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A Stable Potentiostat for Measuring Power From Low Powered Microbacterial Fuel Cells

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1. POTENTIOSTATS AND MICROBACTERIAL FUEL CELLS (MFC)'s

1.1 OVERVIEW

This technical document details our team's research that was focused on harvesting electrical power from the Mudfish. The Mudfish research takes advantage of bacteria that live in the ocean bottom mud to generate electrical power. This document shows how the harvesting of electrical power was done and looks at possible applications of using electrical current attained from the Mudfish.

Our research is based on naturally forming bacteria that grows in the mud. Anode electrodes are placed in the mud with the bacteria. The bacteria living in the mud expel electrons as part of their metabolism.

If the bacteria are isolated from oxygen that is abundant within the first 3 inches of mud in the ocean, then their growth is steady and expelled electrons can be used for many possible applications. One major application is to use the expelled electrons from the MFCs to power sensors. These sensors can be powered for years without the need to replace batteries using the expelled electrons.

To measure the power available from the MFC, we used a potentiostat to perform this measurement. Normally, a potentiostat applies current to a third electrode (called a counter electrode) to reach a desired potential between the working electrode and the reference electrode. However, for low-power systems such as MFCs we had to be careful not to force current into the system.

The reference from Office of Naval Research (ONR) (2010) discusses ONR's effort to support MFC research and the background for this support.

1.2 FIRST-GENERATION POTENTIOSTATS

This section details positive and negative aspects of first-generation potentiostats.

1.2.1 Parameters

As part of our research we built many MFCs based on 6 parameters:

- The electrode material
- The electrode size
- Evaluation of the internal flow of current
- Evaluation of the enclosure
- Serial or parallel connections
- The type of ocean mud the Mudfish lived in.

First Generation Potentiostats

Our first generation of potentiostats were copied from a design from Professor Peter Kaufman (retired) from University of Washington. Figure 1 shows a schematic of the first-generation potentiostats. These potentiostats used an open and close switching cycle to set the potential between the anode and cathode to $\frac{1}{2}$ the open circuit anode to cathode potential. Our experience showed that $\frac{1}{2}$ this value provides the maximum power extracted. A typical open circuit delta is 0.8 V, so the set point is 0.4 V. However, these first-generation potentiostat readings were often unstable. The unstable readings caused uncertainties in MFC designs and uncertainties in our reporting.

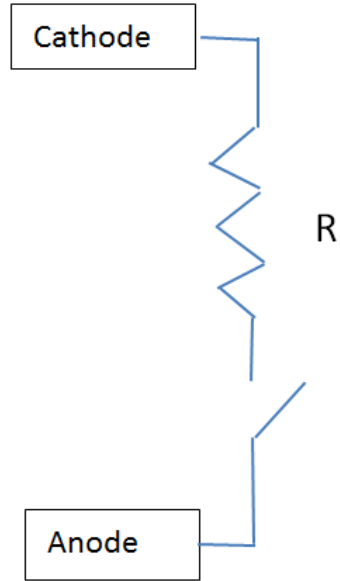


Figure 1. Schematic of first-generation potentiostat. The switch is turned on to reduce the delta and turned off to increase delta, until the average delta is $\frac{1}{2}$ the open circuit delta.

The power measured is calculated from $P = (V_{\text{cathode}} - V_{\text{anode}}) * I$. The power can differ depending on the choice of R. Thus, R is chosen from a bank of resistors, and working experience helps in the selection. The bank of resistors may not have the optimum resistor and the power reading may not be maximized. The V and I are recorded on MadgeTech (Warner, NH 03278) data loggers. Post processing of the V*I product will show the power trend over time.

Some disadvantages of this method are often it takes days for a new MFC to stabilize its power output. Even then the output can become unstable due to touching the electrodes, touching the water, or just moving the system. Figure 2 shows an example of a typical recording with unstable readings.

