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Electricity generation of single-chamber microbial fuel cells at low temperatures

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ABSTRACT

Practical applications of microbial fuel cells (MFCs) for wastewater treatment will require operation of these systems over a wide range of wastewater temperatures. MFCs at room or higher temperatures (20–35 °C) are relatively well studied compared those at lower temperatures. MFC performance was examined here over a temperature range of 4–30 °C in terms of startup time needed for reproducible power cycles, and performance. MFCs initially operated at 15 °C or higher all attained a reproducible cycles of power generation, but the startup time to reach stable operation increased from 50 h at 30 °C to 210 h at 15 °C. At temperatures below 15 °C, MFCs did not produce appreciable power even after one month of operation. If an MFC was first started up at temperature of 30 °C, however, reproducible cycles of power generation could then be achieved at even the two lowest temperatures of 4 °C and 10 °C. Power production increased linearly with temperature at a rate of $33 \pm 4\,mW\,^{\circ}C^{-1}$, from $425 \pm 2\,mW\,m^{-2}$ at 4 °C to $1260 \pm 10\,mW\,m^{-2}$ at 30 °C. Coulombic efficiency decreased by 45% over this same temperature range, or from CE = 31% at 4 °C to CE = 17% at 30 °C. These results demonstrate that MFCs can effectively be operated over a wide range of temperatures, but our findings have important implications for the startup of larger scale reactors where low wastewater temperatures could delay or prevent adequate startup of the system.

1. Introduction

Microbial fuel cells (MFCs) directly convert chemical energy in organic matter into electrical energy using microorganisms, providing a method for simultaneously producing renewable energy while treating wastewater (Ahn and Logan, 2009; Feng et al., 2008; Liu et al., 2004; Min and Logan, 2004). Power densities produced with pure compounds such as acetate have increased by nearly six orders of magnitude through improvements in reactor architecture (Logan and Regan, 2006a,b), optimization of solution chemistry (Feng et al., 2008; Liu et al., 2005), and using new materials and modifying electrode surfaces (Cheng and Logan, 2007; Logan et al., 2007; Park and Zeikus, 2003; Zhang et al., 2009). Characteristics of the substrates and system operation also can greatly affect power densities. These include solution pH (Borole et al., 2008; Fan et al., 2008); wastewater alkalinity, added buffers and their concentration, ionic strength, and solution conductivity (Huang and Logan, 2008a; Liu et al., 2005); operation mode in terms of fed-batch or continuous flow (Ahn and Logan, 2009; Huang and Logan, 2008b); and the specific organic matter species in the different types of wastewater and their degradation by products (Feng et al., 2008; Huang and Logan, 2008a; Liu et al., 2004; Min et al., 2005).

Temperature is another important wastewater characteristic, but most studies have examined performance at a single temperature, with typical temperatures chosen of room temperature or higher (20–35 °C). When temperatures have been varied during a study, different results have been obtained relative to impact of temperature on performance, although in almost all cases lowering the temperature reduced performance. In two different studies with single-chamber MFCs operated in fed-batch mode, the power density decreased by 10% when the temperature was reduced from 32 °C to 20 °C (Liu et al., 2005; Wang et al., 2008). In another study with a single-chamber MFC operated with continuous mode, the power density decreased by 21% when the temperature decreased from 35 °C to 24 °C, but only by 5% when the temperature was decreased from 30 °C to 24 °C (Moon et al., 2006). In contrast, it was reported that when using a two-chamber MFC with a ferricyanide cathode, that the power density was reduced by 39% when for a temperature decrease from 30 °C to 22 °C, and that there was no appreciable power generation at 15 °C (Min et al., 2008). In another two-chamber MFC study with a dissolved oxygen (DO) catholyte, however, current increased from 0.7 mA to 1.4 mA when the temperature decreased from the range of 20–35 °C to 8–22 °C (Jadhav and Ghangrekar, 2009). In this case, the solubility of DO may have

