The Effect of a p-n TiO_2/Cu_2O/ ITO Composite Junction Created using Electron Beam Evaporation on a *Shewanella oneidensis MR-1* Powered Microbial Coupled Photoelectrochemical Fuel Cell

Krishna Gorrepati

Spring Valley High School, 120 Sparkleberry Lane, Columbia, SC 29229

Microbial fuel cells (MFCs) show promise as a renewable energy source that can generate electricity through microbes but suffer from low power densities. A photocathode or photoelectrochemical cell is proposed to be substituted with the cathodic electrode in a MFC to create a microbial photoelectrochemical cell (MPC). It was hypothesized that a TiO_2/Cu_2O/ITO composite photocathode in a MPC would have greater voltage outputs when compared to those of a plain ITO cathodic electrode in a MFC. For, the stability of TiO_2 with the wide absorption spectrum of Cu_2O would increase efficiency because the composite band gap setup correlates to an npn transistor. Forty trials and thirty trials were conducted for the Plain ITO glass control MFCs and the TiO_2/Cu_2O/ITO composite MPCs respectively. In each trial, the voltage output was collected every minute for one week. Using a two-sample t-Test with the means, the results indicated that control MFCs and MPCs were significantly different: $t(51)=13.33$, $p < 0.001$. The MPCs also provided a 335% increase in voltage outputs when compared to those of the MFCs.

INTRODUCTION

Microbial fuel cells (MFCs) have garnered global interest because they harvest electrical energy from organic matter. A MFC gets most of its energy from bacteria, which can be obtained from waste water, rivers, or soil. Once bacteria metabolize organic substrates, MFCs receive their energy in a two-step process: the first step, oxidation, requires the removal of electrons from the bacteria, and the second step, reduction, consists of giving those electrons to something that will accept them, such as the anodic electrode (Rabaey & Verstraete, 2005). As the electrons move across a wire from the anodic electrode to the cathodic electrode, the flow of electrons produce electricity. Unfortunately, during these processes, only a small percentage of electrons travel to the cathode.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 24H^+ + 24e^-$$

Photoelectrochemical cells, unlike MFCs, use the sun instead of organic matter to produce electrons. Fujishima and Honda (1972) published the first article on a photoelectrochemical cell that decomposes water. For the electrochemical decomposition of water, a potential difference of 1.23 V, equivalent to radiation with wavelength of 1000 nm, is necessary. Therefore, light can be harnessed to decompose water (Fujishima & Honda, 1972). The researchers connected a TiO_2 electrode to a platinum black electrode through an external load. They found that the oxidation reaction occurred at the irradiated TiO_2 electrode while reduction occurred at the platinum electrode. The same photoelectrochemical principle was used by Qian et al., (2010) in a MFC, but cuprous oxide was used instead of titanium oxide. However, the cuprous oxide was prone to corrosion. As researchers begin to couple MFCs with photoelectrochemical cells to increase the overall efficiency, their main problem becomes finding the right type of materials to use in photocathodes in combination with MFCs.

A coupled microbial photoelectrochemical cell (MPC) can both increase efficiency and make MFCs closer to being economically viable. The photoelectrochemical cell is usually combined in a MFC as a photocathode. The photocathode is usually made of a p-n junction of a p-type and n-type semiconductor. The distinction between p-type and n-type semiconductors refer to the relative position or distance between electrons in the valence band versus the conduction band. The distance between the valence band and conduction band is commonly known as the band gap of the semiconductor. P-type semiconductors have narrow band gaps that allow them to absorb the solar spectrum effectively, but they are prone to photocorrosion and are not stable. However, n-type semiconductors have a large band gap that stabilizes them, but they only absorb UV light (Siripala et al., 2003). The combination of both p-type and n-type semiconductors stabilizes the photocathode and allows it to effectively absorb the solar spectrum. Finding the optimal n-type semiconductor that works synergistically with the bacteria and the p-type semiconductor requires lots of research and experimentation in this relatively new field. Qian, Wang, and Li were the pioneers of the microbial coupled photoelectrochemical cell systems.

Qian, Wang, and Li (2010) were the first to develop a solar MPC that coupled redox reactions from bacteria and the sun's energy to produce efficient electricity generation. The researchers structurally improved a MFC to incorporate a photoelectrochemical cell. Qian et al., (2010) added p-type cuprous oxide photocathode while using the bacterium *Shewanella oneidensis* MR-1. The researchers chose this specific semiconductor because they needed to match the redox potential of the bacteria and the electronic bands of the semiconductor. As a result, the anode and photocathode will function together to combine the energy from solar light and organic substrates for electricity generation. The solar MPC functions by having the photogenerated electrons at the semiconductor reduce protons in the catholyte. At the same time, the holes in the valence band of the semiconductor recombine with electrons from the anode (Qian et al., 2010). However, the Cu_2O was prone to photocorrosion due to its narrow band gap. So, many scientists have begun to explore photocathodes where the n-type semiconductor protect the photocathode from corrosion.

In spite of the many improvements in MFCs, such as MPCs, it is difficult to compare raw data from various researchers. This is due to the various strains of bacteria, various anode and cathode compartment sizes, and various electrode shapes. However, when compared to a control with the same MFC or MPC structural design, one can understand the impact of their modified fuel cell. MFCs or MPCs, in

the same experiment, are usually compared by voltage output across a resistor. This is because all variables are kept constant except the independent variable, so one can clearly differentiate between the various fuel cells by the voltage output. Furthermore, they can also be compared by the total electric power, which is the voltage squared divided by the external resistor. Finding the power output quantifies and indicates a fuel cell's potential abilities. These methods can be used in tandem to compare between the same research and research from other studies.

