

Compartmentalization studies of a deep-design batch Microbial Fuel Cell assembly

Kristopher Ray S. Pamintuan^{1,2}, Ivan Harold P. Bagumba¹, and Zairus Dref G. Domingo¹

1 School of Chemical, Biological, and Materials Engineering and Sciences, Mapua University, Intramuros, Manila, Philippines

2 Center for Renewable Bioenergy Research, Mapua University, Intramuros, Manila, Philippines

E-mail: krs pamintuan@mapua.edu.ph

Abstract. Microbial fuel cells (MFCs) are a promising technology in bioelectricity production. Water systems may be utilized in producing electricity by bio-electrochemical catalytic activity of its inherent microbial culture while simultaneously treating wastewater. Current studies are focusing on design and material optimization for future up-scaling application. For large-scale application, optimization studies such as compartmentalization and stacking become important. In this study, a membrane-less microbial fuel cell is designed and optimized in terms of optimum electrode distances and optimum surface area ratios. It was found that the specific design yielded a maximum of 25.81 mV at the optimum distance wherein dissolved oxygen is sufficiently low enough in this level. Through the optimization of electrode distance was also found that the MFC designed is anode-limited with a 1:4 ratio of anode to cathode is required to produce its maximum power density output. Multiple electrodes study proves the MFC set-up is stackable even without membrane separation. This paper reports the first known attempt to quantify an optimum surface area to volume ratio at $2.34 \text{ m}^2/\text{m}^3$.

1. Introduction

Wastewater treatment continues to be a vital process in any industry as it is considered a fundamental field in sanitation; in charge of the preservation of water quality and minimizing its impact towards the environment. Current wastewater treatment processes require significant energy inputs in achieving desired conversion targets, leading to large amounts of residual waste and discharge of potential resources available within [1]. An improvement in the methods of treatment is essential as its potential resources have the ability to produce energy capable to treat the process itself as well as to introduce a new renewable source of energy. With the exponential depletion of natural resources, researches on innovative and economical industrial processes are imperative in obtaining sustainability.

In recent years, the dependence on fossil fuels has been discouraged and a demand for cleaner, emission-less and more efficient forms of energy has risen. Simpler, cost-effective methods of energy production are one way to reach sustainability and such example of that is the Microbial Fuel Cell (MFC). Organic wastes are transformed directly into electricity by utilizing the microbes within to catalyze an anodic and cathodic electrochemical reaction [2]. With different types of sources of organic wastes come different variations in the design of the MFC, each suited to generate energy from their respective sources of organic wastes. For example, bioelectric energy is derived from the reaction and may be used as an alternate source of energy; either to power the wastewater treatment



process itself or to be applied to other areas of the industry. Through MFC technology, such practices can be improved and made more efficient while also being environmentally sustainable.

Limited studies have been performed on MFCs concerning the aquaculture wastewater treatment process; thus, a common challenge regarding nutrient reduction continues to arise. Aquaculture effluent is known to have high levels of nitrates and phosphates that contribute to eutrophication when released in bodies of water.

The main objective of this study is to perform compartmentalization studies on a deep-design batch MFC for optimization of material usage and electrode spacing using aquaculture wastewater as the substrate. Compartmentalization curves are constructed to evaluate the MFC's steady-state and maximum power density at different positions, both of which are found to be determining factors for its most efficient configuration and stacking potential. The power at fixed system volume and varying electrode surface area wherein the optimum electrode surface area to wastewater volume is determined. Results of this research can provide new information in the study of novel and low-cost renewable energy sources and wastewater treatment processes. Additionally, the design and data quantified in this study can be contributed to the overall collective of MFC research.