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been a factor. The DO saturation concentration varies with temperature, and DO concentrations will affect cathode performance (Oh et al., 2004). The maximum voltages produced in the study by Jadhav and Ghangrekar (2009) were usually very low (<50 mV), and thus other factors such as high internal resistance, changes in microbial community, and DO could have been important. Sediment MFCs have been operated at low and ambient temperatures of seawater, but power densities in these systems are very low, and the effects of temperature on these systems have not been investigated (Reimers et al., 2006). *Geobacteraceae* isolated at 10 °C have been shown to grow at temperatures as low as 4 °C (Holmes et al., 2004b).

The specific temperature may affect what bacteria are present in the anodic biofilms in wastewater fed systems. Changes in microbial communities in response to different treatment conditions and types of organic matter are being studied (Logan, 2009; Logan and Regan, 2006a; Xing et al., 2009). As yet there have been few direct connections between the types of microorganisms that predominate in these systems and power, except that various *Geobacter* species are often associated with higher power densities (Holmes et al., 2004a; Ishii et al., 2008). Thus, while bacterial growth rate and respiration can change with temperature (Madigan and Martinko, 2006), the community development and structure can also be important. In recent field tests, it was found that a 1000-L microbial electrolysis cell (MEC) reactor (Logan, 2010) had a long startup period when inoculated with wastewater and operated at relatively lower temperatures, compared to reactors typically operated in the laboratory at 20 °C or 30 °C (unpublished results). Therefore, it became important to better understand the effects of temperature on MFC startup and operational performance.

In this study, we examined MFC performance as a function of the initial temperature over a range of 4–30 °C. We compared system performance under these different initial temperatures with performance of systems started up at the same time under more optimal temperature of 30 °C which were then switched to operation at lower temperatures.

2. Materials and methods

2.1. MFC construction

MFCs were single-chamber, cube-shaped reactors having a cylindrical anode chamber 4 cm long and 3 cm in diameter as previously described (Liu and Logan, 2004). The anode was an ammonia gas treated graphite fiber brush (25 mm diameter × 25 mm length; fiber type PANEX 33 160K, ZOLTEK) (Logan et al., 2007). Carbon cloth cathodes (7 cm^2) contained a Pt catalyst (0.5 mg cm^{-2}) on the water facing side, and four polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side (Cheng et al., 2006).

2.2. Inoculation and operation

Reactors were inoculated with the solution from an MFC operated for over 1 year (initially inoculated from the effluent of the primary clarifier of the local wastewater treatment plant). After startup, the MFCs were operated in fed-batch mode using a phosphate buffer nutrient solution (PBS; conductivity of 7.8 mS/cm) containing 1 g/L acetate as the fuel (Cheng and Logan, 2007). Temperatures were set at 4 °C, 10 °C, 15 °C, 20 °C, and 30 °C during inoculation and operation using either a constant temperature room or an incubator (SHAKA4000-7, Thermo Scientific). In the case of the lower-temperature tests (4 °C and 10 °C), separate MFCs were also first inoculated and operated at 30 °C for 500 h before being tested at the lower temperature. Reactors were refilled each time

