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Farming Electrons: Galvanic vs. Microbial Energy in Soil Batteries

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Abstract—Recent work shows the exciting potential for soil microbes as a renewable energy harvesting source. However, the choice of materials in microbial fuel cells (MFCs) significantly impacts where the energy comes from. MFCs with metallic anodes draw energy from both renewable bacterial activity *and* non-renewable galvanic corrosion of cell components. Previous studies do not analyze these two power sources separately. This letter clarifies the behavior of metallic MFCs by characterizing galvanic activity separately from biological activity. We find that the majority of energy attained from prior designs is most likely galvanic, not bacterial, and as a consequence is non-renewable.

Index Terms-MFC, microbial fuel cell, mud battery, soil battery, galvanic cell, energy harvesting.

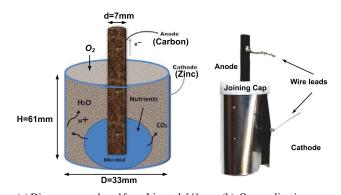
I. INTRODUCTION

The emergence of the Internet of Things and ubiquitous sensor networks have generated a surge of research in energy scavenging techniques. Harvesting RF, solar, or kinetic energy enables the creation of battery-free devices that can be used where frequent battery changes or dedicated power lines are impractical. These traditional harvesting sources can often be unavailable or intermittent, however, which motivates exploring new potential energy sources. One unusual source of power that can be tapped is bacterial colonies.

Microbial fuel cells (MFCs), also sometimes known as mud or soil batteries, are electrochemical cells, with a cathode, anode, and electrolyte. The anode accepts electrons that are produced as a byproduct of naturally occurring redox reactions. These reactions are limited unless electrogenic microbes, such as *Geobacteraceae*, are present to catalyze them [1]. Fortunately, the presence of an electron acceptor encourages a *biofilm* of electrogenic bacteria to form on the cell surface, which can create a non-trivial potential difference across the cathode and anode. MFCs have been a topic of research in civil engineering and ecological biology for decades [2], but are relatively under-explored as a possible power source in electronics research. Most low-power electronics have instead opted for traditional batteries, RF energy, or solar cells. This is changing, however, as researchers seek to power devices in more challenging environments such as underground or underwater.

Most MFCs use carbon and its variants as materials for the electrodes because these materials are low-cost, chemically stable, and do not harm the surrounding microbial ecosystem [3]. However, carbon has orders of magnitude lower conductivity than most metals, which negatively impacts MFC voltage. Recent work investigates the use of metallic and metal-coated carbon anodes [3], but one consequence is the introduction of galvanic potential between the cathode and anode. In practice, this means that metallic MFCs have two sources of power: galvanic corrosion and microbial reactions. This causes challenges in analyzing MFC power output, specifically in isolating

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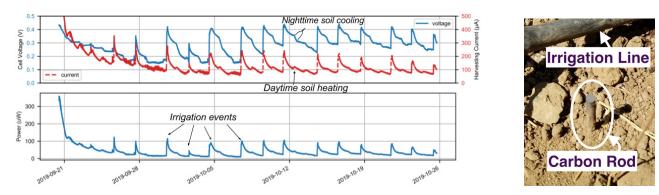


(a) Diagram reproduced from Lin et al. [4] (b) Our realization Fig. 1: A Zn-C soil cell as described by Lin et al. in [4]. (b) is our realization, with the same dimensions. We added a 7mm tall 3D printed plastic cap to join the cathode and anode together and prevent short circuiting. To deploy, the hollow interior is packed with soil.

the relative contributions of microbial activity vs galvanic activity. A 2015 paper by Lin et al. [4] describes a fuel cell that uses a carbon cathode and zinc anode and is capable of producing $60 \,\mu$ W. A similar metallic MFC has been proposed to power an in-situ irrigation control system [5]. These works measure aggregate cell performance, but do not differentiate between the galvanic and microbial power sources. Differentiation is important for long-lived deployments, as microbial energy is renewable, but galvanic contributions have a limited lifetime.

This letter details our initial explorations into MFCs as a power source. We begin with a replication of the cell described by Lin et al. [4] (as seen in Fig. 1), which we deploy for six weeks at the Stanford Educational Farm. We expect cell power to grow over time with bacterial colony growth but see no such result. This prompts an investigation into whether bacterial activity truly is the primary source of power harvested from this cell. We perform controlled experiments to isolate the impacts of electrolyte (soil) and anode selection. We find that MFCs as described in recent literature may actually be solely galvanic cells.