2. Methodology

2.1. Materials and equipment

The batch MFC was of polycarbonate plastic, measuring 12 in x 2 in x 2 in (LxWxH) shown on Figure 1. The usable volume was 4.5 L. The electrodes were arranged in 11 columns and 6 rows, a total 66 electrodes overall. The columns are spaced 1 inch apart while the rows are spaced 2 inches apart. Graphite rods 3 inches in length (2 inches exposed within the MFC) and outer diameter of 0.3 cm were used as cathodes and anodes for the desired electron transfer. Copper wires along with alligator pins are used in connecting the graphite rods to the multimeter (RS Pro RS12) used for the electrical measurements.

With a deep design system, the anode and cathode's distance are incrementally increased therefore properly separating the positive and negative charges in the anode and cathode respectively, instead of using a membrane. An anaerobic system for the anode is promoted due to the MFC's deep design, causing oxygen to be consumed in the upper parts of the set-up where the cathodes are located.

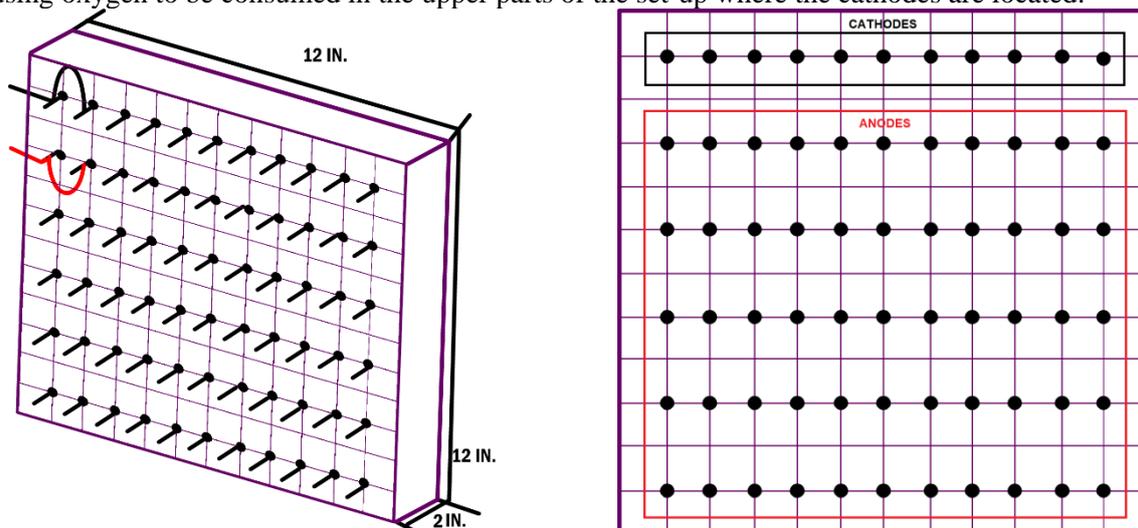


Figure 1. Design of the studied MFC

The wastewater was collected from established aquariums in Manila, Philippines. The acquired wastewater was used immediately upon collection and was let to settle for 5 days in the set-up, giving time for biofilms to develop in the electrodes. Initial measurements revealed that the substrate had a

COD of 8 ppm, nitrates of 59.76 ppm, and phosphates of 2.40 ppm. The suspended and settled solids were not quantified but were included in the MFC as an additional carbon source.

2.2. Compartmentalization studies

The compartmentalization studies were divided into 5 parts, namely: vertical distance optimization, horizontal distance optimization, anode - limiting compartmentalization, cathode - limiting compartmentalization, and multiple-electrode optimization. All of these tests are imperative in determining the efficiency of a MFC.

In vertical distance optimization, the voltage across a constant 1000-ohm external resistance was measured in all columns, with varying depth of anodes. The constructed set-up allowed for up to 10 inches of anode-cathode vertical separation. In horizontal distance optimization, electrodes in the optimized vertical distance were used. Voltages were measured for increasing inter-electrode separation. The set-up allowed for a maximum of 10 inches horizontal distance with 1-inch increments. Anode-limited compartmentalization was performed by fixing the number of connected anode to only one, and subsequently incrementally increasing the number of cathodes (from 1:1 anode:cathode to 1:11). Cathode-limited compartmentalization is the reverse of anode-limited. Multiple-electrode optimization was done by incrementally increasing the number of paired electrodes connected in parallel.

