VOLTAGE SELF-AMPLIFICATION AND SIGNAL CONDITIONING FOR ENHANCED MICROBIAL FUEL CELL PERFORMANCE

THESIS

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ABSTRACT

Microbial fuel cells (MFCs) are bio-reactors in which bacteria undergoing anaerobic respiration, deprived of all common electron acceptors, are able to use a final electron acceptor outside of the cell wall. While MFCs are able to directly convert almost any nutrient source into electricity, the voltage and current produced are too low to power common electrical devices. Due to the biological nature of the electricity production, the traditional method of stacking voltage sources in series to increase the amplitude does not work. This experiment tested the ability of passive circuits to boost the voltage output of MFCs and the effect of those circuits on the MFCs themselves. The circuit known as the Joule Thief successfully boosted the voltage of four MFCs in parallel while also reducing the activation losses of these cells.
To my family, both by blood and by love. Your limitless patience and love supported me through more than many of you know. Your oft stern words motivated me to work ever harder, and your faith in me drove me to finish what I thought I never would. This - as is everything I am proud to have accomplished - exists, because of you.
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CHAPTER 1
INTRODUCTION

1.1 Microbial Fuel Cells

The production of easily distributable and consumable energy has been the single largest contributor to climate change on our planet and caused the devastation of innumerable ecosystems. It is because of this, that regardless of how competitive the cost of renewable and sustainable energy production is, it must continue to be explored, researched, and improved. The microbial fuel cell (MFC), is a technology that is able to directly convert nearly every biodegradable compound into electricity\textsuperscript{[22]}\textsuperscript{[18]}. However, because of the low power output of these bacteria, they were relatively ignored for the better part of the 20\textsuperscript{th} century. That is, until they were shown to function without the addition of external mediators\textsuperscript{[3]}. Since the discovery of these naturally occurring electrochemically active bacteria (EAB), MFCs have risen in popularity exponentially, with over 300 peer-reviewed MFC papers published on them last year alone. This is because, even with the limited outputs of MFCs power production, many believe, including this researcher, that future potential is great and robust enough that the continued improvement of MFC technology is worth the time, energy, and financial investment.
1.1.1 How MFCs Create Electricity

MFCs are bio-reactors in which bacteria undergoing anaerobic respiration, deprived of all common electron acceptors (e.g., oxygen and nitrate), are able to use a final electron acceptor outside of the microbial cell wall. This creates a situation in which the most advantageous acceptor can become the electrode provided. Once this electrode is selected by the bacteria to continuously deposit their electrons, the MFC is able to produce current. The current and voltage able to be produced by the cell is determined by the internal losses that the cell experiences and the external load connected between the anode and cathode. If no load (or an infinite resistance load) is connected between the electrodes, then the cell will rise to its open-circuit voltage (OCV).

1.2 Research Goals and Motivation

Portable consumer electronics are powered by a range of voltages from 1.5 V (AA alkaline battery) to 3.7 V (lithium-ion battery) to 12 V (lead-acid car battery) or some multiple of those values (with multiple batteries wired in series). MFCs, even when operating at OCV, are not presently able to reach this level of performance – and OCV is never the operating voltage of a source. Therefore, even if one attains the ever elusive thermodynamic maximum potential for the electro-chemical reactions occurring within a particular MFC (1.2 V for the most common redox reaction, hydrogen fuel cells), as soon as current begins to be drawn, the voltage will begin to fall. Merely connecting MFCs in series is not a solution, since it has been shown that MFCs wired in series suffer significant losses and are subject to voltage reversal[1]. Therefore some form of signal conditioning is hypothesized to be the only real option
for widespread implementation of MFCs as useful power sources. The proposed signal conditioning technology would need to:

- Have a very low input impedance (to maintain low anode potential and high current production)
- Be able to function with low input voltages
- Be able to function with a varying input voltage
- Have a very high source to load power efficiency.

Previous work done in this area has been able to produce an OCV of nearly 2.5 volts [10] – however, as current increased, the voltage production decayed faster and either merged with the unconditioned voltage-current polarization curve or fell to zero volts before the unconditioned signal. It was, therefore, the goal of this research to find or develop a circuit capable of increasing voltage while not producing a polarization curve that did not return to the non-conditioned values.

1.3 Energy Harvesting

Energy harvesting is a relatively new field of electrical engineering that attempts to live up to its name. Its goal is to collect or “harvest” energy from many sources that have, up until recently, never been considered for use. Some examples include:

- Ambient electro-magnetic radiation
- Piezoelectric effects
- Thermo-electric effects
- Pyro-electric effects
- Electro-static effects
- Residual bio-mechanical energy

The purpose is to gain usable energy from either passive or environmental sources – often from what has previously been considered a “loss” within a system. It was
after delving into the work of this field that the circuits used in this experiment were
discovered – integrated circuits made by Advanced Linear Devices and marketed
specifically as ”Energy Harvesting” chips and a do-it-yourself circuit known as the
“Joule Thief”.

1.4 Hypothesis

The hypothesis of this study was that microbial fuel cell performance could be en-
hanced by the connecting multiple MFCs and an energy harvesting signal conditioning
electronic circuit.
CHAPTER 2
LITERATURE REVIEW

2.1 Internal Losses within MFCs

Fuel cells, including abiotic hydrogen fuel cells (HFCs) and microbial fuel cells (MFCs), experience internal losses which reduce the voltage at which these devices are able to produce current. All losses can be estimated from the data on the voltage versus current plot (i.e., polarization curve) generated from the step test (step test methodology provided in Section 3.2.4). The use of polarization curves (Figure 2.1 – modified from Baker, 2011 [2]) to identify the losses experienced by HFCs and MFCs is common practice[15]. However, estimating the actual value of each type of loss does not appear to be common at all. This quantification can provide insight into both where opportunities for improvement exist as well as specifically what in the fuel cell was affected by a given experiment. Losses are categorized as: 1)activation losses, 2)ohmic losses, and 3)concentration losses.