The overriding problem with current MFCs is the power density, for it is too low to be economically feasible. This is due to the low coulombic efficiency in a MFC, for many of the electrons are unable to reduce at the anodic electrode. To provide greater electrical output, a photoelectrochemical cell or photocathode is proposed to be substituted as the cathodic electrode to create a microbial photoelectrochemical cell (MPC). Unlike a conventional MFC, the MPC's photocathode, under photoirradiation, generates electron hole pairs to make the cathode potential higher than that of the anode. As a result, the electrons from oxidation are continuously driven to the photocathode and reduce the protons to hydrogen at the photocathode (Chen et al., 2013). Indium tin oxide (ITO) with a 4 eV band gap is a n-type semiconductor, but it is not a viable cathodic alternative in a MFC for it can only absorb UV light and electrons are not driven to the cathode. So, Cu_2O (2.2 eV) can be evaporated onto indium tin oxide (ITO) and can act as a photocathode, but Cu_2O is still prone to photocorrosion, so a n-type semiconductor is needed to protect the photocathode (Siripala et al, 2003). As a result, a n-type TiO_2 (3.2 eV)/ p-type Cu_2O (2.2 eV)/n-type ITO (4.4 eV) composite can be tested. It was hypothesized that a novel TiO_2/Cu_2O/ITO composite photocathode would provide greater voltage outputs when compared to those of a plain Cu_2O photocathode developed by Quian et al. (2010) or an ITO glass cathodic electrode. This is because the stability of TiO_2 with the wide absorption spectrum of Cu_2O will increase the efficiency because the composite's setup correlates to a npn transistor and include p-n junctions thereby increasing the voltage output.

Moreover, MFCs continue to generate interest because they use only organic matter to produce "green" electricity. As described by Logan (2012), if MFCs covered only 1% of land at 10% efficiency, one would have enough energy to power the whole world. To approach 10% efficiency, scientists have tried several methods. The most recent developments include the use of various metals on the electrode. Qian et al., (2010) was the first to use a Cu_2O photocathode with a MFC to create a MPC, which increased the electrical output dramatically. Similarly, the purpose of this experiment is to find a way to increase coulombic efficiency in a MFC without using expensive materials. Currently, no one has analyzed the effects of a combination of various metals such as a TiO_2/Cu_2O/ITO composite photocathode in microbial fuel cells. These materials are chosen due to previous studies of photoelectrochemical cells utilizing each of the materials individually. Since the combination of these materials into a MPC has not yet been accomplished, the composite may provide a viable method in improving the MPC's efficiency over both the MFCs and current MPC photocathode alternatives. This novel MPC can thereby become an economically viable alternative to both MFCs and current MPCs.

Research on the composite TiO_2/Cu_2O/ITO photocathode with *Shewanella oneidensis* MR-1 in a MPC was conducted at the University of South Carolina under Dr.Crittenden. This composite consisted of thermally evaporated TiO_2 and Cu_2O on ITO glass and was compared to the photocathode developed by Qian et al. (2010) which consisted of thermally evaporated Cu_2O on ITO glass. Twenty and thirty trials were conducted for the plain Cu_2O/ITO MPCs and the TiO_2/Cu_2O/ITO composite MPCs respectively. The voltage output was measured across a 100-ohm resistor. The data for the novel MPC and Cu_2O MPC was statistically analyzed at alpha equal to 0.001 with a two-sample t-Test for the means of each trial. Based on these results, a single cell scalable prototype was created that could potentially be used to generate electricity from wastewater.

MATERIALS

Shewanella oneidensis MR-1
Autoclave
Fume hood
Incubator
Tryptic soy broth
Bleach
100-ohm resistor
Deionized water
Indium Tin Oxide (ITO) glass
Test tubes
2000 mL jug
Wax
Disposable 25 mL pipettes
Single channel pipettor
60 Watt fluorescent light bulb
Proton Exchange Membrane (PEM)
Steel clips
Copper
Cathode tube
Anode tube
Anode stopper
Steel electrode holders
Graphite electrodes
Silver colloidal solution
Thermodynamic evaporator
Epoxy
Titanium

METHODS

Microbial fuel cells (MFCs) use bacteria to reduce electrons at the electrode, resulting in an electrical output. Moreover, an anode tube and cathode tube, separated by a proton exchange membrane (PEM), were required to separate the oxidation of electrons from bacteria and flow of electrons to the cathode. A combination of the organic substrate, bacteria, and anode/cathode compartments were required to create a functional MFC. However, a microbial coupled photoelectrochemical fuel cell (MPC) functions and is constructed in the same way but requires a cathodic photoelectrochemical electrode and may prove to be a viable alternative to MFCs. A MPC can involve both p-n junction photocathodes or plain p-type photocathodes. In the fuel cells that were constructed, the cathodic electrode acted as the the independent variable. The novel TiO_2/Cu_2O/ITO composite photocathode was compared to the Cu_2O photocathode produced by Qian, Wang, and Li (2010). During MPC construction, aseptic techniques were used and safety precautions were taken, for MPCs include Biosafety Level 1 bacterium, *Shewanella oneidensis* MR-1 that were obtained from stock quantities maintained at -81 °C.