3. Results and Discussion

3.1. Vertical distance optimization

The measured voltage averaged across all electrode pairs as a function of time and averaged across all measurements grouped by distance are given in Figure 2.

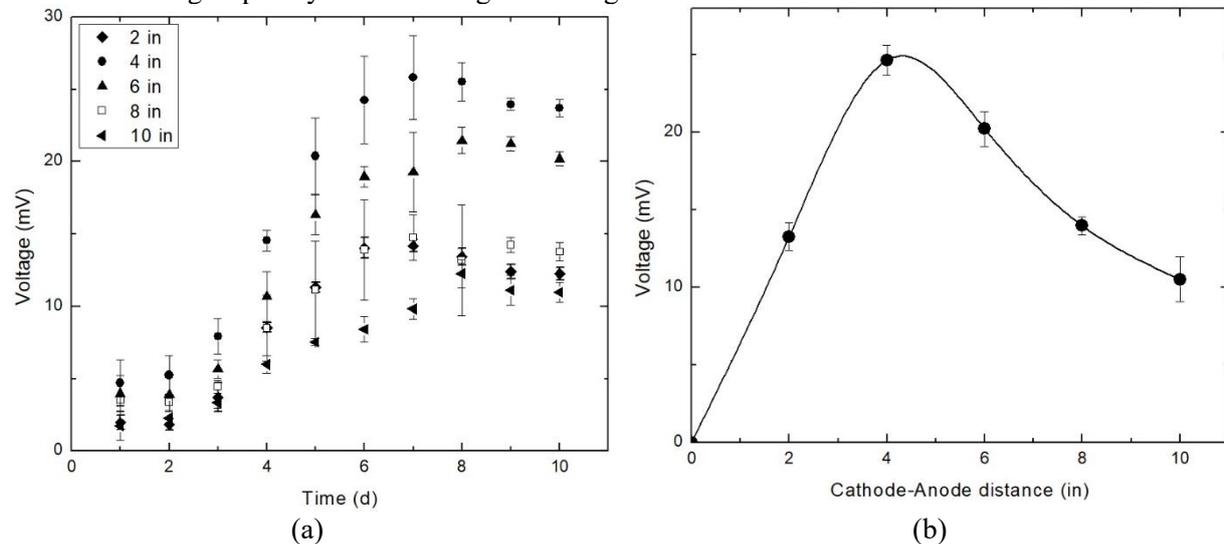


Figure 2. (a) Time-behavior of voltage measurements on different cathode-anode distances and (b) general voltage behavior against cathode-anode distance

The voltage, and subsequently power, peaked at a cathode-anode distance of 4 inches. The nature of the deep-design MFC without a membrane allowed ions to diffuse through the media when the substrate is still; this facilitated charge separation between the cathode and anode. At close distances (i.e., 2 inches), charges tend to be mixed due to their influential attraction and repulsion, leading to poor performance and low efficiency. At large distances, it takes protons longer to travel through the media (increased ohmic losses), making the anodic reaction and subsequent proton transfer rate-limiting, which cannot be remedied by enhancing cathodic conditions. Thus, an optimized cathode-anode distance is vital to obtain a compromise between efficient charge segregation in the absence of a

membrane and lower ohmic losses [3]. The relatively small standard deviation between columns of electrode pairs confirm the consistency of the findings.