2.1.1 Activation Losses

Activation losses have two main causes: 1)anode surface structure and surface area and 2)amount of energy gained by bacteria during metabolism. The single largest contributor is anode surface area[15]. In general, the more surface area the anode has, the better the fuel cell performance and the fewer activation losses that are
observed[15]. The structure of the anode surface can also have an impact on activation losses. A surface that has more biologically active sites will likewise improve the performance of an MFC. Both of these are because the more bacteria that are attached to the anode electrode, the more electrons that electrode can collect.

The bacterial metabolic losses that occur are based on two main components. First, the closer the MFC’s operating conditions match the bacteria’s optimum environment, the better the bacteria’s metabolism, and therefore, fuel cell performance. The second, and more difficult component to alter, is the electrochemical advantage of the bacteria using the electrode as the final electron acceptor instead of other chemical species in the anolyte. The higher the electrochemical potential of the reaction for the given electron acceptor, the more likely the bacteria are choose it. This means that the anode’s potential plays an extremely important role. The closer to zero volts the anode can be maintained, the more energy the bacteria are able to gain.
from using the anode as the electron acceptor, and therefore, the more energy the MFC will be able to produce.

2.1.2 Ohmic Losses

Ohmic losses represent a significant portion, though not all of, the internal resistance of an MFC ([15]) and thus as the name would suggest, are actually measured in ohms. Ohmic losses within MFCs can be caused by any of a great variety of conditions within the fuel cell. A brief, and in no way exhaustive list, includes:

- Bacteria-electrode connection or interface
- Internal resistance of electrodes
- Resistance of electrode-charge collector interfaces
- Conductivity of the anolyte
- Conductivity of the membrane
- Rate of ion transport across the membrane
- Conductivity of the catholyte

Even though ohmic losses have the largest number of causes, most of these can be avoided with careful planning. This is because most of these causes are subject to factors of the fuel cell design and operating conditions.

2.1.3 Concentration Losses

Concentration losses most commonly take the form of mass transfer losses. As bacteria consume nutrients, the concentration of nutrients near the bacteria begins to dwindle. Soon there is a nutrient concentration gradient that spans from the bulk
concentration (maximum) and asymptotically approaches a complete lack of nutrients (minimum) near the bacteria. This is most prevalent in batch systems that are neither stirred nor agitated. Stirring, agitation, or running the fuel cell in a continuous flow mode can all reduce or negate these losses entirely.

2.2 Traditional Methods of Modifying MFC Output Signals

Traditionally, when one wants to increase the voltage produced and has several near identified electrical sources, one is able to merely wire the sources in series (Figure 2.2). This is how nearly all consumer electronics work, and why when putting multiple batteries in many electronics, the battery orientation alternates. However, when MFCs are wired in series, there are several unexpected results. If connected in series for a short period of time, it successfully adds the voltages and averages the electrical current of the MFCs. However, the longer the series connection is maintained, the more detrimental effects appear. First, the voltage production begins to dwindle, next “voltage” or “cell” reversal can occur, and finally voltage production can stop entirely. Voltage reversal is a phenomena that can occur when either there is an inadequate supply of food for the fuel cell or more commonly when the anode voltage gets too high[1].

These issues, however, do not occur when MFCs are connected in parallel[31] (Figure 2.3). When independent MFCs are wired in parallel, they successfully add their electrical current production together and average their voltage production. However, this averaged voltage is still less than 1 volt. Therefore, in order to convert this output so that it can power actual devices, some form of signal conditioning is necessary.


2.3 Signal Conditioning

Signal conditioning is the use of electrical components or circuits to alter an electrical signal. The most common forms of signal conditioning are amplification and filtering. These circuits can either be self-powered (passive) or externally powered (active). Amplification circuits are almost exclusively active devices, using the power supplied to them (usually ±5 volts or ±12 volts) to increase the voltage amplitude while maintaining the same current. However, since the output of the MFCs is intended to be the power source itself, active devices (most traditional amplification devices) are not an option.

At the time of writing, only one previous experiment was found investigating the effects of signal conditioning circuits on MFC performance[10]. In this experiment, four MFCs were wired in parallel and connected to an energy harvesting circuit where two sets of four capacitors switched between parallel and series connections via relays to charge in parallel, disconnect from the fuel cells, then discharge while connected in series. This method successfully was able to add the voltages together while preventing voltage reversal in any of the fuel cells. However, in this experiment,
the energy harvesting circuit increased the ohmic losses so much that the voltage was only boosted at low current production (Figure 2.4 – taken from [10]).

At high current production, the performance was actually hindered. Thus, since there was still room for significant performance improvement, the search for an alternate circuit began.
2.4 Joule Thief

2.4.1 History of the Circuit

The Joule Thief is a circuit designed by Z. Karparnik and released to the public in the 1999 issue of “Everyday Practical Electronics”[9]. The circuit is a self oscillating voltage booster; which, outside of the energy source, contains only four components – and all of them are both inexpensive and easy to acquire (Figure 2.5). The Joule Thief circuits built for this study had an average starting current (i.e., the current required to induce oscillations) of 5 mA.

2.4.2 Mechanism of the Circuit

Once oscillations begin, the peak-to-peak voltage observed is determined by the forward bias voltage of the light-emitting diode (LED) chosen. An example of the
output across the LED can be seen in Figure 2.6; where channel 1 (yellow) is measured across the entire fuel cell, and channel 2 (blue) is measured across the LED. For more information on how to read oscilloscope images, refer to Appendix B.

Each time the voltage surpasses the forward bias voltage of the LED, the diode gate opens. Once open, current follows the path of least resistance, and since the LED side of the circuit has the resistance of only the toroid and vs the transistor side has both the toroid and a resistor. This flow of current through the LED is marked by the beginning of the output voltage peak. The diode gate remains open as long as there is current available at or above the forward bias voltage. The decrease of voltage begins almost immediately and can be seen in the negative slope of the peak’s signal. As soon as the voltage drops below the forward bias voltage, the gate closes, the LED turns off, and the voltage potential begins to build until it is high enough to repeat the process. The duty cycle and the frequency that the LED operates at

Figure 2.5: Schematic of Joule Thief Circuit
is determined by the current available to the circuit. The higher the current, the longer the signal can maintain its high potential, and thus the lower the frequency of oscillations. The duty cycle appears to remain constant regardless of the frequency, input voltage, or input current.

