Capturing power at higher voltages from arrays of microbial fuel cells without voltage reversal†

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Received 23rd August 2011, Accepted 31st August 2011
DOI: 10.1039/c1ee02451e

Voltages produced by microbial fuel cells (MFCs) cannot be sustainably increased by linking them in series due to voltage reversal, which substantially reduces stack voltages. It was shown here that MFC voltages can be increased with continuous power production using an electronic circuit containing two sets of multiple capacitors that were alternately charged and discharged (every one second). Capacitors were charged in parallel by the MFCs, but linked in series while discharging to the circuit load (resistor). The parallel charging of the capacitors avoided voltage reversal, while discharging the capacitors in series produced up to 2.5 V with four capacitors. There were negligible energy losses in the circuit compared to 20–40% losses typically obtained with MFCs using DC-DC converters to increase voltage. Coulombic efficiencies were 67% when power was generated via four capacitors, compared to only 38% when individual MFCs were operated with a fixed resistance of 250 Ω. The maximum power produced using the capacitors was not adversely affected by variable performance of the MFCs, showing that power generation can be maintained even if individual MFCs perform differently. Longer capacitor charging and discharging cycles of up to 4 min maintained the average power but increased peak power by up to 2.6 times. These results show that capacitors can be used to easily obtain higher voltages from MFCs, allowing for more useful capture of energy from arrays of MFCs.

Introduction

A microbial fuel cell (MFC) generates electrical power from organic matter in water, such as wastewater, allowing for renewable energy production. Exoelectrogenic bacteria at the anode degrade organic matter and simultaneously transfer electrons to the anode and into the circuit. At the cathode, oxygen from the atmosphere is reduced to form water. The maximum potential that can theoretically be created is 1.1 V (open circuit conditions, assuming 17 mM acetate as the organic matter, a partial pressure of oxygen of 0.2 atm, and a pH = 7). In practice, the maximum voltage that is produced is only ~0.8 V under open circuit conditions, with working voltages of ~0.5 V. The low voltage has been a large obstacle in energy recovery from MFCs as this voltage is too low to be used directly for many practical applications. For example, a single light emitting diode (LED) requires a minimum voltage of 2 V. Thus, effective methods of boosting MFC voltages are needed.

Broader context

Microbial fuel cells (MFCs) generate electricity using organic matter in water as an energy source, and can be used to treat wastewater while simultaneously producing electricity. However, voltages from air cathode MFCs are generally small (~0.5 V), with a theoretical maximum of ~1.1 V. Conventional DC-DC converters can not be efficiently used to increase voltage as they typically require voltages larger than those produced by MFCs, and they have significant energy losses at low input voltages. Another way to increase voltages is to connect multiple MFCs in series, as done with batteries. However, in-series operation usually fails to produce stable electric power because of a phenomenon called voltage reversal, where overall voltage can decrease. Due to these limitations, practical power applications using MFCs have been limited. It is shown here that a simple electronic circuit can be used to increase voltages using capacitors. Multiple capacitors were frequently (every one second) charged by one or more MFCs, and then discharged in series to achieve two goals: boosting MFC voltages, and avoiding voltage reversal. This simple circuit design produced negligible power losses, resulting in efficient capture of the energy produced by MFCs at higher voltages.
Several approaches have been used to increase MFC voltages. One approach is to connect multiple MFCs in series, forming a stacked system, as is commonly done with hydrogen fuel cells. However, when this is done the stack usually undergoes voltage reversal, resulting in a low or nearly zero stack voltage. Voltage reversal has been shown to occur when anode potentials become unbalanced, for example when substrate concentrations are low in one cell relative to an adjacent cell. The bacteria are less active at the lower substrate concentration; as a result, the anode potential of that cell becomes positive and similar to the cathode potential of the adjacent cell. Voltage reversal can also be driven under high current conditions even without substrate depletion. Voltage reversal occurring in only one of multiple MFCs connected in series results in a failure of the whole system. An alternative approach to increasing the voltage of MFCs is to use a DC-DC converter. This approach has been used to power an underwater alarm system, a wireless sensor, or an electric circuit. The required input voltage to conventional DC-DC converters is generally larger than that produced by an MFC, and therefore an additional voltage boosting system such as a power pump is necessary to produce higher voltages. This dual boosting system results in substantial energy losses, for example 40–60% losses at output currents ranging from 1 to 10 mA. These power management systems also require supercapacitors, resulting in relatively complicated electronic circuits with multiple energy losses. When a supercapacitor was used in a circuit by itself, it was recently shown that voltage could instantly reach 0.3 V with a single MFC (external resistor = 21.4 Ω). However, the lack of a DC-DC converter or another approach precluded higher voltages. MFC voltages can also be increased by integrating a reverse electrodialysis (RED) stack into the cell, but this requires the use of additional salt and fresh water solutions.