3.2. Inter-electrode (horizontal) distance optimization

The measured voltage on two electrode pairs with varying horizontal distance at a fixed and optimized vertical distance of 4 inches is graphically represented in Figure 3. The average voltage drops slightly at about 0.16 mV per inch of horizontal separation with the maximum value at the minimum distance of 1 inch. That translates to less than 1% of voltage loss as horizontal distance is increased. Upon further analysis, the voltages were statistically similar across all separations ($\alpha = 0.05$). This suggests that in larger operations, multiple electrode pairs can be spaced up to 11 inches apart or possibly more to cover larger reactor areas using minimal electrode materials without significantly lowering voltage and power output. If electrode surface area is desired to be maximized, electrode pairs can also be placed near each other without fears of voltage dropping due to short-circuiting or mixing of charges. These results give design flexibility for constructing larger MFC modules.

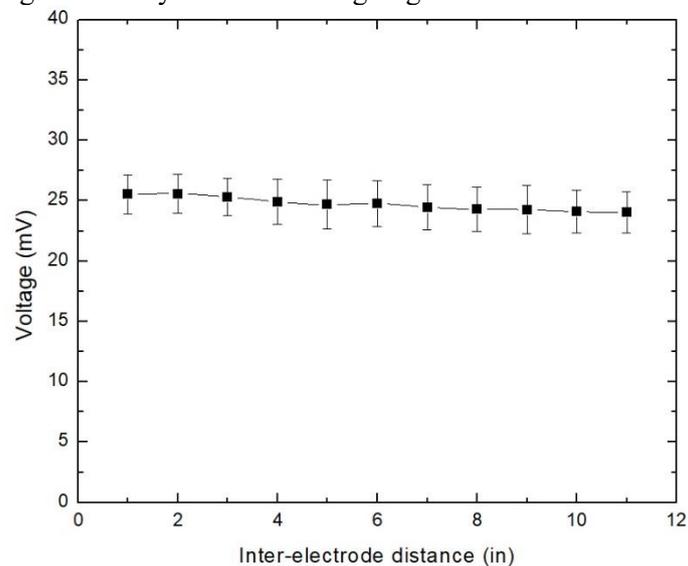


Figure 3. Variability of measured voltage against horizontal inter-electrode distance at a fixed vertical distance of 4 inches

3.3. Anode- and cathode-limited compartmentalization

Shown in Figure 4 are the voltage, power, and power density of anode- and cathode-limited compartmentalization tests. In anode-limited conditions, one anode was paired with incrementally increasing number of cathodes. This simulates a case wherein the available surface area of the cathode is greater than that of the anode. The anode to cathode ratio of 1:1 is often seen used in literature [4][5][6] due to its simplicity, but the results of this study has shown that the power can be improved by changing the ratio to 1:4 or 1:5 (anode:cathode). This means that in order to balance the cathodic and anodic reactions, more cathodic surface area must be provided as the cathodic reaction is slower than the anodic reaction. Providing more cathodic surface area gives more active sites for the reduction of protons. However, beyond 5 connected cathodes to 1 anode, it can be seen that there is a significant decrease in both power and power density. The decrease in power can be attributed to gaining a balanced reaction rate from both electrodes, but the electrons generated in the anode would have more difficulty reaching the protons in the cathode because the probability of the two meeting is lowered by increasing the number of cathodes. For the decrease in power density, it can be attributed to the increased internal resistance offered by the extra electrodes. Even if the absolute power increases, the excess electrode material contributes to the lowering of the power density.

When the power is normalized with respect to surface area to yield power density, the power density remains statistically similar from 1 to 4 connected cathodes ($\alpha = 0.05$). This counters the increase in absolute power as adding more cathodes do not contribute to a significantly higher power density. For large scale operations, the power generation would largely benefit from using the 1:4 anode to cathode ratio as the optimized combination.

