial strains are capable of producing electricity at a very high ionic strength. In the report, a newly isolated strain EP1 was demonstrated, belonging to *Shewanella marisflavi* based on polyphasic analysis, which could reduce Fe(III) and generate power at a high ionic strength of up to 1,488 mM (8% NaCl) using lactate as the electron donor. Using this bacterium, a measured maximum power density of 3.6 mW/m² was achieved at an ionic strength of 291 mM. The maximum power density was increased by 167% to 9.6 mW/m² when ionic strength was increased to 1,146 mM. However, further increasing the ionic strength to 1,488 mM resulted in a decrease in power density to 5.2 mW/m². Quantification of the internal resistance distribution revealed that electrolyte resistance was greatly reduced from 1,178 to 50 Ω when ionic strength increased from 291 to 1,488 mM as shown in Table.1.

The results above demonstrate for the first time that a bacterium from *S. marisflavi* species can transfer electrons to an electrode to generate current at high ionic strength in an MFC. Although it has been demonstrated that the type strain of *S. marisflavi* can tolerate 8% NaCl in aerobic growth (Yoon *et al.*, 2004), there is no evidence for its capacity to produce current at such an ionic strength in an MFC. *Rhodospseudomonas palustris* DX-1, for example, can produce very high current and power density, but the type strain of *R. palustris* cannot generate power under the same conditions (Xing *et al.* 2008). In the present study, strain EP1 isolated from coastal marine sediments could grow and produce electricity at a wide range of solution ionic strengths. Based on our knowledge, this is the first time electricity generation is demonstrated at such a high ionic strength (1,488mM) by a pure culture. Strain EP1 produced 44mA/m² and 9.6 mW/m² at the ionic strength of 1,146 mM, which was maintained at levels of power output comparable with those obtained from similar architected H-type MFCs with other species (Lanthier *et al.* 2008; Bond and Lovley, 2003). Although the amount of power density was very small compared with those produced by different microorganisms in other MFC types (Xing *et al.* 2008; Ringeisen *et al.* 2006), low performance was mainly the result of the architecture of the MFC system but not the bacterium as this H-type MFC had high internal resistance, which could significantly affect the performance (Watanabe, 2008).

Table 1: Summary of experimental and calculated data from two-chamber MFCs with different ionic strengths.

MFC ^a	IS ^b /mM	E _b /mV	R _e /Ω (%) ^c	R _s /Ω (%) ^c	R _{int} /Ω	P _{max} ^d /mW/m ²	P _{max} ^e /mW/m ³
Air 1%	291	449	1,178(60)	789(40)	1,967	5.12	85
Air 2%	462	449	592(43)	789(57)	1,381	7.3	122
Air 4%	804	449	234(23)	789(77)	1,023	9.9	164
Air 6%	1,146	449	72(8)	789(92)	861	11.7	195
Air 8%	1,488	371	50(3)	789(97)	1,551	4.4	74
FeCN 2%	291	787	577(50)	789(50)	1,156	25.8	430
FeCN 6%	1,146	787	65(10)	789(90)	644	28.4	807

- 1) Air and FeCN indicate MFCs using oxygen and ferricyanide as electron acceptor, respectively. The number indicates the NaCl concentration in electrolyte
- 2) Only IS in the table was obtained from experiments and the others were calculated
- 3) Numbers in the parentheses show the percentage contribution in total R_{int}
- 4) Based on the surface area of anode
- 5) Based on the reactor volume

Table 2: Summary of Power density values for MFC-1 and 2 (mW/m²) for the 1st 10 and 20th day.

Time (Days)	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	20th
MFC-1	12.48	7.38	39.02	45.69	10.54	7.21	7.21	0.97	5.27	6.59	0.00
MFC-2	648.51	570.83	408.61	323.37	151.58	131.81	33.84	25.66	32.66	29.00	12.83

MFC-1 without modified cassava PEM

MFC-2 with modified cassava PEM using Sodium aliginate

Table 3: Maximum generated power and current density, and internal resistance obtained from this study at several concentrations of NaCl.

Molarity (M)	Conductivity (mS/cm)	Maximum current density (mA/m ²)	Maximum power density (mW/m ²)	Internal resistance (Ω)
0.0	1.053	87.00	10.08	445
0.2	10.95	210.20	20.90	177
0.4	20.96	266.56	25.25	130
0.6	25.80	281.01	26.94	120
0.8	30.30	294.68	29.13	115

1.0	35.00	316.42	31.41	110
1.2	40.00	330.14	32.76	101
1.4	44.00	319.08	31.05	106

Table 4: Maximum generated power and current density, and internal resistance obtained from this study at several concentrations of KCl.