One liter of the organic substrate or tryptic soy broth (TSB) media was prepared at a ratio of 1000 mL of deionized water to 30 grams of tryptic soy broth. After the organic substrate had been autoclaved, a pipettor with 25 mL disposable pipettes was used to place 10 mL of the TSB media into each of the four disposable test tubes. While wearing gloves to minimize the risk of exposure, *Shewanella oneidensis*

MR-1 was inoculated into each test tube. The test tubes were then placed in an incubator at 33 °C. While the microbes grew, the anode and cathode compartments were set up.

The anode tube, cathode tube, and proton exchange membrane (PEM) were gathered (see Appendix A, figure 1). Wax was applied to the tip of the anode tube. After the PEM was placed between the anode and cathode, they were then connected (see Appendix A, figure 2). A steel clip was placed between the anode and cathode to secure the connection. The MPCs were then autoclaved at 121 °C for 1.5 hours. Once autoclaved, the MPCs were placed in the fume hood to decrease contaminant exposure.

20 mL of TSB media was placed in both the anode and cathode (see Appendix A, figure 3). The pre-cut cylindrical graphite electrode was attached to the steel electrode holder. The graphite electrode was then submerged in the TSB media at the anode (Appendix A, figure 3). The anode stopper was then inserted in the top of the anode compartment to decrease oxygen levels. The novel cathodic electrode was then constructed. ITO glass was cut into 12.5mmX25mm pieces. These pieces were thermodynamically evaporated using e-beam evaporation with 50 nm of Copper and then 50 nm of titanium. To increase electric conductivity, silver colloidal solution was added between photocathode and the steel electrode holders. Two coats of five-minute epoxy was then added to strengthen the bond between photocathode and the steel electrode holders. Next, aluminium foil was placed on the top of the cathode compartment to decrease contamination but allow oxygen. Using a single channel pipettor, 25 microliters of *Shewanella oneidensis* MR-1 was inoculated into the anodic compartment of the MPC from the previously inoculated test tubes. The inoculated MPCs were placed in the incubator, where each MPC was connected to a 100 ohm resistor (see Appendix A, figure 3). Each MPC was also connected to a reference and measuring lead. This enabled the voltage to be automatically collected every minute for seven days. Outside the incubator, two 60 Watt fluorescent light bulbs were directed at the MPCs from 1.5 feet away (see Appendix A, figure 4). These procedures were repeated 30 times with TiO_2/Cu_2O/ITO MPCs.

The MPCs with Cu_2O followed the same procedures as the TiO_2/Cu_2O/ITO MPCs. However, the Cu_2O/ITO MPCs were pieces of ITO glass that were thermodynamically evaporated using e-beam evaporation with just 50 nm of Copper. Data for the Cu_2O/ITO MPCs were automatically collected every minute for seven days for each of the 20 trials. Since previous results showed that the novel MPC performed better than the control MFC, only the TiO_2/Cu_2O/ITO composite MPCs and Cu_2O MPCs were compared and statistically analyzed at alpha equal to .001 with a two-sample t-Test of the means for each after 5,000 elapsed minutes.

Once measurement for each fuel cell was completed, bleach was poured into the fuel cells and disposable test tubes. After sterilization, the remaining TSB media was poured down the drain. The disposable test tubes were then thrown into the trash with the used graphite electrodes and photocathodes; the trash was autoclaved and disposed by the University's biohazard department.

Based on previous results, a scalable MPC prototype was then constructed. The prototype utilized the properties of the novel photocathode into a single cell MPC. The prototype consisted of multiple anodic electrodes, six in all, in a parallel circuit (see figure 1). The photocathode consisted of a TiO_2/Cu_2O/ITO composite 50nmX50nm, placed in the single chamber that also contains the anodic electrodes. The single chamber included 1L of TSB media and included an inoculation of 200 microliters of *Shewanella oneidensis* MR-1. The MPC prototype was connected to a reference and measuring lead. This enabled the voltage to be automatically collected every minute for five days. Outside the incubator, two 60 Watt fluorescent light bulbs were directed at the prototype from 1.5 feet away to stimulate sunlight. Once measurements for the prototype were completed, bleach was poured into the prototype and disposable test tubes. After sterilization, the remaining TSB media was poured down the drain. The electrodes and photocathodes were then thrown in the trash.

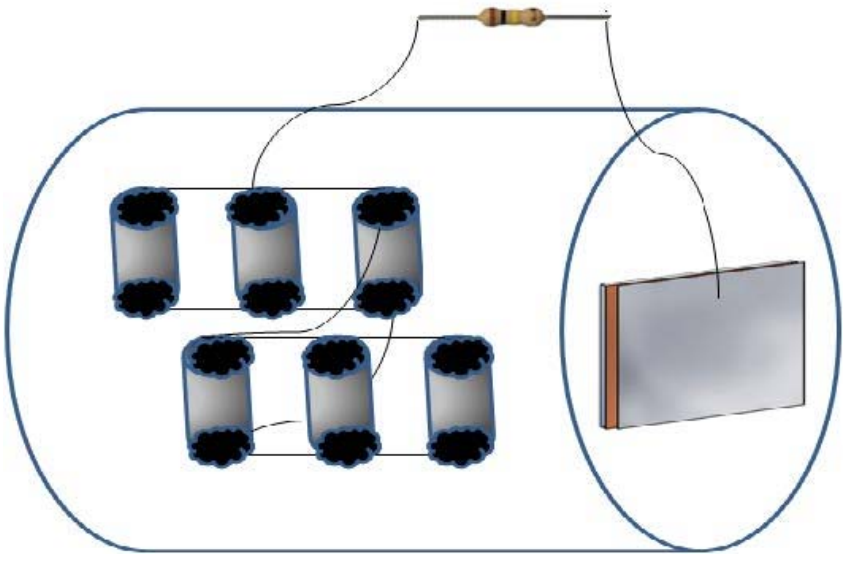

Figure 1. MPC Single Cell Prototype. Six anodic graphite electrodes were connected in a parallel circuit and were connected externally, through a 100 ohm resistor, to the TiO_2/Cu_2O/ITO photocathode. The anodic electrodes were placed in 1 liter of TSB media and the prototype was inoculated with a *Shewanella oneidensis* MR-1.