Several variations of the circuit were constructed using different LEDs and toroids of varying diameters, wound with different gauges of wire, and different numbers of windings. Each of these variations would undoubtedly create different responses, however, given the scope of the experiment, once one that was powering a white LED was found to work well with the actual fuel cells, and that one was then used for the rest of the experiment.
CHAPTER 3
MATERIALS AND METHODS

3.1 Materials

3.1.1 Design Objectives

Many previous iterations of MFCs used in this lab were subject to intense cracking of the end-plates to edge-shearing forces[30]. Moreover, the electrode wires were held in place by expensive stainless steel wire grips with septum gaskets that were required to be replaced each time a cell was stopped and restarted. Finally, the previous designs all required continuous gassing to keep the anode anaerobic any time liquid was removed or added to the anode chamber. This included regular substrate additions and pH adjustment, which meant a significant amount of time was spent gassing the fuel cells and thus inherently both using nitrogen gas and releasing off-gasses and rather noxious odors into the laboratory’s air. The MFC shown below was designed by this researcher to solve these problems and maximize the ease of use in experimentation. The only modification made to increase power production was the use of two cathodes for a single anode (Figure 3.1).

3.1.2 Electrode Preparation

The anode and the cathode electrodes used in this cell were identical. The electrodes were EC-12 grade EDM blank graphite plates (GraphiteStore.com part #MW001021).
They arrived as 2x3x$\frac{1}{4}$ inch smooth blanks that were then cut in half using a wet tile saw to produce 1.5x2$\frac{1}{4}$ inch electrodes. Each of these blanks then had a hole $\frac{1}{16}$ inch in diameter and $\frac{1}{4}$ inch deep drilled into the top of the electrode. The electrodes were then lightly scrubbed under flowing tap water to remove any residual particles from the cutting and drilling processes. After the debris removal, they were soaked in 1N HCl for 24 hours. They were then rinsed in DI water and soaked in 1N NaOH for 24 hours. After being rinsed again, and dried in an oven at 200° F for 60 minutes, the electrodes were allowed to cool to room temperature. After cooling, 6 inch lengths of 24 gauge wire with chemical resistant insulation had the last $\frac{1}{4}$ inch of
insulation removed from each end. The stripped end of a wire was then inserted into
the electrode’s drilled hole, and the hole was then filled with silver epoxy (McMaster
part #7661A13) and allowed to cure. After the silver epoxy had hardened, thus pro-
viding both a physical and electrical connection, a protective epoxy (McMaster part
#74645A77) was applied on top of the joint to prevent degradation of the electrical
and physical connection between the electrode and the wire. After all adhesives had
set and finished curing (at least 24 hours), the electrodes were stored in DI water
until ready for use.

3.1.3 Anode and Cathode Chamber Assembly

Both chambers were fabricated from cast acrylic tube stock that had a 3.5 inch outer
diameter (OD) purchased from AIN Plastics. This tube stock was cut into 1.0 inch
wide rings with two \( \frac{3}{8} \) inch holes and one \( \frac{1}{8} \) inch hole drilled within 3 linear inches that
would then be designated as the top of the chamber (see Figure 3.2). To complete the
anode chamber, the electrode wire was fed through the \( \frac{1}{8} \) inch hole and the hole was
then sealed with room temperature vulcanizing (RTV) liquid rubber gasket. Each
of the two \( \frac{3}{8} \) inch holes were filled with a \#000 rubber stopper with a through-hole
whose purpose is explained below. The cathode chamber was identical to the anode
chamber, however, no stoppers were placed in the drilled holes, and the smaller hole
that passed the electrode wiring was not sealed. The working volume of each chamber
was 125 mL.

3.1.4 Membrane

A \( \frac{1}{8} \) inch thick flat-ring gasket was placed on the inside edge of both the anode and
cathode chambers. The gaskets were Buna-N rubber (Durometer hardness rating
of A55) that was made and custom cut by Fournier Rubber in Grandview, OH to
match the inner and outer diameter of the chamber rings. Flat-ring gaskets were used because the support provided by a flat ring was far superior than that provided by the o-rings mentioned below (which were unable to hold the membrane in place without buckling or rolling). Between these two gaskets was placed the membrane that separated the two chambers. It was a 0.45 mm thick Strong Acid Cation Exchange Membrane from Membranes International (part #CMI-7000S), hand cut to match the dimensions of the chamber rings and gaskets and pretreated in a mineral solution (Appendix C.1) for 24 hours. The prepared membrane was then trimmed as necessary to fit after the expansion caused by membrane hydration.

3.1.5 Check Valve Placement

In one of the rubber stoppers was placed a Lee’s “New Technology Check Valve” (part #12400). The addition of a check valve to this lab’s MFCs was made by Alan Yost during his research after it was discovered that this easily allowed the off-gasses to escape the anode. This solved two separate issues: firstly, it prevented pressure build-up in the anode chamber which often caused problems and spills when the pressure
was unknowingly released during MFC maintenance. Secondly, it allowed the carbon
dioxide that was produced by the bacteria to escape the chamber. This prevented
further acidification of the anode chamber from dissolved CO$_2$ in the anolyte forming
into carbonic acid.

3.1.6 Feeding Tube Assembly and Placement

Through the second #000 rubber stopper was fed $\frac{1}{8}$ inch OD anti-microbial tubing
(McMaster-Carr part #9334T12). This tube was connected to the barb connection
of a Barb-to-Male Luer-lock fitting, which in turn was connected to a female-female
Luer-lock stopcock. This system allowed for the removal or addition of fluid to the
anode chamber while maintaining anaerobic conditions without the need for gassing
of the chamber.

3.1.7 End-plate and O-ring Placement

In each previous MFC fabricated and used in the lab, the end-plate and the chamber
were fused with either epoxy or a plastic adhesive that chemically bonded to the two
pieces. To successfully bond the two pieces, they first had to be made incredibly
smooth which took significant time. Moreover, this created a very strong, permanent
air and liquid seal between the chamber and the end-plate - but too rigid of a joint
that was unable to flex. This rigidity caused the most critical problem: cracking
at the corners of the end-plates. This cracking occurred because the large amount
of force applied by the bolts in the corners that was required to prevent any leaks
where the membrane sat between two gaskets was more than the shear strength of
the fabrication material.