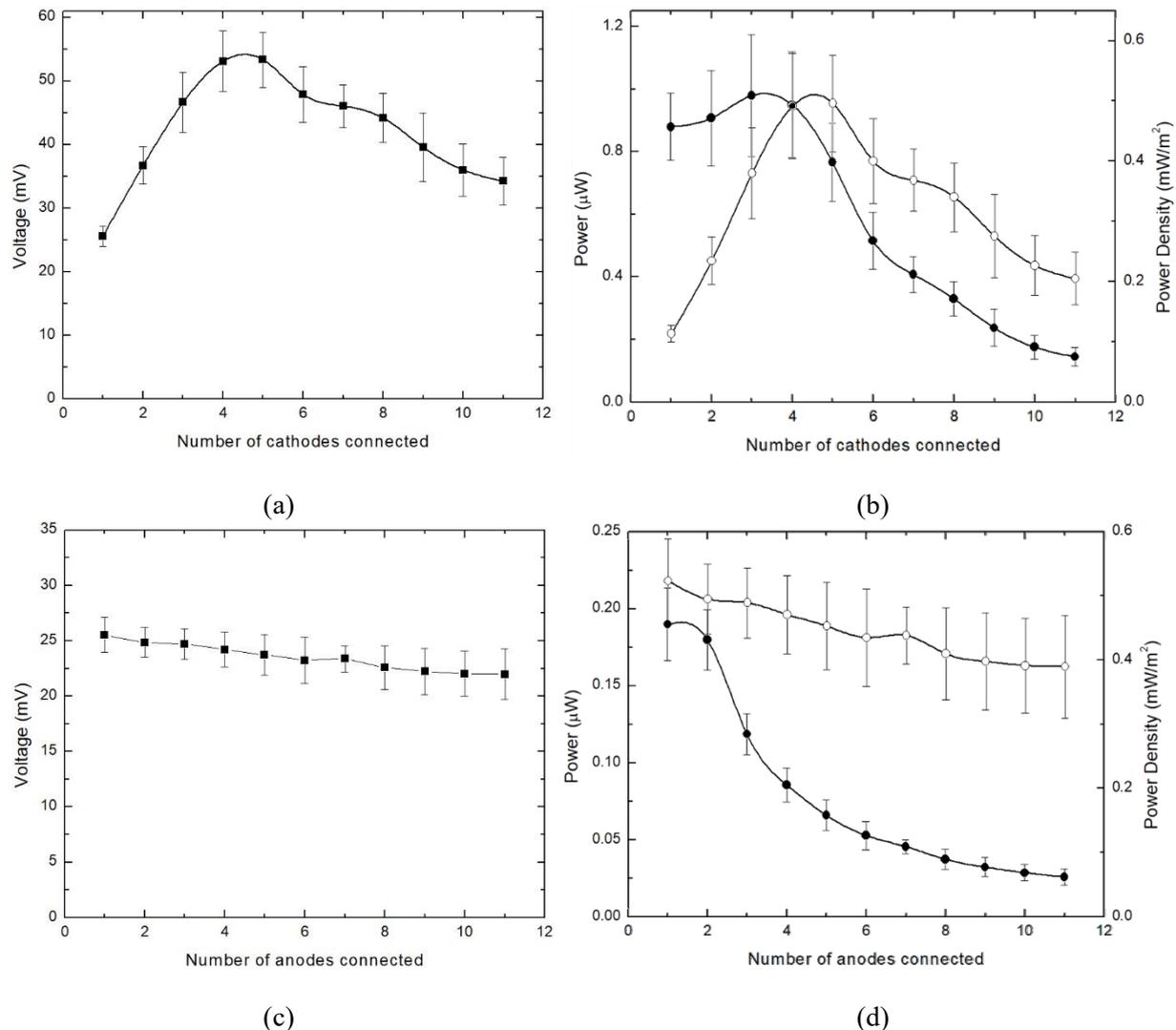


Figure 4. (a) Voltage measurement for one fixed anode and increasing number of cathodes, (b) Power (\circ) and power density (\bullet) for one fixed anode and increasing number of cathodes, (c) Voltage measurement for one fixed cathode and increasing number of anodes, (d) Power (\circ) and power density (\bullet) for one fixed cathode and increasing number of anodes