Hypothesis TiO_2/Cu_2O/ITO composite MPCs will provide a greater voltage output than Cu_2O MPCs because the composite material works as a npn transistor and includes p-n junctions. **H_o**: There is no difference in voltage outputs of the Cu_2O MPCs and TiO_2/Cu_2O/ITO MPCs. **H_a**: There is a significant difference between the voltage outputs of Cu_2O MPCs and the novel MPCs.		
Levels of Independent Variable	TiO_2/Cu_2O/ITO cathode (MPC)	Cu_2O/ITO cathode (MPC)
Number of Repeated Trials	30	20
Independent Variable: The different cathodic electrodes used in the fuel cells. **Dependent Variable:** The voltage output in the fuel cells in volts. **Constants:** The amount of TSB media, the amount of water, the amount of inoculated bacteria in the anode, constant incubator temperature at 33 °C ± .05 ºC, same fuel cell setup, the type of bacteria: *Shewanella oneidensis* MR-1, and the same data collection method.		

Figure 2. Experimental Design Matrix

RESULTS

The research consisted of two data sets of fuel cells: novel MPCs with TiO_2/Cu_2O/ITO cathodic electrodes and MPCs with Cu_2O/ITO c athodic electrodes. Twenty trials and thirty trials were conducted for the novels MPCs and current MPCs respectively. Data or voltage outputs (mV) were collected every minute for approximately seven days for each fuel cell (see Appendix B). The first 5,000 minutes were then taken out of data analysis, for analysis was conducted only after the bacteria had stabilized. An average was taken for each individual trial when the bacteria had stabilized, giving more meaningful results. A two-sample t-Test was then conducted with the calculated means for each trial (see Table 1) at alpha equal to 0.001.

Table 1. Means of each trial for novel MPCs and Cu 2 O/ITO MPCs in millivolts. Shows the mean voltage output in millivolts of each trial after 5,000 elapsed minutes. Means are calculated after stabilization of bacteria.

Cu_2O/ITO Cathodic Electrode MPCs Means:				
25.47	14.18	20.98	10.39	24.12
9.44	19.87	19.60	17.22	16.32
16.27	7.75	18.93	16.32	16.33
19.78	16.33	19.65	10.79	26.04

TiO_2/Cu_2O/ITO Cathodic Electrode MPCs Means:				
121.67	222.95	135.02	135.01	112.26
116.27	168.11	144.81	165.71	81.67
123.68	108.82	103.03	193.49	117.49
185.24	178.81	139.73	144.01	172.27
141.85	98.98	160.93	186.47	132.11
134.44	184.08	122.95	129.00	82.60

The descriptive statistics clearly show that the mean voltage outputs for TiO_2/Cu_2O/ITO cathodic electrode MPCs are greater than the Cu_2O/ITO cathodic electrode MPCs. For, the novel photocathode has greater values for Q1, median, and Q3. There is also a 818% increase from the mean Cu_2O/ITO MPC voltage output to the mean novel MPC voltage output. Also, the standard deviation for the novel MPCs are greater, so the voltage output in the novel MPCs are more varied than the photocathode produced by Qian, Wang, and Li (2010). The general trend shows that the novel MPCs have a higher voltage outputs but are more varied.

Table 2: Descriptive Statistics of Means. Descriptive statistics for the Cu_2O/ITO MPCs and TiO_2/Cu_2O/ITO MPCs are given. The descriptive statistics were performed using data from Table 1.

Variable	Cu_2O/ITO Cathode (MPCs)	TiO_2/Cu_2O/ITO Cathode (MPCs)
Number of Trials	20	30
Mean (mV)	17.29	141.45
StDev (mV)	5.06	34.25
Minimum (mv)	7.75	81.67
Q1 (mV)	15.22	117.19
Median (mV)	16.78	135.02
Q3 (mV)	19.83	169.15
Maximum (mV)	26.04	222.95

A two-sample t-Test was conducted to see whether TiO_2/Cu_2O/ITO cathodic electrode MPCs had significantly greater voltage outputs than the Cu_2O/ITO cathodic electrode MPCs. The test showed that there was a significant difference between the populations for the Cu_2O/ITO MPCs* (M=17.29, SD=5.06) and the novel MPCs* (M=141.45, SD=34.25), t(48)=-16.04, p <0.001. As a result, the hypothesis is supported, and the novel MPC photocathode and the Cu_2O/ITO photocathode can be considered two different populations. This is further supported by the MPCs greater mean voltage output.

Table 3: t-Test: two-sample. A two-sample t-Test was conducted between Cu_2O/ITO MPCs and TiO_2/Cu_2O/ITO MPCs with alpha at 0.001. The test yielded a low p-value and a high t-value which indicates a significant difference between the populations.