O-rings have a circular cross-section and therefore seal on a tangential line with
the two surfaces they are between; this provides a better seal than a flat cross-section
gasket when the same amount of force is applied. Moreover, because the o-rings purchased were of a very soft rubber, the force needed to seal the chambers was reduced even more. These two characteristics working together completely resolved both of the previous cell’s problems of cracking and leaking at the interfaces.

Thus, the final design included end-plates which were $\frac{1}{8}$ inch acrylic sheet cut into 3.5x3.5x$\frac{1}{4}$ inch square sheets with one Buna-N o-ring (Durometer hardness of A45) placed between each end-plate and its chamber. The entire unit was held together by 4 inch $\frac{1}{4}$-20 galvanized steel hex-head bolts and wing-nuts with a washer between the bolt head and end-plate as well as a washer between the wing-nut and the end-plate.

### 3.1.8 Inoculum

The enriched inoculum used in this experiment was derived from bovine rumen fluid. The original rumen fluid was stabilized, clarified, and stored in 50 mL plastic bottles. This fluid was used as inoculum for four MFCs that were operated for approximately four months. After the first month of standard operation, the pH of the MFCs was continually adjusted to maintain a neutral pH environment at the previous rate, but the feeding schedule was altered. The time between introduction of new feedstock was continually increased in an attempt to force the bacteria to consume more of the cellulose being fed to the MFCs. The now enriched anolyte from these cells was removed, mixed together, and used to inoculate a new ”feeder” cell that would provide all subsequent inoculum for this experiment.
3.2 Methods

3.2.1 Preparation and Inoculation

All acrylic components were washed with Sparkleen and dried before assembly. Once fully assembled, the mineral solution used to prepare the membrane was placed in the chambers to test the fuel cell for leaks. Upon passing the leak test the MFC was then ready for inoculation. Enriched inoculum was taken from a running MFC. Each fuel cell’s anodic chamber received 30 mL of enriched inoculum from a continuously running MFC and 95 mL of feeding solution (see Appendix C.2).

3.2.2 Monitoring Cell Performance

After inoculation, each fuel cell was connected to a simple resistive load of 1000 ohms. The voltage produced across this load was recorded every three minutes with an Agilent 34970A data-logger, and a computer running the software program Benchlink Datalogger 3. These voltages were taken continuously over a period of several weeks, during which additional tests were completed and are described later in this chapter.

The initial voltage measurements were plotted against time on a regular scale, a natural log scale, and a log 10 scale. These data were used to determine how long the MFCs were able to effectively produce voltage from a single feeding. Once this value remained consistent (approximately 48 hours) the signal conditioning experiments were timed such that the bacteria had consumed the majority of the feed stock, but had not yet ceased electricity production.

3.2.3 Feeding of the Cells

Each time the fuel cells were fed, the following protocol was used. One at a time, the MFCs were first removed from the incubator, then the spent potassium ferricyanide
was removed from each of the two cathode chambers, and the chambers were then filled with freshly made potassium ferricyanide which had been adjusted to pH 7. The three way Luer-Lok stopcock that was connected to the check-valve was then connected to a gas bag filled with nitrogen, and turned to select that port. The gas bag’s valve was then opened, allowing the pressure in the anode chamber to remain constant while fluid was removed, without continuously gassing the chamber and the bacteria. The anode chamber was mixed well and 10 mL was removed by Luer-Lok syringe through the feeding tube. The consumption of substrate, production of off-gasses, and evaporation caused an average loss of 5 mL every 3 days. Therefore while using a different syringe, 15 mL of the feed stock solution was added to the anode chamber through the same feeding tube.

The anode was once more mixed well, and 15 mL was removed. While being continuously gassed with nitrogen, the pH of this 15 mL was measured with a Russell LP060 meter. To this same 15 mL aliquot, drops of 1M HCl or 1M NaOH were added by dropper to correct the pH. The adjusted 15 mL was then returned to the anode, which was mixed again, and a second volume of 15 mL removed. The pH of this 15 mL was measured, and the method above was repeated until the nominal pH of 6.8 was achieved.

### 3.2.4 Determining Power Density

The most common method for determining the performance of an MFC is to create a Polarization Curve from the data obtained from a Step Test. The step tests were performed using a resistance decade box functioning as the external fuel cell’s load. Beginning at 1 MΩ, the voltage rate of change was allowed to stabilize to within a rate of 0.2 mV/s. This voltage was recorded, and the process repeated for each successive “step”. Following this pattern, the resistance was systematically reduced.
from the initial 1 MΩ down to 5 Ω. At each step, the voltage measurement and resistance value were used to calculate both the current through the resistor, and the power dissipated by the resistor, thus determining what was produced by the MFC.

These data were then normalized by either anode electrode surface area (usually the projected surface area) or by the anode chamber working volume to create a “density” value. From there, two graphs are created: the first plots voltage on the y-axis against current density on the x-axis. This plot helps to determine where any voltage or power losses may be occurring in the fuel cell (described in Section 2.1) as well as provide a reference of how much current can be drawn out of the fuel cell at any given voltage. The second graph plots power density on the y-axis against current density on the x-axis. This shows both the maximum power able to be produced by the MFC and at what current it occurs. Since, in a simple resistive circuit, maximum power occurs when the external resistance matches the internal resistance of the source, this also provides an approximation of the MFC’s internal resistance. It is, however, important to note that the internal resistance of an MFC is in constant flux. Ignoring any changes that might be occurring within the culture on the anode itself, conductivity of both the anolyte and the catholyte are constantly changing as the feed stock is consumed by the bacteria and the catholyte oxidizes the cations that are passing across the membrane.

A step test was conducted first on each individual MFC, then all of these cells MFCs wired in parallel, and then on the MFCs wired in parallel while connected to the Joule Thief circuit. When testing the Joule Thief Circuit, the resistance decade box replaced the fixed value resistor($R_1$ in Figure 2.5). Moreover, the resistance of the Joule Thief’s toroidal inductor is directly based on the frequency of the voltage
oscillations; this means that the input impedance is not simply the decade box value, but is in fact:

\[ (R_{\text{Decade Box}} + L_{\text{Toroid Inductor}} \times 2\pi\omega) \text{ Ohms} \]  

(3.1)

A table of the calculated input impedances can be found in Appendix D.1 based on the observed frequencies ranging from 15.09 kHz to 81.77 kHz.