Molarity (M)	Conductivity (mS/cm)	Maximum current density (mA/m ²)	Maximum power density (mW/m ²)	Internal resistance (Ω)
0.0	1.037	61.65	4.93	490
0.2	8.59	144.24	17.46	211
0.4	14.0	197.24	24.23	158
0.6	18.92	215.08	26.88	147
0.8	25.10	234.16	28.79	129
1.0	31.00	238.63	28.20	130

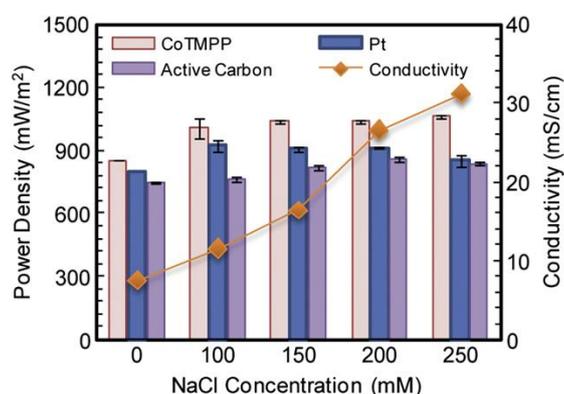


Fig 1: Effect of NaCl addition on power generation and electrolyte conductivity.

Impact of Salinity (NaCl) on cathode catalyst performance in MFCs

Several alternative cathode catalysts have been proposed for microbial fuel cells (MFCs), but effects of salinity (sodium chloride) on catalyst performance, separate from those of conductivity on internal resistance, have not been previously examined. Three different types of cathode materials were tested here with increasingly saline solutions using single chamber, air-cathode MFCs by Logan *et al.*, 2011. The best MFC performance was obtained using a Co catalyst (Cobalt tetramethoxyphenyl porphyrin; CoTMPP), with power increasing by $24 \pm 1\%$ to 1062 ± 9 mW/m² (normalized to the projected cathode surface area) when 250 mM NaCl (final conductivity of 31.3 mS/cm) was added (initial conductivity of 7.5 mS/cm). This power density was $25 \pm 1\%$ higher than that achieved with Pt on carbon cloth, and $27 \pm 1\%$ more than that produced using an activated carbon/nickel mesh (AC) cathode in the highest salinity solution. Linear sweep voltammetry (LSV) was used to separate changes in

performance due to solution conductivity from those produced by reductions in ohmic resistance with the higher conductivity solutions. The potential of the cathode with CoTMPP increased by 17-20 mV in LSVs when the NaCl addition was increased from 0 to 250 mM independent of solution conductivity changes. Increases in current were observed with salinity increases in LSVs for AC, but not for Pt cathodes. Cathodes with CoTMPP had increased catalytic activity at higher salt concentrations in cyclic voltammograms Compared to Pt and activated Carbon. These results suggest that special consideration should be given to the type of catalyst used with more saline wastewaters. While Pt oxygen reduction activity is reduced, CoTMPP cathode performance will be improved at higher salt concentrations expected for wastewaters containing seawater or high salinity as shown in Fig 1.

It was shown that the CoTMPP catalyst provided improved performance of the MFC at all salinities tested, although this change was not a linear function of salt concentration. Pt catalyst performance decreased for NaCl additions above 100 mM. This finding with Pt is consistent with previous reports that elevated NaCl concentrations decrease the oxygen reduction activity of Pt (Schmidt *et al.*, 2001) due to a decrease in the oxygen reduction rate in the presence of adsorbed Cl ions (Stamenkovic *et al.*, 2001). Considering its lower cost and the enhanced performance at a higher salt concentration, CoTMPP is therefore a better choice than Pt for several reasons when using MFCs with more saline solutions. Using CoTMPP in MFCs not only eliminates the need for a precious metal like Pt but it also takes advantage of the positive effect of the higher salinity on catalyst performance. The cost of CoTMPP, while lower than that of Pt, is still considerably more than that of AC. Although MFCs with AC cathodes produced less power than those with CoTMPP cathodes, the advantages of substantially reduced cathode costs for the AC could make it a better choice than CoTMPP in practice.