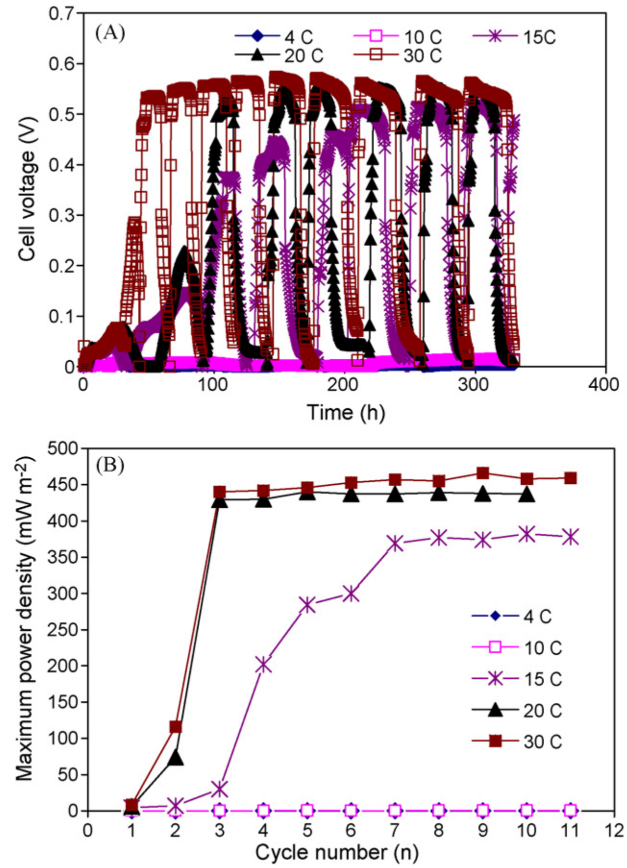

Fig. 1. Voltage generation of MFCs as (A) a function of time and (B) the maximum power density produced in each cycle during the startup period at different temperatures.

when the voltage decreased to <20 mV, forming one complete cycle of operation.

The polarization and power density curves were obtained by operating MFCs for 20 min at different fixed external circuit resistances (1000–50 Ω). Electrode potentials were measured using an Ag/AgCl reference electrode (RE-5B; BASi, West Lafayette, IN), with all potentials corrected and reported here versus a normal hydrogen electrode (NHE). CODs were measured using standard methods (APHA, 1998).

2.3. Calculations and measurements

Voltage (E) across the external resistor (1 kΩ, except as noted) was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current, power and coulombic efficiency (CE) were calculated as previously described (Logan et al., 2006), with the current density and power density normalized by the projected surface area of the cathode.

3. Results

3.1. Startup under different initial temperatures

At 30 °C, MFCs required only ~50 h (three cycles) before reaching maximum power production (Fig. 1). Cell voltages over subsequent cycles were then reproducible in terms of maximum voltage, with an average of 563 ± 6 mV. When the MFC was initially operated at 20 °C, the time required to reach the first maximum power cycle was still three cycles, but the time required

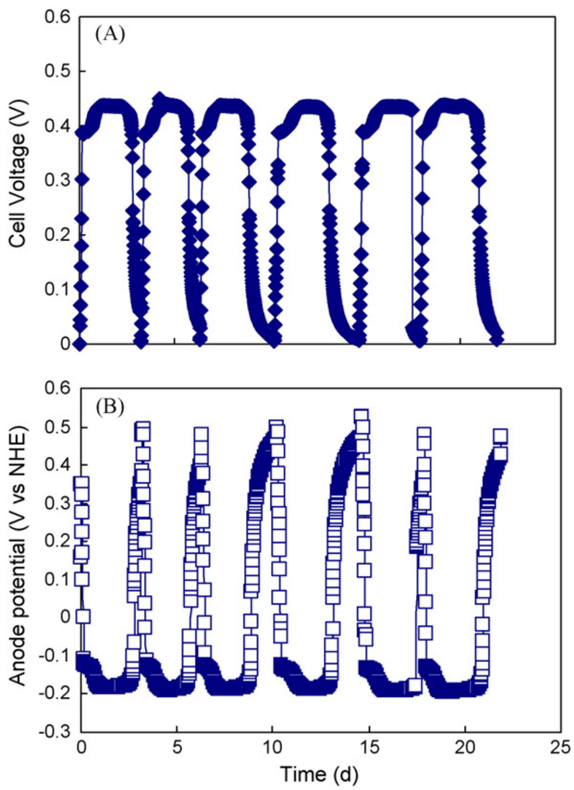

Fig. 2. (A) Cell voltage and (B) anode potential of MFCs operated at 4 °C after initial startup at 30 °C (1 kΩ fixed resistance).