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(a) Voltage, current, and power output from a six-week deployment on a farm with sandy clay loam soil. "Soil heating" (orresponds to a soil temperature high of 22° C at 5 cm (air temp 31° C). "Cooling" marks a soil low of 10° C (air 16° C).

(b) Deployed cell.

Fig. 2: Zn-C cell (reproduction of [4]) deployed at a drip-irrigated farm. As in [4], we find power output depends on soil moisture. Initial voltage and current are high as we seeded the deployment with soil at field moisture capacity (30-35% moisture). After a week, moisture returns to normal (10-25%) resulting in reduced power. Irrigation at a rate of 1 gal/hr occurs in 1hr increments on Mondays, Wednesdays and Fridays, visible as large periodic spikes. There was no rain. Changes in peak falloff slope occur diurnally due to day/night temperature fluctuations.

II. INITIAL STUDY

For our initial study, we replicated an MFC as described and characterized in prior literature [4] to observe its performance. The cell consists of a 7 mm thick graphite rod surrounded by a sheet of zinc metal 61 mm in height and 33 mm in diameter, joined by a plastic cap (see Fig. 1). The overwhelming majority of MFCs are constructed using graphite and other forms of carbon because it is cheap, biocompatible, and chemically and microbially stable [2], [3]. This design is notable because it uses a metallic anode, and metal electrodes are generally avoided since most metals produce an oligodynamic (antimicrobial) effect due to their heavy ions. However, researchers have successfully built MFCs with healthy biofilms using silver and copper as anodes [3]. We wanted to see how this novel anode material (zinc) behaves when deployed outdoors. As we will see, however, the results of this initial study lead us to suspect that this cell is primarily driven by galvanic reactions, and *not* microbial.

Our construction uses off-the-shelf materials [6],[7], and is connected to an energy harvesting circuit built on a TI BQ25505. The harvester is configured with a maximum power point (MPP) of 80% of the open circuit voltage and charges a rechargeable battery. We use a RocketLogger [8] to collect low-side current sensing and voltage measurements. The components are then sealed inside a watertight box and deployed on an actively irrigated farm field for 6 weeks. The cell is buried in soil at a depth of 4 cm (see Fig. 2b).

Figure 2a shows the current, voltage, and power harvested from the cell over the six week deployment. On the surface, our results largely agree with those reported by Lin et. al [4]: a similar output voltage of less than 1 V and harvesting currents on the order of 100 μ A. However, we were surprised to observe that the power output does not increase over time, which would indicate microbial colony growth. The starting moisture of the soil surrounding the cell is high, about 35%; the initial large power output is due to the high moisture content increasing the conductivity of the soil electrolyte. After this initial spike, our harvester was able to recover an average 33 μ W from day 5 onward. While these results are interesting, they also invite skepticism that the observed cell operation is driven by microbial interactions.

First, biofilm formation on MFCs takes several days to a week before they produce a stable voltage and current [2]. Biofilm power output begins at zero and steadily increases over time. In contrast, our study witnesses stable voltage and current immediately, as soon as water is introduced to the system. The presence of water creates a sufficient electrolyte to allow the passage of ions between the anode and cathode. We also do not see a steady increase in average power output over time. These observations suggest that, at least initially, the cell produces electricity through a purely galvanic process.

Second, we are concerned with the choice of electrode materials. Baudler et al. note that copper can be used as an anode because *Geobacteraceae* are resistant to the oligodynamic effect of heavy metal ions [3]. Although not a heavy metal, silver is also a successful anode as it is a "noble" metal, which means that it is resistant to the antimicrobial processes of oxidation and corrosion, However, zinc is not a noble metal. Instead, zinc is often utilized specifically for galvanic reactions. For example, one common galvanic reaction [9] has zinc serve as an anode and the graphite rod as the cathode:

$$\operatorname{Zn} \longrightarrow \operatorname{Zn}^{2+} + 2 e^{-}$$
 (1)

$$O_2 + 2 H_2 O + 4 e^- \longrightarrow 4 O H^-$$
⁽²⁾

$$Zn + 2OH^{-} \longrightarrow Zn(OH)_{2}$$
 (3)

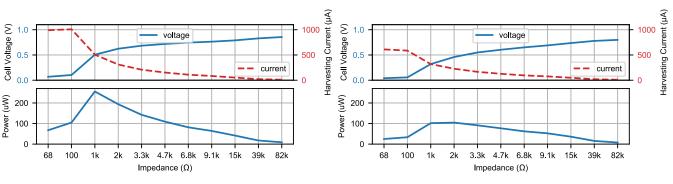
In Eq. (1) the zinc oxidizes, forming aqueous zinc (Zn^{2+}) and two free electrons. At the cathode, these free electrons are involved in a water or oxygen reduction reaction, producing OH^- ions, in Eq. (2). The result is electrons flowing from the Zn anode to the C cathode.