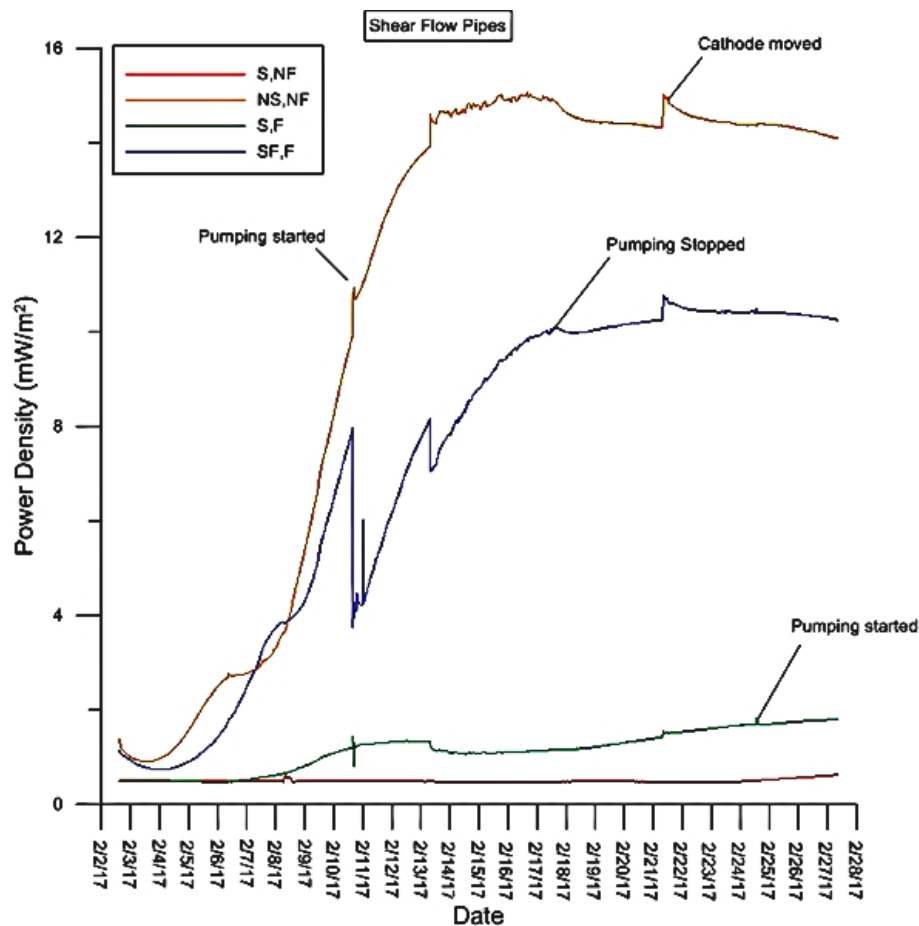


Figure 2. Recording from four MFCs, with a number of unstable jumps.

Re-design of the Potentiostats

We attempted to improve the stability of the potentiostat circuit by incorporating more robust circuit elements. However, the main cause of instability came from the on off switching. Another source of instability came from the high-speed transition of the switching transistor, which introduced harmonics into the data.

To overcome these issues it was decided to re-design the potentiostat. This led to the first prototype of the new potentiostat being designed, and the team created a final product from this design that was stable and accurate.

1.3 SECOND GENERATION OF POTENTIOSTATS

This section details improvements made to overcome limitations of first-generation potentiostats. The main concern of the re-designed potentiostat was stability. The switch mode operation (an integral part of the first generation of potentiostats) was not used in the new design. Instead the cathode to anode pathway was initially loaded by a very high resistance of a NMOSFET transistor. The gate of the NMOSFET was slowly turned on to slowly extract electrons from the anode. The resistance of the source drain channel was a sweep from several mega-ohms to a few ohms over a period of several minutes. When the measured delta matched the set point ($\frac{1}{2}$ the open circuit delta) the circuit would lock on to this resistance. The circuit would follow changes in the power if there

were changes to the circuit or to the environment (such as temperature changes). Figure 3 shows the new circuit as a smart device.