Variables	Plain ITO Cathode (MFCs)	TiO_2/Cu_2O/ITO Cathode (MPCs)
Mean	17.29	141.45
Variance	25.60	1173.20
Observations	20	30
df	48	
t Stat	16.037	
Standard Error of Difference	7.742	
P(T<=t) one-tail	<0.001	

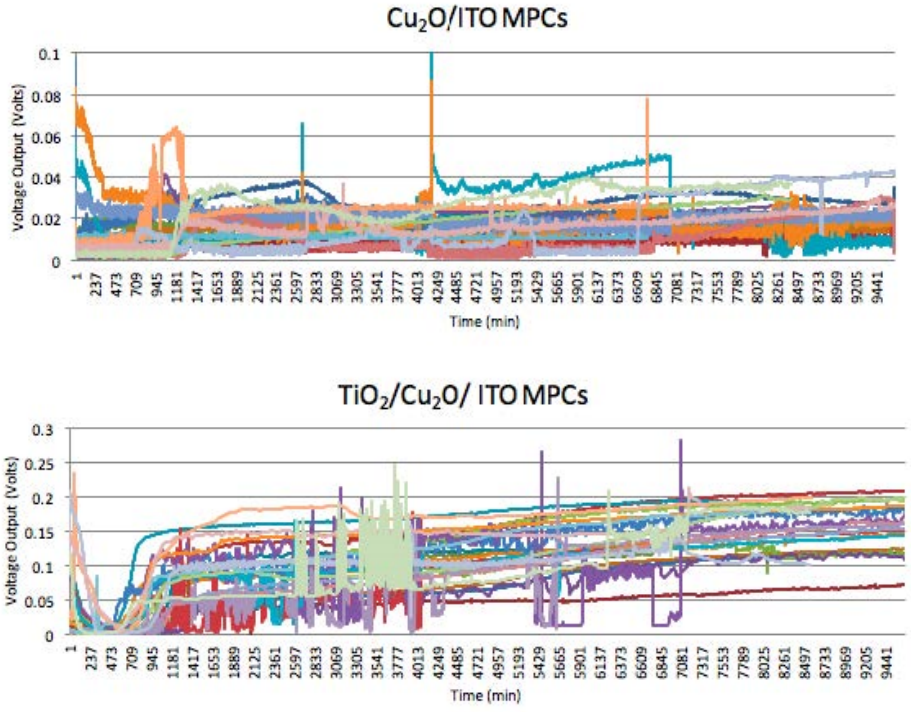

Figure 3: Graph of Fuel Cells' volts per minute. Graph of all fuel cell's volts per minute over approximately seven days. A visual trend shows that TiO_2/Cu_2O/ITO MPCs have higher voltage outputs compared to those of Cu_2O/ITO MPCs. Also, the bacteria do not seem to completely stabilize across all fuel cells till after 5,000 elapsed minutes.

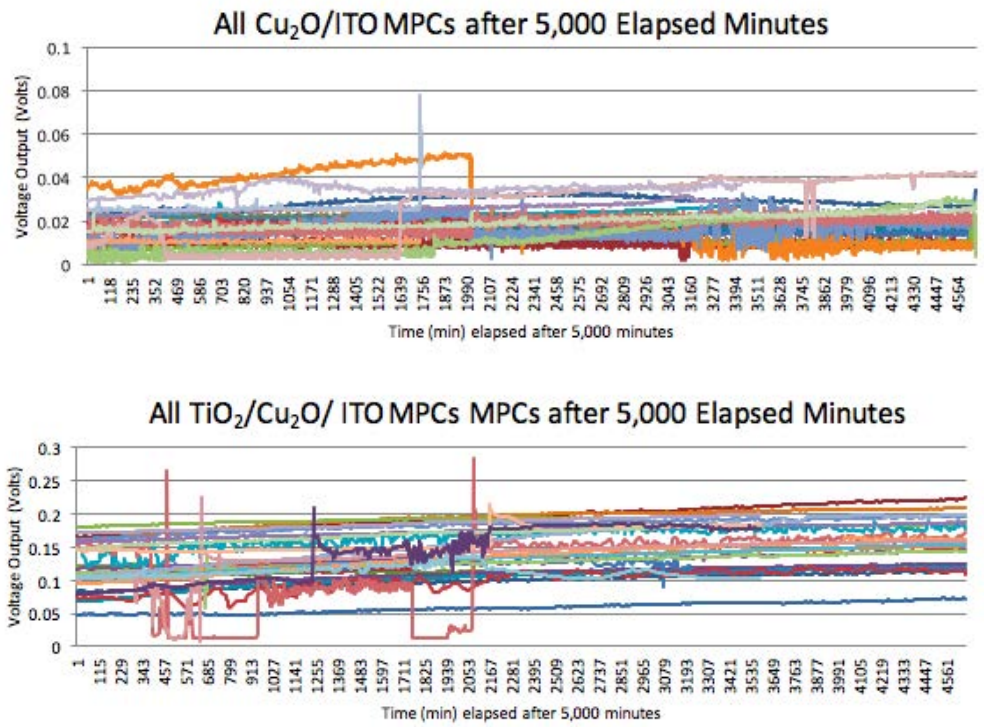

Figure 4: Graph of Fuel Cells' volts per minute after 5,000 elapsed minutes. Graph of fuel cells' volts per minute after bacteria had stabilized. A general trend shows that the fuel cells have a large standard deviation due to the varied metabolism of the bacteria. Also, the bacteria appear very stable after the 5,000 elapsed minutes.