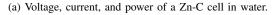
Finally, after recovering the buried cell, we attempted gene sequencing¹ on samples from the electrodes. This is how microbial ecologists determine the microorganism(s) responsible for electricity generation in MFCs. 16S RNA gene sequencing [10], [11] revealed that there were no significant populations of electrogenic microbes². Due to these surprising observations, we decided to further study the Zn-C cell in a controlled laboratory environment, and compare it against a more traditional C-C cell.

III. CONTROLLED LAB EXPERIMENTS

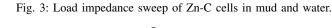
The results of our initial study motivate more controlled experimentation to understand the means of electricity generation of the Zn-C soil cell. To isolate the effects of soil bacteria, we deploy a

¹George Wells' lab at Northwestern University assisted with sequencing ²*Sporosarcina* was the dominant taxa at about 7%.





(b) Voltage, current, and power of a Zn-C cell in mud.



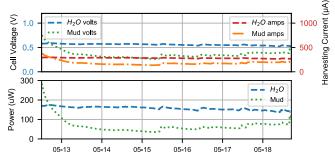


Fig. 4: Zn-C cells with $2k\Omega$ loads in mud and water. Voltage, current, and power are measured over six days. Starting electrical conductivities (ECs) were equalized by adding salt to the distilled water before beginning measurements. Initial soil moisture was 33%. After six days, moisture decreased to 11% due to evaporation. EC and moisture levels were determined by a TEROS-12 soil sensor [12].

sterilized Zn-C cell in distilled water alongside a cell in mud and measure power output over time. We also sweep cell load impedance and measure power to determine the maximum power point of each electrolyte. Next, to isolate galvanic activity, we deploy a conventional carbon-carbon (C-C) cell in mud and measure its power output over time, as well as across load impedance. From these experiments, we confirm our hypothesis that power recovered from the Zn-C cell deployed in our initial study was galvanic, not microbial.

A. Mud Versus Water

To isolate the effects of soil microbes and galvanic corrosion in the Zn-C cell, we create two new Zn-C cells. After sanitizing both cells with ethanol, we place one in sterilized distilled water, and another in mud³ and measure the voltage and current for six days. As seen in Fig. 4, both cells immediately exhibit a voltage potential and current, which supports the hypothesis that the power output of a Zn-C cell is mostly a chemical process driven by galvanic corrosion. After six days, the surface of the cell submerged in water is covered in significant amounts of precipitate (see Fig. 7b).

While the mud cell initially outputs 300μ W, it decreases to a steady $50-100 \mu$ W as the soil absorbs water [13]. In contrast, the water cell remains stable with an average output of $150-175 \mu$ W. Both cells exhibited fluctuations in power output due to changes in the ambient temperature caused by sunlight, but the average power output does not grow over time. Prior work has shown that load characteristics

³Sandy clay loam; collected Jan '20 from Stanford Farm; used in all experiments.

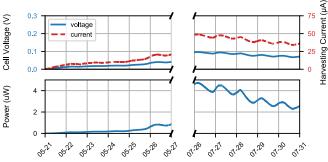


Fig. 5: Voltage, current, and power of a C-C cell in mud with a $2 k\Omega$ load, from day zero. As there is no galvanic difference between two pieces of carbon, there is no initial potential. As the biofilm forms, the cell potential and power output rises. After two months, the biofilm is able to provide a consistent power output of 2-4 μ W.

can affect energy recovered from harvesting sources [14]. To test the impact of load on cell performance, in Fig. 3 we sweep load impedance from 68Ω to $82 k\Omega$. Both batteries achieve a maximum power point around 1-2 k Ω , which agrees with the results from [4].

B. Carbon-based Microbial Fuel Cell

We create a conventional carbon-carbon (C-C) MFC to compare its behavior against the Zn-C cell. This also serves to demonstrate that the soil used has a sufficient electrogenic microbe population to encourage timely biofilm growth. The carbon-based cell is built from a MudWatt educational kit [15], and consists of two pieces of graphite felt; one of which is submerged in mud, the other is placed on top of the mud to be exposed to air.