In cathode-limiting conditions, one cathode is paired with an increasing number of anodes. The results indicate that by disproportionately increasing the anodic surface area, both power and power density will continue to decrease. This is in agreement with the results from anode-limited compartmentalization that the cathodic reaction is rate limiting. When the number of anodes were increased, almost no change in power occurs but the power density drastically lowers due to the increased surface area and internal resistance offered by the additional anodes. In summary, a larger cathodic surface area is to be provided for optimum MFC operation. Similar results were obtained from Plant-Microbial Fuel Cells (PMFCs) [7].

3.4. Multiple electrodes connection

The voltage, power, and power density generated by the MFC set-up with increasing number of paired electrodes is shown in Figure 5. Both power and power density continuously increased, but they do differ in their behavior at the inflection point of the curve. For power, the trend suggests a continuous increase as the number of paired electrodes are increased beyond 11 pairs. For the power density, however, the trend suggests that a maxima would soon be reached as more pairs beyond 11 are added. This means that there exists a maximum number of paired electrodes that can be connected in parallel wherein power density is also maximum. Beyond that maximum point, it is expected that the power density would decrease due to the increased resistance offered by the additional electrodes. When that happens, it would be better if other types of connections would be used, or separate the other electrodes in another compartment. The results of this study is in contrast with a previous study wherein power increased but power density steadily decreased as the number of electrodes were increased [8].

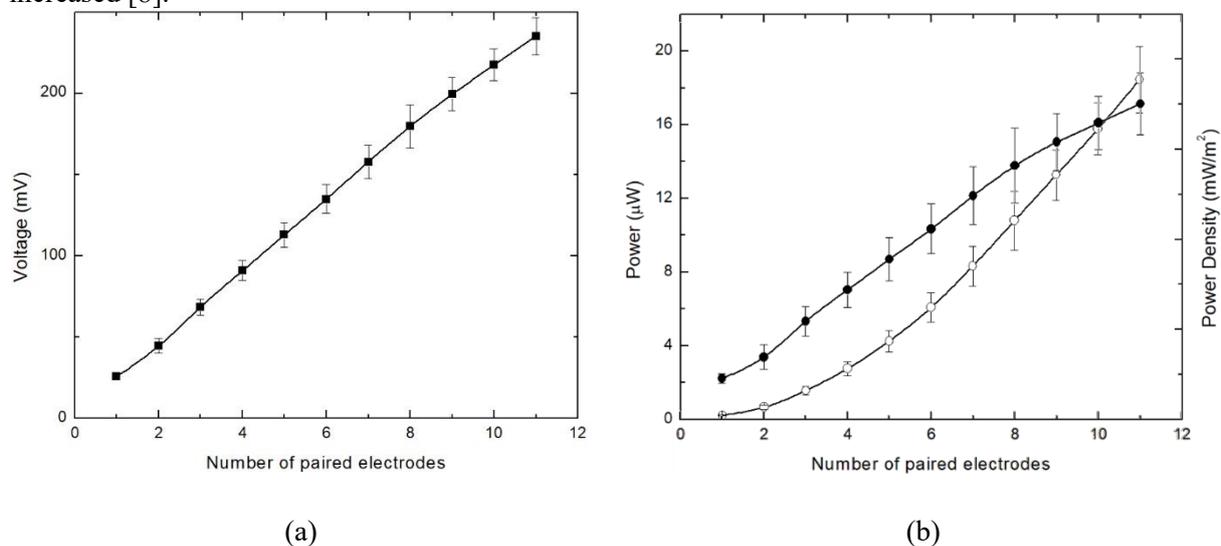


Figure 5. (a) Voltage measurement for incrementally increasing number of paired electrodes, (b) Power (○) and power density (●) for incrementally increasing number of paired electrodes

The term compartmentalization refers to the optimization of electrode surface area to volume ratio (SA/V). To date, there are no mentions in literature about the optimal or maximum allowable ratio for MFCs. For this study, the ratio was computed to be $2.34 \text{ m}^2/\text{m}^3$. Generally, higher values of this ratio is preferred to translate to more electrode surface area being properly utilized in a given volume of MFC. More research this to be done to improve this ratio before MFCs can become viable for scale-up..