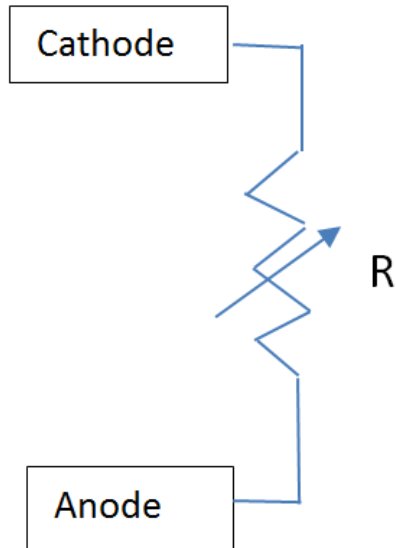


Figure 3. New potentiostat is a smart device where the resistance is varied to obtain the optimal delta.

The sweep of the NMOSFET gate was done from the voltage of a capacitor with a time constant of several minutes. This capacitor charged when a PMOSFET was turned on and slowly discharged when the PMOSFET was turned off. The charging and discharging was controlled by a comparator that compares the set point to the instantaneous delta. A high-level schematic of the circuit is shown in Figure 4.

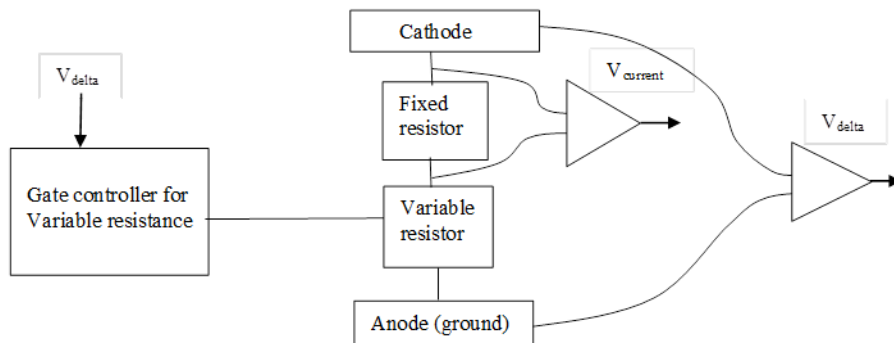


Figure 4. High-level schematic of the second-generation potentiostat.

A more detailed low-level schematic is shown in Figure 5. The schematic in Figure 5 also includes a reference out, if the user wants to add a reference probe to the MFC. The 10 ohm resistor (R7) is used for the current measurement.