It is shown here that MFC voltages can be increased by using arrays of supercapacitors in relatively simple circuits. Practical applications of MFCs, for example power generation from organic matter in a wastewater treatment plant, will likely require the use of multiple MFC modules. Thus, any practical application of MFCs will have a large number of MFCs that could be arranged so as to maximize energy recovery. To achieve higher MFC voltages and eliminate voltage reversal, we designed an electronic circuit with MFCs that charge multiple supercapacitors in parallel but discharge these capacitors in series. By excluding the use of power pumps or DC-DC converters, we avoided substantial energy losses encountered with previous approaches. Energy losses of the capacitors were minimized by using relatively short time periods for charging and discharging the capacitors. Stable and continuous power generation was shown using up to four MFCs and eight capacitors, compared to that produced by individual MFCs or MFCs operated in series prior to the onset of voltage reversal. This approach will make it technically feasible to apply MFCs more widely for energy recovery from wastewater.

Materials and methods

MFC preparation and operation

MFCs were built from 4-cm cubic Lexan blocks with an inner cylindrical chamber (~27 mL; 7 cm² in cross section). Graphite fiber brushes (2.7 cm in diameter and 2.3 cm in length, Mill-Rose Lab Inc., OH) were used as anodes. Carbon cloth cathodes had a platinum catalyst (3.5 mg over 7 cm²) in a mixture of carbon black and Nafion on the water side, and four diffusion layers on the air side.

The MFCs were inoculated with the effluent of an operating MFC originally started with domestic wastewater, and the inoculated MFCs were operated in fed-batch mode. Sodium acetate was provided as substrate at 1 g L⁻¹ (12.2 mM) unless otherwise noted. The medium was a 50 mM phosphate buffer solution (32.3 mM Na₂HPO₄; 17.8 mM NaH₂PO₄-H₂O; 5.8 mM NH₄Cl; 1.7 mM KCl; conductivity of 7.4 mS cm⁻¹, pH = 7.1) containing minerals and vitamins except as noted. All experiments were performed at room temperature (23.6 ± 0.3 °C).

Electronic circuit design

The circuit was made using 1-F supercapacitors (M-series, Cooper Bussmann, MO) and relay switches (SVDC1A SPDT Micro Relay, RadioShack, TX) on a standard breadboard. Relay switches were controlled by a programmable microcontroller (Mega2560, Arduino, Italy). In a relay switch, signal currents from the microcontroller were completely separated from MFC-induced currents. For more practical applications, more energy efficient switches, such as transistors could be used.

To avoid voltage reversal, MFCs charged capacitors in parallel (Fig. 1) while capacitors discharged in series through a resistor. As shown in Fig. 1B, the left set of capacitors (C1 through C4) was charged in parallel by four MFCs, while the right set of capacitors (C5 through C8) discharged in series to the external resistance. While this example circuit consists of 4 MFCs and 8 capacitors, the experiments were also performed with a single MFC using various numbers of capacitors. The charging and discharging of these capacitor sets were alternated every one second (unless otherwise noted). With the one second of charging and discharging, stable and continuous power generation was achieved.

![Fig. 1](https://www.rsc.org/content/dam/energyenviro/energyenviron_sci/2011/4/4662-4667/4663/1-energyenvironsci4662-4667-4663-f1.gif)
Voltage reversal test

In order to demonstrate the adverse effects of voltage reversal on power generation, four MFCs were initially operated in series (external resistance of 1000 Ω) without capacitors. One MFC was fed a lower concentration of sodium acetate (0.5 g L⁻¹) compared to the other MFCs (1.0 g L⁻¹) as substrate imbalances are known to induce voltage reversal. When voltage reversal was observed, all four MFCs were changed from a series connection to the circuit with 8 capacitors in order to demonstrate that a high voltage could immediately be restored using this approach even after MFCs had exhibited voltage reversal. To confirm this approach avoided voltage reversal, additional fed-batch cycle was run with 8 capacitors at a smaller external resistance (250 Ω) as small resistors are also known to trigger voltage reversal with multiple MFCs arranged in series.