Once the Joule Thief was in use, several more measurements were needed. All multi-meters used in this study were Tenma model 72-7730, and the oscilloscope was a Tektronix model TDS 3014C. The following measurements were all taken simultaneously:

- Total voltage produced by the MFC, mV
- Total current supplied by the MFC, mA
- Voltage and frequency across the LED as captured by digital oscilloscope
- Current through the LED, mA

This way power through the LED and total power could both be calculated. As white LED’s require significant power to produce a visible quantity of light, all Joule Thief experiments were done with the four MFCs in parallel.

**Ground Loop Problems**

The first several step-tests conducted with the Joule Thief attached provided data where the voltage readings on the oscilloscope did not match those on the data acquisition system. After investigation, it was discovered to be caused by a ground loop. This occurs when two points that are supposed to be at the same potential, for one reason or another, are not. This occurred in the experiment because the oscilloscope ground probe was directly linked to the safety ground plug in the power cord and
therefore maintained at earth ground. Since MFCs produce a relative voltage, earth
ground is not used as a reference, and this caused errors in the data. This was solved
by attaching all instrumentation to a backup universal power supply (UPS), which
separates the devices it powers from earth ground, thus allowing accurate measure-
ments by all instruments.

3.2.5 Estimating Losses from the Step Test

Activation Losses
The activation losses were estimated by applying a power based regression line to the
low current data points(Figure 3.3). The data points used were chosen by applying
the regression to all of the data points and removing the higher current points one
by one until a proper fit was achieved. While the regression line formed from the
experimental data does not flatten out quite as much as the example(Figure 2.1), it
also takes place over a significantly shorter operating range of current production.
The horizontal asymptote of this line is estimated to be the lower bound of the
activation losses experienced by the MFCs.

Ohmic Losses
The ohmic losses were estimated by applying a linear based regression line to the high
current data points(Figure 3.3). The data points used were chosen by applying the
regression to all of the data points and removing the lower current points one by one
until a proper fit was achieved. This method proved very effective as the estimated
ohmic losses were very close to the estimated internal resistance of each fuel cell.
Concentration Losses

The concentration losses were not estimated for any of the experimental data sets collected. Each experiment was conducted while the MFCs were continuously agitated on a shaker table. As can be seen in the experimental polarization curve for the four MFCs wired in parallel (Figure 3.3), the exponential decay associated with concentration losses was not observed, nor was it observed in any of the individual fuel cells performances.
4.1 Individual Cells

To date, the most common performance benchmark for MFCs in the body of research has been individual fuel cells powering a simple resistive load. As such, the four MFCs’ individual performances were held as the control of this experiment. Therefore, all following configurations and their tests were compared against the performance of, and losses experienced by, these individual fuel cells attached to their simple resistive loads. Since these fuel cells’ performance was to determine the baseline or expected values, it was important to determine the consistency of their performance.

4.1.1 Voltage

The open-circuit voltage of a fuel cell is the maximum voltage that can be attained, given the particular operating conditions and electrochemical reactions. These MFCs reached an average OCV of 710 mV, and as Table 4.1.1 shows, all of the fuel cells deviated from this average by less than 6.5%. Maximum power was achieved while the MFCs produced 80-90 mV.
<table>
<thead>
<tr>
<th>Cell</th>
<th>Open-Circuit Voltage, mV</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Average</td>
</tr>
<tr>
<td>1</td>
<td>707</td>
<td>710</td>
</tr>
<tr>
<td>2</td>
<td>681</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>697</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>756</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Open Circuit Voltage Produced by Individual MFCs

4.1.2 Internal Losses

The performance of fuel cells during a step test can provide insight into which internal losses are present and are having the largest impact on an MFC’s performance[15]. Though created as a reference for hydrogen fuel cells, Figure 2.1 demonstrates how the voltage versus current density (or simply current) polarization curve can show the three types of internal losses that occur within all Polymeric Exchange Membrane(PEM) fuel cells and how each losses affects the fuel cell’s performance.

By comparing the reference chart (Figure 2.1) to the actual performance of the individual MFCs (Figure 4.1), one is able to see that these MFCs experienced large activation losses. The steep decline at low current production clearly accounts for the majority (approximately 86%) of voltage loss in the MFCs. The final ~14% was due to the ohmic losses within the fuel cell. The MFCs were continuously agitated on a shaker table to minimize mass transfer losses, and from the graph this strategy appears to have been entirely successful. The concentration and mass transfer losses are imperceptible on this graph.
4.1.3 Power

The individual power production (as calculated using Equation 4.1), like the voltage production, of the four MFCs followed similar curves (Figure 4.2) and had similar maximum values (Table 4.2).

\[
\text{Power} = \frac{\text{Voltage}^2}{\text{LoadResistance}} 
\]  

(4.1)

The largest deviation from the average maximum power produced was just over 13% – twice the deviation of the voltages. It should be noted that any variances in voltage create larger variances in the power curves due to the squaring of the voltage. Moreover, since each MFC produces its OCV at the maximum load resistance, but
each has a slightly different internal resistance, each MFC did not produce maximum power at the same load resistance, thus altering which MFCs deviated from the average performance.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Maximum Power, mW</th>
<th>Average</th>
<th>Deviation, %F.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>284</td>
<td></td>
<td>-8.7</td>
</tr>
<tr>
<td>2</td>
<td>312</td>
<td>311</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>353</td>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td>4</td>
<td>296</td>
<td></td>
<td>-4.9</td>
</tr>
</tbody>
</table>

Table 4.2: Maximum Power Produced by Individual MFCs
Figure 4.2: Power Produced by Individual MFCs
4.2 Parallel Cells

4.2.1 Voltage

The second test was conducted with all four of the MFCs wired in parallel, thus only one decade box was needed for the test. To compare the relative performance, the current of the four individual MFCs was added together while the voltage was averaged in order to predict what the MFCs should produce when wired in parallel. The OCV of the fuel cells in parallel was observed to equal the exact average of the four individual fuel cells: 710 mV. When comparing the predicted Voltage versus Current curve to the observed results, they are very similar with the largest deviation occurring at very low currents (Figure 4.4).