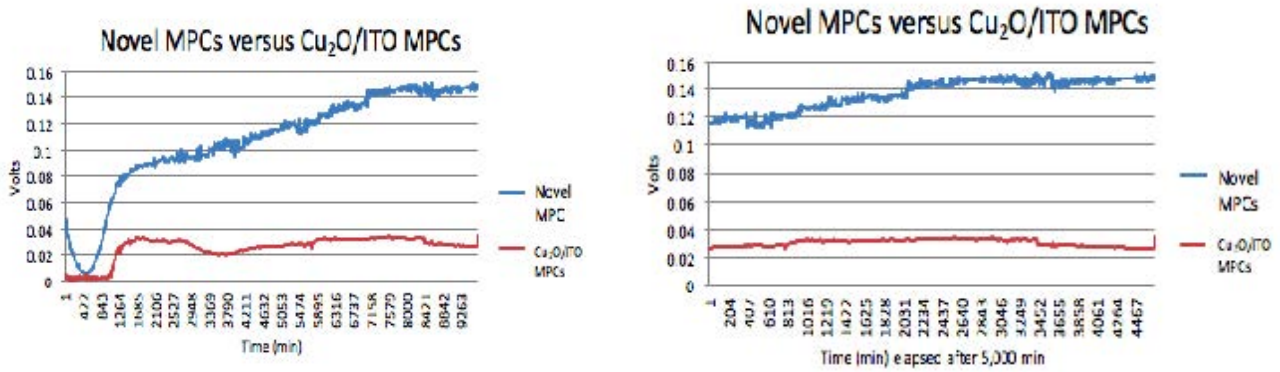

Figure 5: Graph of Average Fuel Cells' volts per minute. Average for each point at the associated time across all fuel cells were taken for the two different MPCs. The general trend of both graphs indicate that the average novel MPC had higher voltage outputs than the average Cu_2O/ITO MPC during the entire run. The X-axis indicates time, and the Y-axis displays the voltage output in volts.

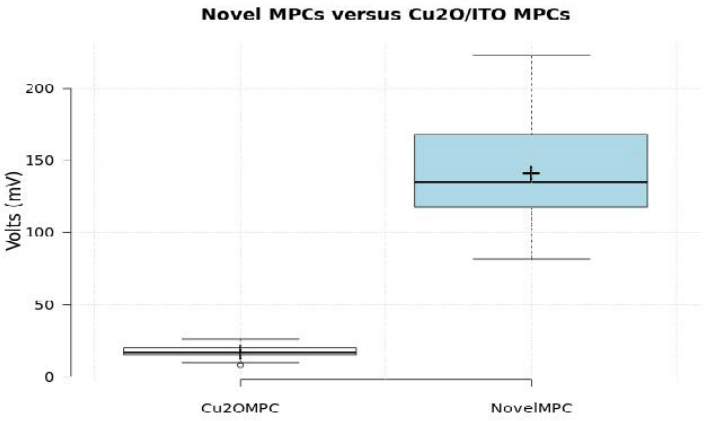

Figure 6: Boxplots Comparing the Control MFCs and MPCs. Boxplot comparing the novel MPC versus the Cu_2O/ITO MPC. The X-axis indicates the different treatments while the Y-axis displays the voltage output in millivolts. A visual trend in the boxplots in Figure 4 shows that the TiO_2/Cu_2O/ITO MPCs have higher voltage outputs. For, the novel MPC has a greater Q1, median, and Q3 values than those of the Cu_2O/ITO MPC. While the novel MPCs outperform the Cu_2O/ITO MPCs, the are also more varied.