Analyses

MFC performance was examined for individual MFCs and reactors operated as an array by standard polarization and power density curves obtained using the single cycle method. MFCs were first set under open circuit conditions for at least 20 min before the external resistance was sequentially increased from 7 Ω to 4 MΩ, with at least 20 min per resistance until the voltage drop across the resistor becomes stable. Voltages produced by MFCs and capacitors were recorded using a digital multi-meter (Agilent 34792A, Agilent Technologies, CA) every 10,050 s unless otherwise noted. The potential drop across an external resistance was also monitored to determine current using Ohm’s law.

The change in the chemical oxygen demand (COD) over a fed batch cycle was measured according to standard methods (Hach Co., CO). The Coulombic efficiency (CE) for capacitors discharged in series, when the capacitors were charged by multiple MFCs in parallel, was determined from the change in COD (ΔCOD) over a fed batch cycle using

\[
CE = \frac{8N_C \int |i| dt}{FV_{an} \Delta COD}
\]

where \(i\) is the current passing through the external resistance, \(F\) the Faraday constant, and \(V_{an}\) the total liquid volume. The calculation of the Coulombic efficiency was modified from that used for a single MFC by including the number of capacitors (\(N_C\)) because the capacitors are charged in parallel but discharged in series, thereby proportionally changing the charge transferred during the capacitor discharge. \(N_C\) was set to be unity for MFCs operated without a capacitor.

Results and discussion

Voltage increases

The open circuit voltage produced by a single MFC was increased by 340% to 2.5 V using 8 capacitors in the circuit, compared to operation of the same MFC without the capacitors (0.7 V) (Fig. 2A). In addition, the open circuit voltage increased in proportion to the number of capacitors used in the circuit. The use of capacitors increased working voltages as well. For instance, the voltage under maximum power conditions increased by ~4 times from 0.25 (no capacitor) to 1.05 V (8 capacitors). This enhanced voltage was achieved by the series arrangement of the capacitors during discharging and thereby the degree of voltage enhancement was more pronounced with more capacitors in the electronic circuit (Fig. 2A).

There was no noticeable reduction in the maximum power with the increased number of capacitors as the resulting maximum power from a single MFC was similar, between 0.73 and 0.78 mW (1035 and 1116 mW m⁻², normalized by 7-cm² cathode), regardless of the number of capacitors (Fig. 2B). This result indicates negligible power losses during the repetitive charging and discharging of the capacitors in the circuit. In addition, currents corresponding to the maximum powers were found to decrease approximately by half with an addition of one capacitor. These results show that voltages and currents from an MFC can be controlled simply by adding more capacitors, and the capacitor circuit can be used without major power losses.

Operation with arrays of MFCs

With four MFCs, the output voltage from 8 capacitors was almost identical to that produced by the same four MFCs arranged in series in the absence of voltage reversal (Fig. 3A). As a result, the corresponding power curves were very similar with the maximum power at ~2.9 mW (1048 mW m⁻², normalized by total cathode area of 28 cm²) (Fig. 3B). These results indicate that 8 capacitors, where two sets of four capacitors were alternately charged in parallel but discharged in series, can convert performance of four MFCs into that of the same MFCs arranged in series. In addition, the similar maximum power values confirm negligible power losses in the circuit. It should be noted that the experiment with the four MFCs in series (without the capacitor circuit) was incomplete as there was a significant drop in voltage.
and power due to voltage reversal at higher currents, even though the test was performed using fresh substrate medium.

Control of voltage reversal

Voltage reversal was intentionally induced with four MFCs arranged in series by starting a fed batch cycle with a lower substrate concentration in one of the MFCs (MFC-2). The output voltage was initially stable at ~1.5 V (for 12 h) at a low current using a high external resistance (1000 Ω) (Fig. 4). However, after 12 h voltage reversal in MFC-2 limited overall power generation by the system. Following this onset of voltage reversal, at 14 h the four MFCs were disconnected from series operation and connected to the circuit containing 8 capacitors. As soon as the capacitor circuit was used, voltage reversal in MFC-2 was eliminated and the output voltage was instantly restored to ~1.4 V (Fig. 4). This result confirms the capability of the capacitor circuit to avoid voltage reversal.