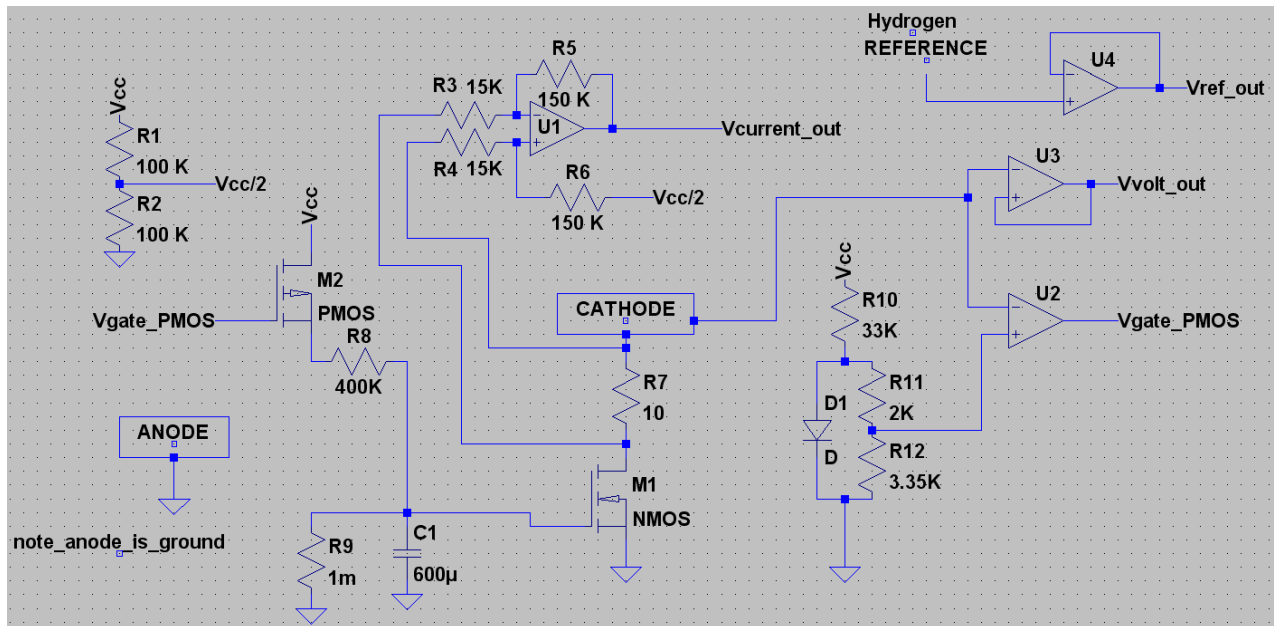


Figure 5. Low-level schematic of second-generation potentiostat.

1.3.1 Second-Generation Potentiostat Circuit Design

A brief description of the circuit operation is as follows. The cathode and anode of the MFC were connected to the circuit at the points shown. The anode is ground for the circuit. Amplifier U3 measures the delta ($V_{\text{cathode}} - V_{\text{anode}}$). The output, $V_{\text{volt_out}}$, was recorded on channel 1 of the data logger. The current flowing through R7 was measured by amplifier U1 (with a gain of 10). The output, $V_{\text{current_out}}$, was recorded on channel 2 of the data logger. The NMOSFET (M1) provided variable resistance to the current flowing between cathode and anode, and is in series with R3. The gate of M1 was controlled by the voltage at C1. When the circuit was initially turned on, C1 was discharged and at 0 V. At that moment the gate of M1 was at 0 V and the resistance of the drain source channel was high, usually several mega-ohms. Initially the delta was around 0.8 V and the set voltage was 0.4 V. The set voltage of 0.4 V was provided by the combination of D1, R11, and R12. We set it up for R12 to be variable so the set voltage could be set to any desired value. The resistor R10 was set up to limit the current to prolong battery life. The set voltage was sent to the positive terminal of the comparator U2. The negative terminal of U2 was connected to the delta line (i.e., cathode). Initially the delta was set to be greater than the set point so that U2 would output a signal at negative rail (i.e., 0 V). With time, as the delta became less than the set point, U2 would output a signal at positive rail (i.e., V_{cc}). The output of U2, $V_{\text{gate_PMOS}}$, drives the gate of the PMOSFET transistor, M2. When the gate of M2 was set at 0 V, the drain source channel was open and conducts provided current to C1 through the resistor R8. The resistor R8 is shown as 400 k Ω , but could be varied to control the time constant $R8 \cdot C1$. When the delta has decreased at or below the set point, comparator U2 would output a signal of positive rail to the gate of M2. The positive rail signal would then immediately close the drain source channel and no current would flow to C1. The capacitor C1 then was discharged through resistor R9. The discharge of C1 then lowered the voltage to the gate of M1 which increased the M1 resistance, which then increased delta. This feedback process continued and the delta will actively followed the set point.

Originally, the LM324 operational amplifiers were used as the operational amplifiers in the circuit. They worked reasonably well but were not accurate for low-powered MFCs. This problem has to do

with the high input voltage offset (3 mV) of the LM324 device. Recently, they were replaced by the NCS2325DMR2G operational amplifier made by ON Semiconductors. The potentiostat using the NCS2325DMR2G chips were tested by comparing the potentiostat power reading directly to a power reading taken off a resistor whose resistance corresponds exactly to the NMOSFET resistance. The result was a 1% difference between the potentiostat reading and the direct reading.