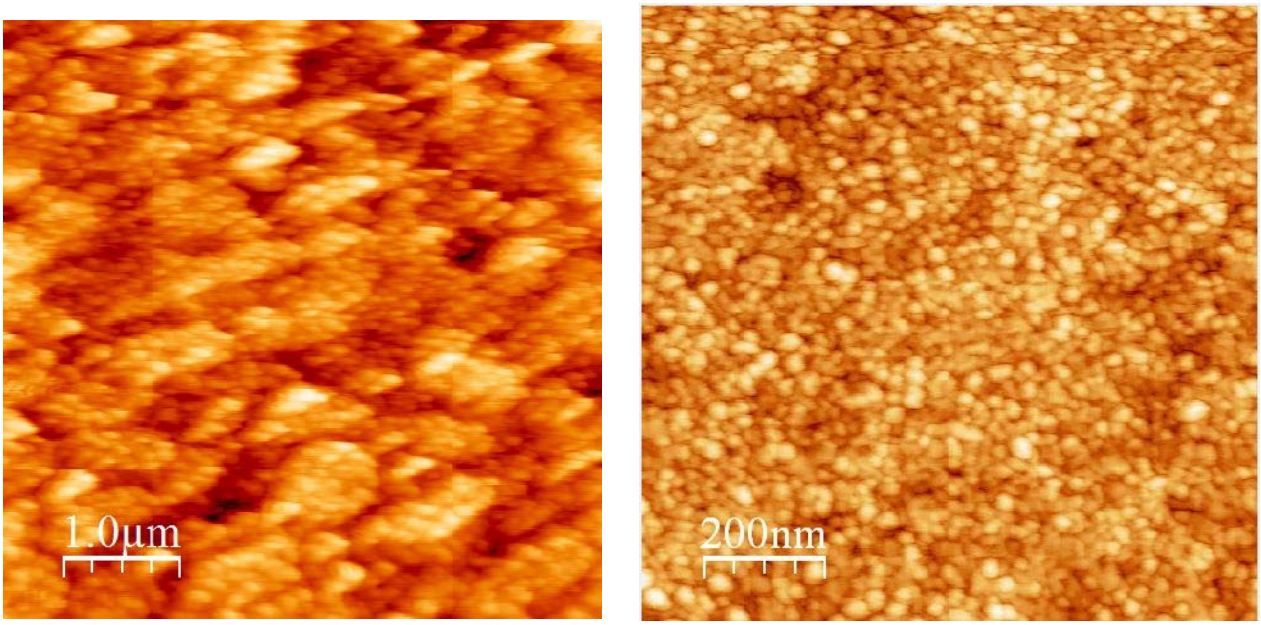

Figure 7: AFM Images of Cathodic Electrodes. A) Plain ITO Cathodic Electrode and B) TiO_2/Cu_2O/ITO Cathodic Electrode. AFM images comparing the cathodes used in the Cu_2O/ITO MPC versus the novel MPC. A) From black space to the surface, there is a height difference of 2 nm. B) After the evaporation of TiO_2/Cu_2O/ITO, the semiconductor substance appeared as dots on the ITO surface due to e-beam evaporation. Each dot is 10 nm in height.

DISCUSSION

The purpose of this study was to increase the efficiency of current MFCs by including a photocathode. A photoelectrochemical cell was added to a MFC to create a MPC because it can both increase efficiency and make MFCs more economically viable. An MPC would increase efficiency because the photocathode acts as a npn transistor. A npn transistor consists of a p-type semiconductor sandwiched between two n-type layers. The p-type semiconductor acts as the base while one n-type semiconductor will be the emitter and the other the collector. So, a small current entering the base is amplified to large collector and emitter currents. The combination of both p-type and n-type semiconductors also stabilizes the photocathode and allows it to effectively absorb the solar spectrum (Siripala et al., 2003). As a result, the anode and photocathode will function together to combine the energy from solar light and organic substrates for electricity generation. The goal was to compare the novel p-n junction TiO_2/Cu_2O/ITO composite cathodic electrode with the p-type Cu_2O/ITO composite cathodic electrode produced by Qian, Wang, and Li (2010). The novel MPC was tested to also understand the capability of TiO_2/Cu_2O/ITO composite under photoirradiation and as an electron acceptor. If found to achieve high voltage outputs, it can increase power density while lowering cost.

A two-sample t-Test was then conducted with the means at alpha equal to 0.001. The results indicate that the two populations are significantly different: $t(48)=13.33$, $p<0.001$. The results further support the alternative hypothesis: the novel MPCs have significantly greater voltage outputs than the Cu_2O/ITO MPCs. Also, AFM imaging in Figure 7 shows the height difference of the bumps on cathodes at 200 nm of the two different MPCs. The bumps are 2 nm to 10 nm in height, proving their is a difference at a microscopic level of both cathodes and that the electron beam evaporation of TiO_2 and Cu_2O on the MPC cathode was successful on both photocathodes.

In Figure 5, the average of all fuel cells were taken for each minute. This graph shows that both MPCs continuously increased in voltage outputs overtime. The average of the MPCs with a TiO_2/Cu_2O/ITO composite cathodic had a relatively higher voltage output than the average of the Cu_2O/ITO MPCs during the entire duration of the trials. Moreover, in Figure 6, the novel MPCs had greater Q1, median, and Q3 values for both with and without outliers. Based on the means, the average novel MPC provided a 818% increase in voltage output when compared to the average novel Cu_2O/ITO MPC.

Qian, Wang, and Li (2010) constructed a Cu_2O/ITO based MPC because they needed to match the redox potential of the bacteria and the electronic bands of the semiconductor. Though the same bacteria is used in this study, a n-type TiO_2 (3.2 eV)/ p-type Cu_2O (2.2 eV)/n-type ITO (4.4 eV) composite cathodic electrode achieved greater voltage outputs than the p-type cuprous oxide with 2.2 eV band gap photocathode developed by Qian et al. This is because a photocathode based on a npn transistor can, under photoirradiation, generate electron hole pairs to make the cathode potential higher than that of the anode. As a result, the electrons from oxidation are continuously driven to the photocathode and reduce the protons to hydrogen at the photocathode (Chen et al., 2013). Therefore, the novel photocathode was able to greatly increase the efficiency in comparison to the Cu_2O/ITO photocathode. Even though this study did not use nanowires for the cathodic electrode like Qian, Wang, and Li (2010), the results still illustrated that the novel MPCs provided greater voltage outputs when compared to the MPCs without a p-type electrode sandwiched between two n-type electrodes. Future research should be conducted on combining nanowire with this novel photocathode to further increase efficiency of MPCs.

Some sources of error in this study include voltage outputs picked up from the incubator and the measuring leads not being tightly secured to the fuel cell, so this may account for ± 0.00015V error. Also, the bacteria may be at different relative conditions when inoculated into the fuel cells. So, it would take different times for the bacteria to reach stabilizing conditions. Bacterial strains in the air may have also affected the result. These procedures can be improved by sanding the measuring leads every time before use. Also, all fuel cells can be inoculated at the same time and run over the same period of time, thus increasing confidence in the controls. Further research must be done to increase confidence in results and explore band gap structures that match the redox potentials of wide ranges of bacteria because of the novelty of MPC.

A single cell MPC prototype was constructed because the MPC provided 335% increase in voltage outputs when compared to MFCs. This prototype utilized the effectiveness of the TiO_2/Cu_2O/ITO photocathode. Receiving roughly 500mV, it proved to be a viable solution to current MFCs. The structure could be scaled and used in tandem with wastewater treatment plants. For, the photocathode could be placed on top of the treatment structure and increase efficiency under photoirradiation by sunlight while the anodic electrodes collected electrons from bacteria in the wastewater.