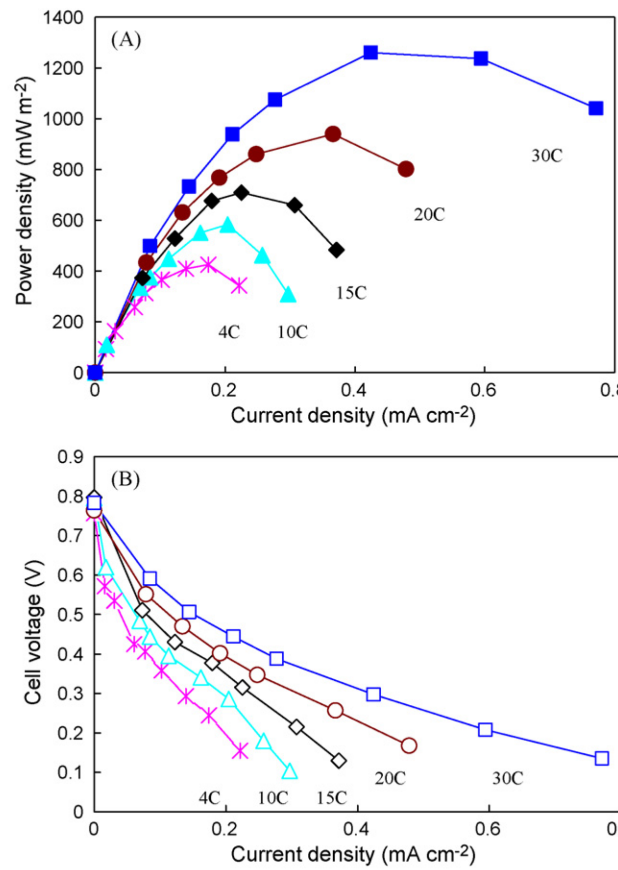

Fig. 3. (A) Polarization and (B) power densities of MFCs operated at different temperatures. MFCs for the two lower-temperature conditions (4 °C and 10 °C) were originally started up and operated at 30 °C before these tests.

increased to ∼110 h. The maximum voltage under these conditions was 545 ± 3 mV. Decreasing the initial temperature to 15 °C further increased the time for stable operation to ∼210 h and required seven cycles, and the maximum voltage was even lower at 512 ± 2 mV. MFCs initially operated at 10 °C and 4 °C did not show appreciable voltage (∼5 mV) even after 800 h (refueled 30 times).

3.2. Startup at a different higher temperature

When MFCs were initially operated at 30 °C, and the transferred to 4 °C or 10 °C, stable power generation was obtained at these lower temperatures. A maximum voltage of 425 ± 2 mV was obtained at 4 °C, while 484 ± 3 mV was produced at 10 °C. The anode potentials at both of these low temperatures paralleled the changes in cell voltage, with a minimum anode potential of −190 ± 2 mV at 4 °C (Fig. 2), and −232 ± 3 mV (data not shown) at 10 °C.

3.3. Overall performance

The performance of the reactors that were always operated at a fixed temperature (15–30 °C) and those first operated at 30 °C and then switched to the lower temperatures (4 °C and 10 °C) were examined in terms of polarization and power density curves, and CEs. The maximum power density of the MFC always operated at 30 °C was 1260 ± 10 mW m^{-2} (Fig. 3). Power densities decreased at lower temperatures, with 940 ± 6 mW m^{-2} at 20 °C and 709 ± 10 mW m^{-2} at 15 °C. Although the MFC initially operated at 4 °C did not produce any power, the MFC first acclimated at 30 °C and then switched to 4 °C produced 425 ± 10 mW m^{-2}, a power density about one-third of that at achieved at 30 °C.