Another study on impact of NaCl on the generation of electricity from dual-chambered microbial fuel cells was carried out by Shanmuga *et al.*, 2014 using raw sago-processing wastewater with an organic load of 14,400 mg COD/l as substrate. Four dual chambered MFCs were constructed and the study aimed to find out the impact of addition of NaCl, which is carried out for effective MFC performance. Interestingly, it was found that the MFC in which NaCl was added to its cathode chamber was best in performance compared to other three MFCs, with a maximum voltage of 603mV and current of 6.03mA. It also documented that the maximum COD removal efficiency of 83% with a total reduction of carbohydrate and

starch content from the wastewater was obtained. Utilizing sago wastewater for the production of bioelectricity from MFC technique is considered as a feasible and sustainable process.

Electricity generation was estimated in all the four MFCs and the effect of NaCl addition was studied. The performance of the MFCs was monitored up to 34 days. The open and closed circuit voltage values generated in all the MFCs was measured. The MFC- 4 documented the maximum open and closed circuit voltages of 610 mV and 603 mV on the 18 day of the experimental period. The details of power (mW) produced in the fourth MFCs are depicted. Consistent increase in voltage and current output was observed in the fuel cells with exhaustion of time, accounting for a maximum power production of 3.63 mW in MFC-4 after 17 days of startup. Power output of 1.67 mW was observed in MFC-1 on 26th and 27th day, whereas MFC-2 and MFC-3 produced 1.25 mW on 26th day and 1.4 mW on 27th day, respectively. The experimental data revealed that the fuel cell with NaCl addition in its cathode chamber showed better power production than the other MFCs.

Effect of Sodium salt on the performance of PEM in MFCs

The type and nature of Proton Exchange Membranes (PEMs) applied in a MFC can be a limiting factor in determining its overall power performance. Hence, MFC with high performance, low cost material and good scalable is necessary and preferred for commercial application (Chai *et al.*, 2010; Min *et al.*, 2005). Most studies have used relatively expensive Nafion-117 as proton exchange membrane (PEM) in MFCs (Liu and Logan, 2004), but cassava starch (a cheaper alternative) can also be used. The use of cassava starch as a proton exchange membrane in MFCs reduces the cost of the cell considering its low relative cost, cheap availability and low energy requirement during treatment and installation (Obasi *et al.*, 2012). In the research reported by Obasi *et al.*, 2013, Sodium alginate was used to improve the performance of cassava starch as proton exchange membrane. In the study the effect of sodium alginate, $(\text{NaC}_6\text{H}_7\text{O}_6)_n$, on the proton conductivity of cassava starch in a dual chamber microbial fuel cell using two cell set-ups operating at room temperature ($27\pm 30\text{C}$) was investigated. The performance of MFC-1 with unmodified pure starch PEM showed a maximum power density of 45.69mWm^{-2} with overall

Coulombic efficiency (CE) of 8.70% after a ten-day useful life. MFC-2 containing starch PEM modified with sodium alginate produced a maximum power density of 648.51mWm^{-2} , with overall coulombic efficiency of 18.93% and COD removal efficiency of 72.8% over a

20 day study period. It was thus observed that the cell whose PEM was modified with sodium alginate showed a tremendous increase of over 100% power density generated with longer useful life than in the case of the unmodified form as shown in Table 2 below. Hence by this way, power production in MFCs could be improved in a more sustainable manner at a cheaper operating cost.

From the result above using the MFC-1, it was possible to produce as much as 45.69mW/m^2 power density and corresponding current density of 35mA/m^2 at the fourth day after inoculation, with swine house effluent used as the substrate (fuel). This peak power value may have resulted from the effectiveness of proton conductivity by the starch PEM which has direct linkage with electron recovery. This may have been made possible as a result of the net electrical pressures on the protons by the cyanide ions (CN^-) present in the starch molecules. However, the cell performance dropped gradually to a minimum value of 6.59mW/m^2 on the tenth day, after which the power production dropped to zero. This short useful life of the cell due to loss of efficiency of the PEM could have been as a result of several factors which may include: activity loss caused by increasing concentration of acidic fermentation product (such as alcohol) during bacteria activity (Mathuriya and Sharma, 2009); developed impedance on proton transfer due to high water absorption and retention; collapse of PEM mass due to bacteria and potassium ferricyanide (catholyte) gradually eating up the PEM surface; gradual build-up of hydrogen gas around the graphite anode; breaking up of intermolecular forces between starch molecules with attendant effect of oxygen diffusion through the PEM; and proton clogging in the available pores, thus leading to polarization of the cell as an overall effect while in MFC-2 the cell was operated with the PEM treated with sodium Alginate. The peak current and voltage of 0.6mA and 1.23v (power density - 648.51mW/m^2 and current density - 527.24mA/m^2) was observed about 3 hours of inoculation on the first day. This indicates a major power improvement suggesting a better proton transfer and subsequent increase in electron recovery due to improved PEM properties via modification. This value was however lower than the maximum power value, 3600mW/m^2 so far reported in literature (Liu and Logan, 2004). The cell performance later showed an exponential decrease in voltage production with time up to 20 days study period. This sustainable power generation and relative longevity could have been attributed to certain factors that are connected with the presence and properties of the alginate such as: exceptional ability of sodium alginate to lyophilize (absorb water from the starch and expand) thus maintaining the PEM strength and stability; its ability to immobilize enzymes (bacteria) by inclusion and