4.2.2 Internal Losses

The reason for the above mentioned deviations can be seen in Figure 4.3. This shows ohmic losses that occurred in the individual MFCs compared to when the MFCs were wired in parallel. Since the slope of the ohmic losses is \( \frac{\text{Voltage}}{\text{Current}} \), it is equal to the actual ohmic resistance (a part of, but not equal to the total internal resistance) of the MFC in ohms. If the expected equivalent resistance of the individual fuel cells is calculated (5.17 Ω – via Equation 4.2), it is a higher value than that seen experimentally, 4.31 Ω for the fuel cells connected in parallel. While more research is needed to confirm the phenomena, there appears to be an additional benefit to connecting multiple MFCs in parallel beyond the ability to add the currents. Future research will attempt to characterize and conclusively determine this effect’s source.

\[
R_{Cell \, Array, \, Equivalent} = \left( \frac{1}{R_{Cell \, 1}} + \frac{1}{R_{Cell \, 2}} + \ldots + \frac{1}{R_{Cell \, n}} \right)^{-1} \quad (4.2)
\]
Figure 4.3: Activation and Ohmic Losses of Individual and Parallel Cells
4.2.3 Power

Because the fuel cells wired in parallel had lower than expected ohmic losses at low current production, more power was generated than that calculated by adding the four individual MFCs’ power together. Outside of this new phenomena, the performance of the MFCs in parallel followed the expected curve very closely (Figure 4.4). These results confirm other researchers’ previous findings that MFCs wired in parallel suffer few if any losses over a short period of time([31]). Planned future experiments will help to determine if any losses occur due to long term parallel connections.

Figure 4.4: Expected and Observed Voltage and Power Production of Parallel MFCs
4.3 Advanced Linear Devices Energy Harvesting Circuits

Several tests were conducted using the Advanced Linear Devices (ALD) energy harvesting chips: EH-4295 with 950Ω input impedance, and EH-4205 with 50Ω input impedance. While these chips were certainly capable of performing their designed function, for unknown reasons, when connected to the MFCs, they did so very unreliably. Their specification sheets implied that they should have been able to easily function on the current provided by a single MFC, however, even with all four cells wired in parallel, the results were often intermittent or non-existent. The problem is suspected to have been caused by either poor electrical connections, a ground loop problem, or perhaps unknown damage to the circuits themselves. Due to the comparatively larger expense of these chips and the significant problems regarding their implementation, they cannot be recommended for use with MFCs at this time, and no future experiments with them are currently planned. Each passing day, new energy harvesting circuits are either launched on to the market or their schematics released to the public. As such, any future work in this area will be done with these newer, less expensive circuits.
4.4 Joule Thief

4.4.1 Circuit Effect on Output Voltage

As soon as the parallel MFCs were connected to the Joule Thief circuit, the oscillations – and with them – the voltage amplification, began. Before the voltage was high enough to power the LED, it acted as an open circuit connection and did not affect the output voltage (Figure 4.5). However, once the voltage surpassed the forward bias voltage of the LED, it began to light. At this point the signal changed significantly (Figure 4.6). The effect of adding the LED was:

- Peak-to-peak output voltage was now determined by the forward bias voltage of the LED

![Figure 4.5: Joule Thief Output Before LED is Powered](image-url)
• The oscillation frequency, total voltage, and total current all dropped significantly and then increased as the input impedance was reduced

• The duty cycle of the LED was almost completely unaffected by the total voltage

These trends can be seen by referring to the oscilloscope screen capture images in Appendix D.1.2 taken during the step test. The peak-to-peak voltage is, of course, not actually how much voltage was being produced – that will be referred to as “total” or “cell” voltage. It was, instead, equal to the amount of power it would take to create a similar effect with no voltage signal conditioning. Please note, this was entirely a function of the circuit and is in no way being claimed to be the MFC power production levels. The root mean squared (RMS) power and voltage, however, can be considered
actual production values. Observing the overall voltage results (Figure 4.7), the circuit functioned as expected – boosting the voltage by parasitically using current.

![Figure 4.7: Effect of Joule Thief on MFC Voltage Signal](image)

The Joule Thief was able to boost the RMS voltage by nearly 50 percent. Due to the unique nature of the circuit’s output, its peak-to-peak voltage effectively emulated a signal boosted more than 425 percent above the original MFC output voltage. Moreover, when the Joule Thief portion of the graph is enlarged (Figure 4.8), it can be seen that the amount of current produced by the MFCs while attached to the Joule Thief never reached the levels of that while during the traditional step test. This is because the input impedance of the Joule Thief never reached the load impedances that were tested using just the resistance decade box as the load (Appendix D.1).
4.4.2 Circuit Effect on Internal Losses of MFCs

While connected to the Joule Thief, the MFCs were able to follow one of two different polarization loss curves(Figure 4.9). The first curve (marked A on Figure 4.9) occurred when there was enough current to power the transistor and begin oscillations, but not enough to power the LED. Curve B is observed when the LED is also consuming power. While connected to the Joule Thief, the activation losses that the MFC experienced appeared to actually decrease. There was a significantly larger reduction in these losses during lower current draw before the LED turned on; but even when the LED was powered, there was a reduction in activation losses as compared to the MFC output with no Joule Thief signal conditioning. It is currently hypothesized that this is caused by a reduction in the bacterial metabolic losses that occur due to reduced anode potential. Further research to confirm this hypothesis and expand the knowledge surrounding this phenomena is planned.
Once the LED was on, the current demand of the circuit increased drastically – this is likely the cause of the response resembling a second polarization curve superimposed on the first. This curve (curve B) had its own, new estimation of activation and ohmic losses, completely different from those while connected to the Joule Thief before the LED was powered (curve A) or the simple resistive load (curve C). Why this curve never merged with that of the simple resistive load curve is currently unknown. Neither is it known what caused the reappearance of concentration losses, which were not observed in any of the other tests. This test, like those before it, was conducted on a shaker table to increase mass transfer within the anode and cathode chambers (Section 3.2.5 and Section 4.1.2).
4.4.3 Circuit Effect on Power Produced by MFCs

Because of the MFCs response to the addition of the LED, instead of following the same power production curves as the previous tests, the step test derived power curves also reflected the decrease in losses. (Figure 4.10).