Another fed-batch cycle with the four MFCs with 8 capacitors was followed using a smaller external resistance (250 Ω), since it has been found that voltage reversal is also triggered by a small external resistance during series operation. The resulting voltage was stable at ~0.8 V across the 250-Ω resistor and voltage reversal was not observed throughout the cycle (Figure S1 in Supplementary Information). The resulting Coulombic efficiency (CE) was 67%, while the MFCs operated individually without capacitors resulted in CE of 38%. This comparison indicates that stable operation of MFCs at boosted voltages can also improve the Coulombic efficiency.

Additive maximum powers

The maximum power produced by the MFCs was not altered by external factors such as the use of capacitors or series arrangement of MFCs in the absence of voltage reversal (Fig. 2B and 3B). The sum of maximum power produced by the four MFCs operated individually (0.77 + 0.68 + 0.70 + 0.69 = 2.84 mW; Figure S2 in Supplementary Information) was similar to the maximum power from the four MFCs with the capacitors circuit (2.94 mW; Fig. 3B). This shows that the maximum power reproduced using capacitors can be predicted based on individual maximum power of used MFCs.

Fig. 3 Comparison in voltage and power from 4 MFCs between with and without capacitors. The circuit of 8 capacitors consisted of two sets of four capacitors alternately charging and discharging every one second. Power production with four MFCs in series was not stable due to voltage reversal, resulting in a failure to produce the expected voltages at a current ~4.8 mA. In addition, the results at lower currents than 4.8 mA could only be obtained with fresh substrate medium.

Fig. 4 Voltage reversal with four MFCs in series occurred between 12 and 14 hours. The voltage was restored by changing the operation of the MFCs from series operation with a capacitor circuit (after 14 hours). The circuit of 8 capacitors consisted of two sets of four capacitors alternately charging and discharging every one second. The initial substrate concentration was varied to ensure voltage reversal (0.5 g L⁻¹ sodium acetate in MFC-2 and 1.0 g L⁻¹ in the other MFCs).

Fig. 5 Additive maximum power from individual MFCs and the maximum power when using the same MFCs with a capacitor circuit. The circuit of 8 capacitors consisted of two sets of four capacitors alternately charging and discharging every one second. The concentration of the phosphate buffer solution (PBS) was 50 mM in one MFC and 5 mM in the other.
losses, compared to previous circuits built with a DC-DC converter, the capacitor circuit design has a significant potential for these different applications.

Conclusions

Voltage reversal was eliminated here by using arrangements of multiple capacitors in the circuit. While a DC-DC converter requires a minimum input voltage that is typically larger than the working voltage of an MFC (~0.5 V), even a very small voltage at the end of a fed-batch cycle (e.g., <0.01 V) could be boosted here using the capacitor-based circuit. In addition, based on maximum power densities produced using the capacitors in the circuit, there were minimal energy losses. In comparison, a power management system with a DC-DC converter can lose 40% of the produced power under similar current conditions. Therefore, the circuit design described here can be used to boost MFC voltages in a stable and efficient way.

This circuit is also capable of producing higher power densities over shorter time intervals by controlling the time interval for charging and discharging the capacitors. With a four-minute interval, the peak power reached 2.5 times the maximum power from a MFC. Even with this substantial power oscillation to produce a high peak in power, average power was stationary, confirming that there were negligible energy losses in the circuit over longer time intervals. This finding shows that the capacitor circuit design will enable MFCs to power electronic devices that require higher electrical power over non-continuous time intervals.

Acknowledgements

This research was supported by funding through the King Abdullah University of Science and Technology (KAUST) (Award KUS-I1-003-13).

References


Effect of charging and discharging period

The circuit with capacitors can be used to further increase the maximum power over a short time period by increasing the charging and discharging cycle time. A single MFC was connected to an external resistance (1000 Ω) through the electronic circuit of 8 capacitors. As the time period for charging and discharging (dt) increased from 1 to 4 min, the magnitude of the voltage oscillation increased from 30 to 110% of the average voltage (0.85 V) (Fig. 6A). Even with the substantial voltage oscillation, the average voltage was stable and varied by only ±3% for the various time intervals. The peak voltage reached 1.39 V, and the peak power was 1.95 mW, with a 4-minute time interval (Fig. 6). This peak power is 2.5 times the maximum power with the one-second time interval (0.78 mW as shown in Fig. 4B). These results show that the capacitor circuit can be used as a power management system to harvest lower MFC power densities over a relatively longer time and then release high power over a shorter time interval to operate electronic devices. Considering the relatively simple design and negligible power