Figure 6 shows the output from the new potentiostat. The reading has no sharp discontinuities and the MFC reached its peak within the first day rather than over many days as with the old potentiostat.

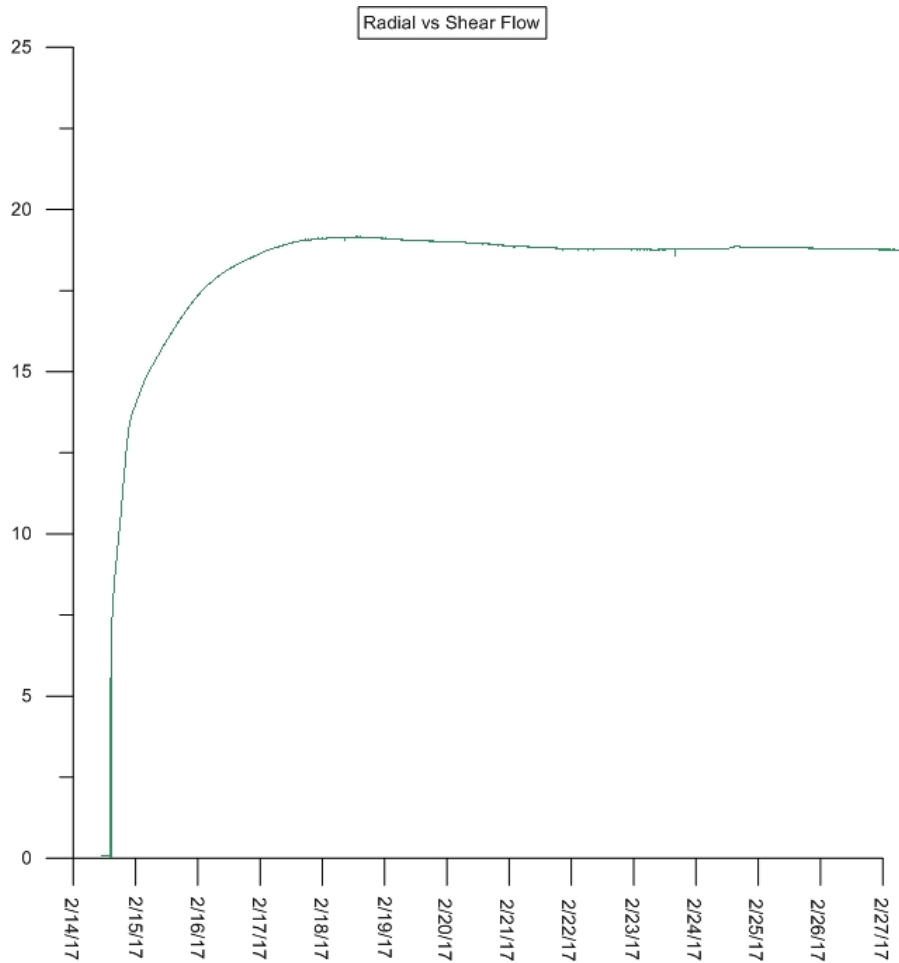


Figure 6. Output of the new potentiostat. The plot is power versus time.

The new potentiostat was used with success for 6 months and helped speed up designing new MFCs and improved the quality of the data saved.

The new potentiostat was also used to scan for the ideal load resistance (i.e., load for maximum power). If the set point is set not at 0.4 V, but set at a low value such as 0.1 V, the potentiostat would sweep through the whole range of load resistances, from mega-ohms through fractions of an ohm. Figure 7 shows a sweep showing the power peak at 0.3556 V. The result shows that the assumption of 0.4 as the best power point is not always correct.