![Figure 4.10: Effect of Joule Thief on Power Density Curve of Parallel Cells](image)

While the maximum total current and maximum total power for the parallel MFCs connected to the Joule Thief were lower than when connected to the simple resistive load, they were able to produce more current at a given voltage and more power at a given current than when connected to a simple resistive load.
4.5 Light

The original reason the Joule Thief was selected for use with MFCs was its final output: light. The Joule Thief made it possible for MFCs to directly power white LEDs. The forward bias voltage of a white LED (at least 3.2 volts) is higher than MFCs could ever produce on their own, however, since the peak-peak voltage is this high, the LED is lit during for the high parts of the oscillations. The LED’s low duty cycle means that it is consuming significantly less power than would normally be required to light the LED, but does translate into a lower lumen light output from the LED. Moreover, since humans can only visually perceive frequencies up to approximately 60-65 Hz[28], the LED appears to be constantly on.

The MFCs produced 0.7 mW maximum total power while the LED was on and the maximum power through the LED was 0.5 mW. This means that the Joule Thief had over 71% power efficiency from the source to the load, and the remaining power drove the amplification process. With optimization of the circuit design, even higher MFC power outputs could be attained, which would translate into more light from the LEDs (as the current production increased, shown in Figure 4.10, the LED became brighter) or the ability to drive brighter LEDs. Moreover, with optimization of MFC design for power production, a single MFC could likely power each LED. Future research will attempt to further this type of directly implementable use of MFC technology.
CHAPTER 5
CONCLUSION

It was observed during this research that when MFCs are wired in parallel, very few losses – if any, are suffered over a period of several weeks. In addition there appeared to be an hereto unknown benefit from the connection seen as a reduction of ohmic losses. There are technologies currently available and more being developed and released all the time that are capable of modifying the low voltage and low current production of MFCs to into a more useful signal, able to power low current technology. Moreover, since this project began, there has been a veritable explosion of the energy harvesting field. Where before there were only a few freely available circuit schematics available for those wishing to build their own, and even fewer available for purchase, there are now many options with varying ranges of required input voltage and/or current and input impedances. Understanding the nuances of how MFCs interact with these circuits and optimizing designs based on that understanding will play a pivotal role in the future adoption of these promising technologies.

That is why future experiments will focus on delving deeper into several of the topics covered explored during this research:

- An in-depth look into the effect of wiring MFCs in parallel to determine:

  1. If the apparent reduced ohmic losses continue to appear.
2. What relationship that reduction might have with the quantity of MFCs wired in parallel.

- A longer study of the Joule Thief’s effect on MFCs and an optimization of this or similar circuits.

- In an attempt to rule out any factors that might arise in the bacterial metabolism due to the complex consortia and feedstock, these future experiments will likely be done with a pure culture and much more simple feedstock.

- Finally, future experiments will be conducted using reference electrodes so that the estimated internal losses can be characterized not only by type and quantity, but also by which electrode is causing them.

After all, the strength of microbial fuel cells do not lie in how quickly they produce power, but from what and how they are able to extract energy. Since MFCs are able to directly convert several sources that would otherwise be considered waste streams directly into electricity – the only expense is the initial investment. This means that as MFCs power production increases, their cost of production decreases, and circuit designs improve, MFCs will become better options for a continually increasing number and variety of implementations. Even though 60 mW (the maximum recorded individual MFC power production[29]) is not a significant amount of power, continually fed MFCs are able to produce electricity indefinitely. Thus this small amount of power can build to significant quantities over the life of the fuel cell, or when stacked together with other fuel cells. If we, as a society and world, are truly going to rise to the challenge of filling the enormous energy demands that we are making with sustainable sources, then MFCs must certainly be a piece – however, large or small that might be, of the energy puzzle.
Appendix A

GLOSSARY OF TERMS

A brief note on the glossary of terms: a significant portion of this document was taken from the corresponding articles available at http://en.wikipedia.org. This source was chosen because of its universal accessibility and the depth of information available for the content area covered by this glossary.

- \( j: \sqrt{-1} \)

- \( \omega: \) Angular frequency, measured in \( \text{radians} \ \text{second} \) and calculated using the equation:
  \[ \omega = 2 \pi f \]

- **Duty Cycle:** The ratio of time the signal is high to the time the signal is low, reported as a percent. In Figure B.1 it would be equal to \( \frac{\text{Period ON}}{\text{Total Period}} \times 100 \).

- **Forward-bias Voltage:** The voltage required to allow current to flow through the junction of a diode or similar component. This voltage is used to keep the junction open and the signal after the junction is reduced by it’s value. For example, since a white LED has a forward-bias voltage of 3.2 V, if a signal is 5 V before the LED, it will be 1.8 V after the LED.

- **Frequency:** \((f)\) A ratio of the number of complete signal cycles over the time passed (in seconds). Reported as Hertz (Hz), where 1 Hz = \( \frac{1 \text{ cycle}}{1 \text{ second}} \) also equal to \( \frac{1}{\text{Total Period}} \) in Figure B.1.
• **Inductor:** “Also called a coil or reactor, is a passive two-terminal electrical component which resists changes in electric current passing through it. It consists of a conductor such as a wire, usually wound into a coil. When a current flows through it, energy is stored in a magnetic field in the coil. When the current flowing through an inductor changes, the time-varying magnetic field induces a voltage in the conductor.” Excerpt taken from and more information available at: http://en.wikipedia.org/wiki/Inductor

• **Toroidal inductors:** “These are passive electronic components, typically consisting of a circular ring-shaped magnetic core of high magnetic permeability material such as iron powder or ferrite, around which wire is coiled to make an inductor. Toroidal coils are used in a broad range of applications in AC electronic circuits, such as high-frequency coils and transformers.” Excerpt taken from and more information available at: http://en.wikipedia.org/wiki/Toroidal_inductors_and_transformers

• **Input Impedance:** “The impedance as “seen by” or measured across the source inputs when that source is connected to a circuit. Does not equal the circuit equivalent resistance.” More information available at: http://en.wikipedia.org/wiki/Input_impedance

• **LED:** Light Emitting Diode - functions like a standard diode, with the addition of outputting light. The color of LEDs are based on junction chemistry, not color of plastic coating. This junction chemistry likewise determines the forward-bias voltage of the LED - thus making the value different for each LED color.