When first constructed, the C-C cell has a near zero power output. This is expected, as it should take a few days to a week for microbes to sufficiently colonize the submerged graphite mesh [16]. Fig. 5, shows the current and voltage over six days of the cell, starting from the initial construction. The cell shows progress towards a colony that produces a stable voltage and current. After six days, however, the resulting microbial power ($\sim 1 \mu$ W) is still two orders of magnitude less than that of the Zn-C cell (100 – 300 μ W). This supports our hypothesis that that the Zn-C cell primarily produces electrical power through chemical instead of microbial processes, as it does not require a biofilm-growth period before producing a useful amount of power.

In Fig. 6, we perform a load impedance sweep of the C-C on day 14, at which point the biofilm is established. We note several differences between the microbial and Zn-C galvanic sweep. First, the

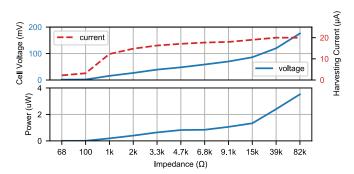


Fig. 6: Load impedance sweep of a 14-day old C-C cell in mud.



(a) Initial Zn-C cells. (b) Used Zn-C cell. (c) Used C-C cell.

Fig. 7: A white precipitate, likely $Zn(OH)_2$, is visible on the used Zn-C cell cathode. No precipitate is visible on the used C-C cell.

maximum power point for the microbial cell is at a much higher load impedance. Second, the peak power of the microbial cell (~4 μ W) is still orders of magnitude lower than that of the established Zn-C cell (~100 μ W). Even at the worst power point (82 k Ω), the ZN-C water cell still produced 9 μ W, nearly double that of the C-C microbial cell.

To understand the harvesting possibilities of an established colony, we allow this C-C cell to develop for sixty days. As seen at the end of the experiment from Fig. 5, cell power output stabilizes after the initial exponential phase, and is slightly higher (2-4 μ W) than the six-day-old cell (<1 μ W). Even with this extended period to grow the biofilm, the C-C power output is still several orders of magnitude less than the Zn-C cell.

C. Analysis of Results

From our two experiments that isolate the influence of soil microbes in the Zn-C cell, and a comparison to an actual carbon-based MFC, we can conclude that the Zn-C cell operates primarily due to galvanic corrosion. Our conclusion is supported by the following evidence from our experiments:

- 1) The Zn-C cell does not depend on microbes to produce electricity.
- The Zn-C cell produces a precipitate during operation, which suggests a chemical reaction.
- 3) The Zn-C cell produces electricity as soon as there is a sufficient electrolyte (water).

The reaction is as described in Eqs. (1) to (3). The result is electrons flowing from the Zn anode to the C cathode. The ions generated in the reactions, Zn^{2+} and OH- react to form $Zn(OH)_2$, the likely precipitate observed on the Zn electrode (see Fig. 7).

IV. LOOKING FORWARD

MFCs remain a potentially exciting energy harvesting source. From a fairly small carbon-carbon cell, we are able to recover enough purely microbial energy to preserve modern microcontrollers in sleep, with sufficient excess to support periodic, banked, higher-power events.

There is much opportunity for future study in this space. We do not yet have the answers to questions such as, "Can zinc eventually form a biofilm?", "How do soil-based MFCs react to changes in soil moisture and temperature?", "What makes biofilms weaker, and what nutrients in soil can help keep them healthy?" and "How do we sustain the growth of the bacterial colony outside laboratory settings?" . As we and others investigate MFCs further, we propose two checks:

- Isolate galvanic interactions test in deionized/distilled water, and/or sterilized soil.
- Validate evidence of biofilm techniques to do this include optical microscopy [3], chemical analysis, and gene sequencing.

V. CONCLUSIONS

As we explore the MFC design space, it is important to carefully characterize where the energy comes from. From our experiments, we believe that zinc-carbon-based MFCs actually behave primarily as non-renewable earth batteries [17]. These types of batteries still may be useful, but more study is needed to determine how long these batteries last and what benefit they might bring compared to traditional dry cell batteries. Finally, it is worth noting that it is possible that a biofilm could eventually form on a zinc anode. However, there was no evidence to suggest that biofilms were formed in prior studies on Zn-C cells, nor in our reproduction.

ACKNOWLEDGMENTS

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