encapsulation thereby stopping it from eating up the starch; being a gum it boosts the bonding strength of starch molecules with themselves and the walls of the pipe (Raymond, 2009; Remminghorst and Rehm, 2009), coupled with improved conductivity, gelatinization and electrostatic cross-linking due to the presence of calcium chloride in the solid matrix. The cell reached a current and voltage values of 0.02mA and 0.73 volts giving a current and power densities of 17.57mA/m² and 12.83mW/m² respectively on the 20th day.

Effect of Electrolyte Conductivity on Performance of Sediment MFC

Rahimnejad *et al.*, (2015) in his research investigated the effect of electrolyte conductivity on power generation from Sediment Microbial Fuel Cells. Electrical conductivity was adjusted at 6 different levels by adding several concentrations of NaCl and KCl, which are abundant and economic salts. By adding NaCl, the performance of SMFCs improved about 3.25 fold. Maximum generated power and current density of 32.76 mW/m² and 330.14 mA/m² are obtained, respectively after NaCl addition. The results are shown in Tables 3 and 4.

From the results above, it was seen that when catholyte solution was prepared with concentration of 0.2M NaCl, internal resistance decreased intensively from 445Ω to 177Ω (Table 3). As a result, the power generation significantly increased from 10.08 mW/m² to 20.90mW/m². The maximum power and current density at each concentration of NaCl is summarized in table 1. The table indicates that the conductivity of cathode solution is an important parameter in SMFC. With NaCl addition, which is a cheap and economic substance, the performance of SMFC improved. In addition, Table 1 indicates NaCl with concentration of 1.2M has the best ability of transferring produced protons to cathode surface. This concentration of NaCl in aerobic cathode

Compartment increased produced power more than 3.25 times greater than when NaCl is not used in SMFC. Furthermore, NaCl addition to 1.2M caused decrease of internal resistance and increase of power density; but after that with increasing the concentration of NaCl, internal resistance increased and power density decreased. Catholyte conductivity cannot increase more than 1M KCl because bacteria's growth influenced significantly (Oh *et al.*, 2006). The results of experiments with KCl addition were similar to NaCl. At first, with adding KCl the internal resistance rapidly decreased and power generation increased same as the previous experiments, but with more KCl the varying intensity in the internal resistance and power generation decreased. This trend continued until the concentration of 1M KCl, after that by adding the salt, internal resistance and power generation slightly increased. The

maximum power and current density obtained in 0.8M KCl, 28.79mW/m² and 234.16mA/m², respectively, which are 5.8 and 3.79, fold greater than before the use of KCl. The maximum power and current density at each concentration of KCl is summarized in Table 4. Also the minimum resistance was observed in 0.8 M. Further increases of salt concentration, however, reduce power production by inhibiting bacterial growth (Liu *et al.*, 2005). Salt (NaCl and KCl) addition consistently decreases the overall R_{int} of the SMFCs. R_{int} can be separated into electrolyte, anode, and cathode resistances. Electrolyte resistance is directly related to the solution conductivity, and decreases when adding salt (Table 3 and 4). Anode resistance arises from the bio-electrochemical reaction at anode, and thus the activity of the electricity generating bacteria. Salt addition did not produce appreciable changes in anode potentials except at the very highest salt concentration.

CONCLUSION

The effect of Sodium salt has shown to be of outmost important on the performances of different kind of microbial fuel cells and in a number of ways. From affecting the salinity of the catalyst used to its effect on improving PEM performance and to its effect as electrolyte on the conductivity of the MFCs. This shows that Sodium salt especially Sodium Chloride which is readily available at a very cheap price can be used in improving the performance of different MFCs.

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