As the power density and coulombic efficiency of fuel cells continue to increase, they will become a more reliable form of green energy. The energy can be used to generate power from wastewater plants with its various forms of microbes and decrease fossil fuel consumption. If 1% of land on earth was covered by MFCs at 10% efficiency, that would be enough energy to power the world (Logan, 2012). As the field reaches closer to 10% efficiency with improvements such as MPCs, they come closer to transitioning the world to green energy.

ACKNOWLEDGMENTS

I would like to thank all of those people who helped make this research possible. First, I would like to thank Dr. Crittenden for all the help and guidance he has given me through this research, for letting me work in his lab under his supervision, and providing me the necessary materials and equipment to carry out my research at Sumwalt College in USC. Secondly, I would like to thank Mrs. Spigner for her advice and reviewing my papers. Finally, I would like to thank my parents for their support through the many phases of research and giving me a ride to USC every week. Without these people and many others, this research would not have been possible.

REFERENCES

Chen, Q., Liu, J., Liu, Y., & Wang, Y. (2013). Hydrogen production on TiO_2 nanorod arrays cathode coupling with bio-anode with additional electricity generation. *Journal of Power Sources, 238*, 345-349.

Fujishima, A., & Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature, 238*, 37-38.

Rabaey, K., & Verstraete, W. (2005). Microbial fuel cells: Novel biotechnology for energy generation. *Trends in Biotechnology, 23*(6), 291-298. doi: 10.1016/j.tibtech.2005.04.008

Logan, B. E., Call, D., Cheng, S., Hamelers, H. V., Sleutels, T. H., Jeremiasse, A. W., & Rozendal, R. A. (2008). Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environmental Science & Technology, 42*(23), 8630-8640.

Siripala, W., Ivanovskaya, A., Jaramillo, T. F., Baeck, S., & McFarland, E. W. (2003). A Cu_2O/TiO_2 heterojunction thin film cathode for photoelectrocatalysis. *Solar Energy Materials & Solar Cells, 77*, 229-237.

Qian, F., Wang, G., & Li, Y. (2010). Solar-Driven microbial photoelectrochemical cells with a nanowire photocathode. *Nano Letters, 10*, 4686-4691. doi:10.1021/nl102977n

APPENDIX

Figure 1: Anode/Cathode Compartments

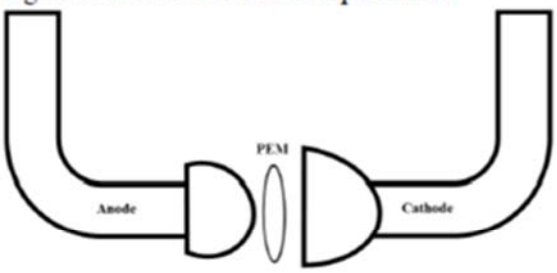

Figure 2: Fuel Cell

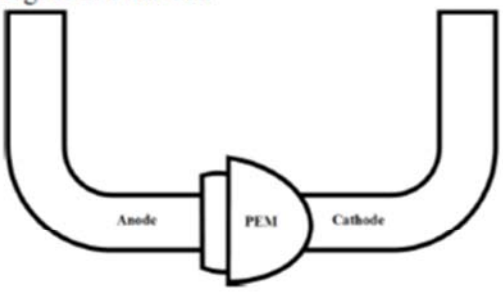

Figure 3: Functional Fuel Cell

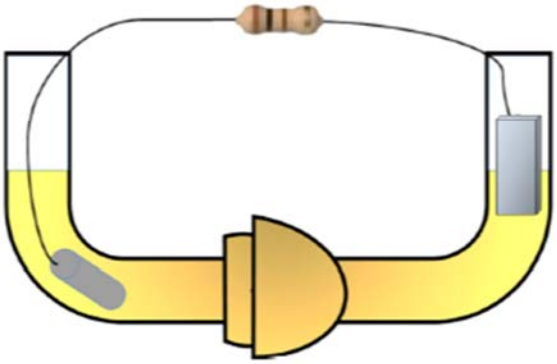

Figure 4: Fuel Cells and Light Setup

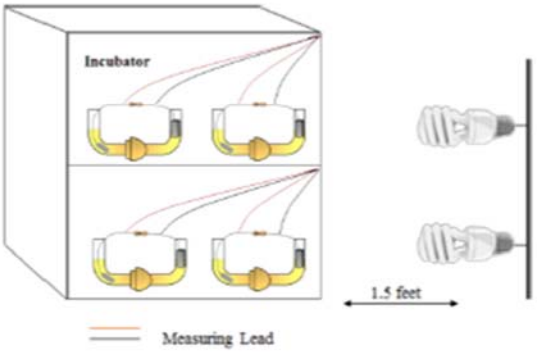

Figure 5: $TiO_2/Cu_2O/ITO$ composite cathodic

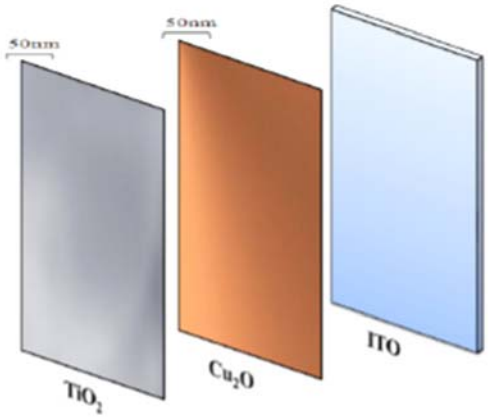

Figure 6: $TiO_2/Cu_2O/ITO$ composite versus Cu_2O/ITO composite