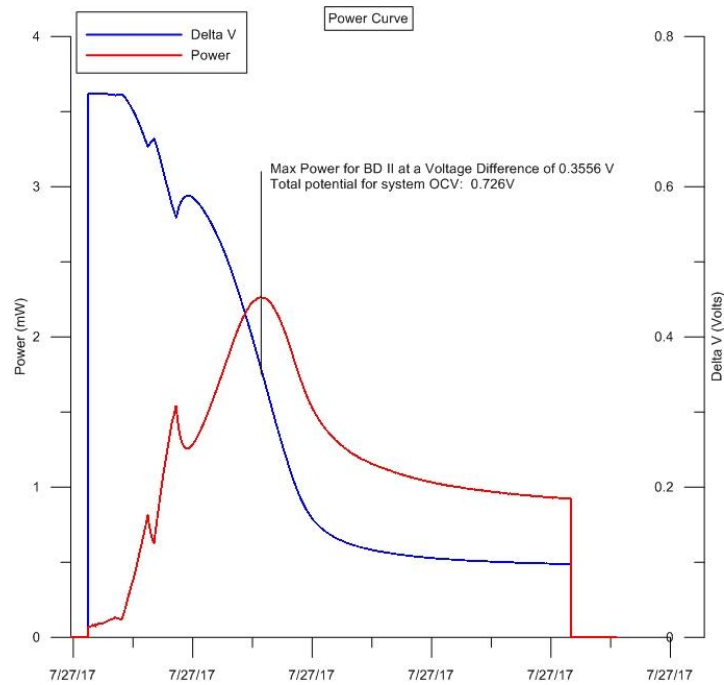


Figure 7. Resistance sweep yields the power peak (left axis). The delta is read using the right axis.

The circuit was sent to a printed circuit board (PWB) manufacturer. The manufactured PCB was smaller than the bread board circuits. A picture of the potentiostat PCB is shown in Figure 8. More recent PCBs are even smaller than the one pictured in Figure 8.

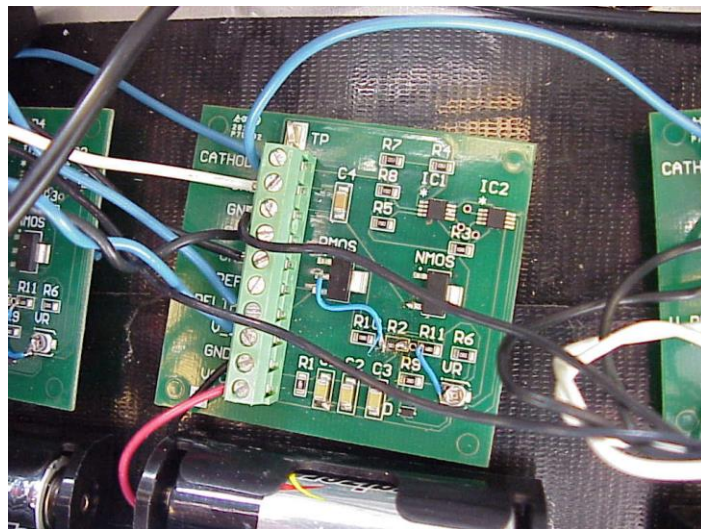


Figure 8. New potentiostat PCB.

Moving ahead in our research we are modifying the potentiostat to measure high-powered fuel cells and solar cells. In the future the goal is to enable the potentiostat to be able to automatically find the peak power point.

2. CONCLUSION

The Mudfish project has used potentiostats to measure the power output of MFCs. Several years' of data has been collected, this includes data that has sharp discontinuities and long settling times. Section 1.1 described the issues with the old potentiostat that led to a re-design of the potentiostat. The sharp on/off switching of the old potentiostat was replaced by a slow resistance sweep that slowly loads the MFC over several minutes. This new mode of operation resulted in much more stable data and shorter settling time. This newly developed potentiostat should be useful for other groups engaged in measuring power from low-powered sources.

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Office of Naval Research (ONR). 2010. "Microbial Fuel Cell: A New Source of Green Energy." Available online at <https://www.onr.navy.mil/Media-Center/Press-Releases/2010/Microbial-Fuel-Cell.aspx>. Accessed on September 7, 2017.

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