4. Conclusions

Designing and engineering a small-scale batch MFC utilizing low cost materials such as graphite rods for electrodes and aquaculture wastewater for the substrate yielded favorable optimization results. In optimizing MFCs, electrode distances, internal resistances and surface area to volume ratios should be considered. In the specific MFC designed, the optimal vertical distance is 4 inches. This provides a compromise between efficient charge segregation and low ohmic losses. In terms of horizontal optimization, there seems to be a minimal drop in voltage as same electrodes are separated horizontally. This is advantageous in large set-ups where multiple electrode arrays are to be installed. The cathodic reaction was found to be rate-limiting and its surface area to volume ratio should be optimized to achieve maximum power from the fuel cell. An anode to cathode ratio of 1:4 or 1:5 was found to yield the maximum power and power density. Multiple electrode stacking has showed that power will continuously increase as paired electrodes are connected, but the power density would be

expected to reach its maximum soon and would suffer from increased internal resistance as more paired electrodes are connected. This paper reports the first known attempt to quantify surface area to volume ratio ($2.34 \text{ m}^2/\text{m}^3$) which will be useful in the scale-up of MFCs.

5. References

- [1] D. Cecconet, D. Molognoni, A. Callegari, and A. G. Capodaglio, "ScienceDirect Agro-food industry wastewater treatment with microbial fuel cells : Energetic recovery issues," *Int. J. Hydrogen Energy*, vol. 43, no. 1, pp. 500–511, 2017.
- [2] C. Santoro, C. Arbizzani, B. Erable, and I. Ieropoulos, "Microbial fuel cells: From fundamentals to applications. A review," *J. Power Sources*, vol. 356, pp. 225–244, 2017.
- [3] S. Cheng, H. Liu, and B. Logan, "Increased Power Generation in a Continuous Flow MFC with Advective Flow through the Porous Anode and Reduced Electrode Spacing," *Environ. Sci. Technol.*, vol. 40, no. 7, pp. 2426–2432, 2006.
- [4] H. Liu, B. Zhang, Y. Liu, Z. Wang, and L. Hao, "Continuous bioelectricity generation with simultaneous sulfide and organics removals in an anaerobic baffled stacking microbial fuel cell," *Int. J. Hydrogen Energy*, vol. 40, no. 25, pp. 8128–8136, 2015.
- [5] L. Zhang, J. Li, X. Zhu, D. Ding Ye, Q. Fu, and Q. Liao, "Response of stacked microbial fuel cells with serpentine flow fields to variable operating conditions," *Int. J. Hydrogen Energy*, vol. 42, no. 45, pp. 27641–27648, 2017.
- [6] I. A. Ieropoulos, J. Greenman, and C. Melhuish, "Miniature microbial fuel cells and stacks for urine utilisation," *Int. J. Hydrogen Energy*, vol. 38, no. 1, pp. 492–496, 2013.
- [7] N. Ueoka, N. Sese, M. Sue, A. Kouzuma, and K. Watanabe, "Sizes of Anode and Cathode Affect Electricity Generation in Rice Paddy-Field Microbial Fuel Cells," *J. Sustain. Bioenergy Syst.*, vol. 6, no. 1, pp. 10–15, 2016.
- [8] J. Zhang, J. Li, D. Ye, X. Zhu, Q. Liao, and B. Zhang, "Tubular bamboo charcoal for anode in microbial fuel cells," *J. Power Sources*, vol. 272, pp. 277–282, 2014.