The maximum power densities produced by these MFCs were inversely proportional to temperature, with a slope of 33 ± 4 mW m^{-2} °C^{-1} ($p < 0.001$) (Fig. 4). The decreased power density was due to both reduce performance of the anode and the cathode (Fig. 5). For example, at a current density of 0.145 mA cm^{-2}, reducing the operating temperature from 30 °C to 4 °C reduced anode performance as shown by an increase in the anode potential by 34% (from −268 mV to −177 mV). The cathode potential decreased by 37% (from 239 mV to 150 mV) over the same temperature range.

CEs generally increased as temperature decreased, except for the MFCs operated at 20 °C (Fig. 4) (1 kΩ). The CE was 17% at 30 °C, decreasing to CE = 15% at 20 °C. CEs increased to 22% at 15 °C, 26% at 10 °C, and 31% at 4 °C. The increased CEs resulted despite additional operation times at lower temperature (85 h at 4 °C versus 20 h at

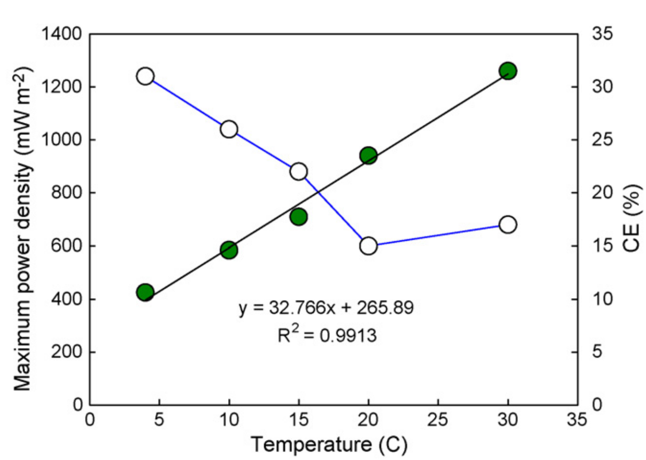

Fig. 4. Maximum power density (filled circles) and CE (open circles) as a function of operating temperature.

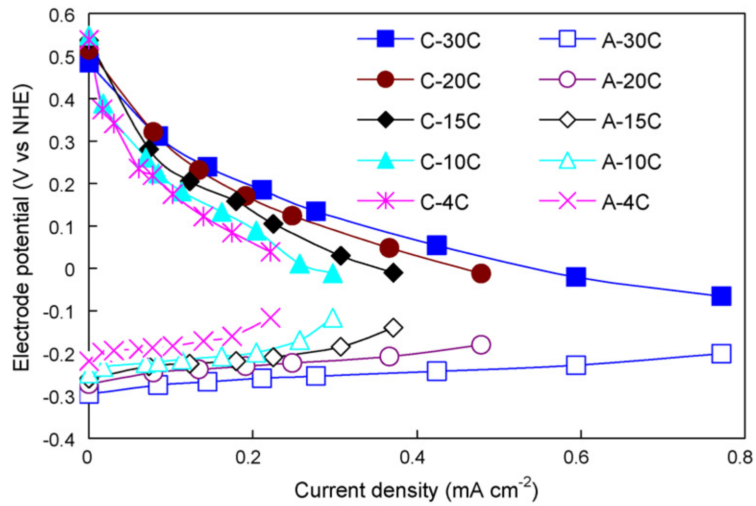

Fig. 5. Anode (open symbols) and cathode potentials (filled symbols) as function of current density at different temperatures.

4 °C). This indicates that in general less substrate was consumed by non-exoelectrogenic bacteria at lower temperatures than that at high temperatures. In all the experiments the COD removals were 92–95%.