• **Open-circuit Voltage:** The voltage that is measured when there is no electrical connection between the anode and the cathode. This voltage is often
maintained if there is an electrical connection with very high resistance (usually greater than 1 M Ω)

- **Oscilloscope**: “A type of electronic test instrument that allows observation of constantly varying signal voltages, usually as a two-dimensional graph of one or more electrical potential differences using the vertical or y-axis, plotted as a function of time (horizontal or x-axis).” Excerpt taken from and more information available at: http://en.wikipedia.org/wiki/Oscilloscope

- **Peak-to-Peak**: “Peak-to-peak amplitude is the change between peak (highest amplitude value) and trough (lowest amplitude value, which can be negative). With appropriate circuitry, peak-to-peak amplitudes of electric oscillations can be measured by meters or by viewing the waveform on an oscilloscope. Peak-to-peak is a straightforward measurement on an oscilloscope, the peaks of the waveform being easily identified and measured against the graticule. This remains a common way of specifying amplitude, but sometimes other measures of amplitude are more appropriate.” Excerpt taken from and more information available at: http://en.wikipedia.org/wiki/Amplitude

- **Resistance Decade Box**: This box enables precision variance of resistance via manual switches that connect or remove precision resistors from the circuit (Figure A.1). The range of resistance available in the model used was 1 Ω to 11 MΩ

- **RMS**: “Root mean square (abbreviated RMS or rms), also known as the quadratic mean, is a statistical measure of the magnitude of a varying quantity. It is especially useful when variates are positive and negative, e.g., sinusoids. RMS is used in various fields, including electrical engineering.” Excerpt taken from
and more information available at:
http://en.wikipedia.org/wiki/Root_mean_square

- **Transformer**: “A transformer is a static electrical device that transfers energy by inductive coupling between its winding circuits. A varying current in the primary winding creates a varying magnetic flux in the transformer’s core and thus a varying magnetic flux through the secondary winding. This varying magnetic flux induces a varying electromotive force (emf) or voltage in the secondary winding.” Excerpt taken from and more information available at: http://en.wikipedia.org/wiki/Transformer

![Figure A.1: Resistance Decade Box](image)
Figure B.1: Explanation of Oscilloscope Screenshot Data
Appendix C

CHEMICAL SOLUTIONS

C.1 Multi-Purpose Solutions

C.1.1 Mineral Solution I

K$_2$HPO$_4$: 3 g
DI Water: 1000 mL

C.1.2 Mineral Solution II

KH$_2$PO$_4$: 3 g
NH$_4$Cl: 4.86 g
NaCl: 6 g
MgSO$_4$: 0.6 g
DI Water: 1000 mL

C.1.3 Uses

- Membranes are pretreated by soaking in a mixture of Mineral Solutions I and II and DI water.
- Feedstock solution uses both Mineral Solutions I and II
- Inoculum processing broth uses Mineral Solutions I and II
C.2 Feedstock Solution

Cellulose Medium Preparation: Initial Feed

To create: 1000.00 mL

Tryptone: 5.88 g
Yeast Extract: 2.94 g
Mineral Solution 1: 150.00 mL
Mineral Solution 2: 150.00 mL
Cellulose (3% w/w): 250.00 mL
Reducing Agent: 20.00 mL
DI Water: 430.00 mL

C.3 Catholyte

Potassium Ferricyanide (50 mM $K_3Fe(CN)_6$ in 100 mM $K_2HPO_4$)(pH 7)

To create: 1000 mL

$K_3Fe(CN)_6$: 16.46 g
$K_2HPO_4$: 17.42 g
DI Water: 1000 mL
Appendix D

DATA

D.1 Joule Thief

D.1.1 Input Impedance

Table D.1: Joule Thief Input Impedances

<table>
<thead>
<tr>
<th>Decade Box Impedance (Ω)</th>
<th>Frequency (Hz)</th>
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Figure D.1: Joule Thief Affect on Voltage versus Input Impedance for Parallel Cells
D.1.2 Step Test Oscilloscope Images

Figure D.2: Joule Thief Step Test: Decade Box Resistance = 1 MΩ
Figure D.3: Joule Thief Step Test: Decade Box Resistance = 0.5 MΩ

Figure D.4: Joule Thief Step Test: Decade Box Resistance = 0.25 MΩ
Figure D.5: Joule Thief Step Test: Decade Box Resistance = 0.1 MΩs

Figure D.6: Joule Thief Step Test: Decade Box Resistance = 50 kΩ
Figure D.7: Joule Thief Step Test: Decade Box Resistance = 10 kΩ

Figure D.8: Joule Thief Step Test: Decade Box Resistance = 7.5 kΩ
Figure D.9: Joule Thief Step Test: Decade Box Resistance = 5 kΩ

Figure D.10: Joule Thief Step Test: Decade Box Resistance = 2.5 kΩ
Figure D.11: Joule Thief Step Test: Decade Box Resistance = 1 kΩ

Figure D.12: Joule Thief Step Test: Decade Box Resistance = 900 Ωs
Figure D.13: Joule Thief Step Test: Decade Box Resistance = 800 Ω

Figure D.14: Joule Thief Step Test: Decade Box Resistance = 700 Ω
Figure D.15: Joule Thief Step Test: Decade Box Resistance = 600 Ω

Figure D.16: Joule Thief Step Test: Decade Box Resistance = 500 Ω
Figure D.17: Joule Thief Step Test: Decade Box Resistance = 400 Ω

Figure D.18: Joule Thief Step Test: Decade Box Resistance = 300 Ω
Figure D.19: Joule Thief Step Test: Decade Box Resistance = 200 Ω

Figure D.20: Joule Thief Step Test: Decade Box Resistance = 100 Ω
Figure D.21: Joule Thief Step Test: Decade Box Resistance = 50 Ω

Figure D.22: Joule Thief Step Test: Decade Box Resistance = 25 Ω
Figure D.23: Joule Thief Step Test: Decade Box Resistance $= 10 \, \Omega$
BIBLIOGRAPHY


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