4. Discussion

The initial operating temperature of an MFC was found to be important here in terms of the amount of time needed for startup, the maximum power generated, and it determined whether the system could reach stable power generation. We were able to achieve stable power production for initial operating temperatures between 15 °C and 30 °C. However, startup times were four times longer at 15 °C than at 30 °C. More importantly, we found that the MFCs started up at the lowest temperatures of 4 °C and 10 °C did not produce appreciable power even after very long operation times. This shows that the initial temperature will have an important impact on the initial formation of an exoelectrogenic biofilm. If reactors were first operated at a higher temperature of 30 °C, and then transferred to these lower temperatures, their performance was consistent based on trends in power generation at other temperatures. This shows that once formed, the bacteria were capable of functioning at different temperatures. Overall, we found that there was a linear relationship between operating temperature and the maximum power produced based on polarization data, with a change of $33 \pm 4\,\mathrm{mW\,m^{-2}\,{}^{\circ}C^{-1}}$. The linear relationship between operating temperature and the maximum power should aide in the development of biosensors as the response to temperature changes would be easily predicted.

A decrease in maximum power densities observed here is generally in agreement with that found in other studies, although the amount of this decrease is larger here than typically reported. For example, there was a 25% decrease in maximum power here (1260–940 $\mathrm{mW\,m^{-2}}$) for a decrease from 30 °C to 20 °C, compared to <10% obtained in three other studies (Liu et al., 2005). This difference could be due to lower power densities (<700 $\mathrm{mW\,m^{-2}}$), and therefore higher internal resistances, in these previous MFC tests compared to those achieved here. When the internal resistance is large, anode performance may be less important than other factors such as cathode performance. We observed here that both the anode and cathode performance affected power production (Fig. 5). If only anode performance was important we would have expected to see an optimum in power production at the optimum growth temperature of the bacteria. For example, Holmes et al. (2004b) found that two *Geobacteraceae* isolates from a marine sediment grew over a range of 4–30 °C, with an optimum growth rate of 22 °C. Here, we did not observe an optimum over the same temperature range but rather a continuous increase in power. Other factors may also be important that can affect cathode performance, such as reduced kinetics for rates of oxygen reduction at lower temperatures.

Factors other than temperature can also affect startup time. For example, ammonia treatment of carbon cloth anodes reduced the time and number of cycles needed to achieve reproducible cycles of power generation in an air-cathode MFC, and also increased the amount of power generated (Cheng and Logan, 2007). Heat treatment of graphite brushes at 450 °C has been found to reduce acclimation time (Feng et al., 2010). The use of a pre-acclimated cultures or pure cultures also reduces acclimation time, although the acclimation times vary between different types of reactors (Ishii et al., 2008; Watson and Logan, 2010).

CEs were also affected by the temperature. We found that they decreased from 17% to 15% when the temperature was decreased from 30 °C to 20 °C, with similar changes found by others. For example, when the temperature was decreased from 32 °C to 20 °C (Liu et al., 2005) found that CE decreased from 25% to 17% (fixed resistance of 1 kΩ), and Min et al. (2008) reported a decrease from 43% to 8%. Within this temperature range it may be that the CE is mainly influenced by cycle time and competition between exoelectrogenic bacteria reducing the anode compared to aerobic bacteria using oxygen diffusing through the cathode. However, at the lower temperatures (<20 °C) the exoelectrogenic bacteria may compete better for substrate with other microorganisms, thus increasing the CE. The CE measured at 4 °C was 82% larger than that at 30 °C (31% at 4 °C versus 17% at 30).

These results have important implications for application of MFCs for wastewater treatment. It is clear that MFCs can operate over a wide range of temperatures, but it is also evident that startup procedures can dictate system performance. Our results suggest that optimal startup of reactors requires wastewater temperatures of at least 15 °C. Furthermore, it may be desirable to heat the wastewater during startup in order to reduce acclimation times as reproducible power cycles took four times longer at 20 °C than at 30 °C. The use of higher water temperatures during startup may further aid in more rapid development of the exoelectrogenic population compared to other microorganisms. The lack of any appreciable current generation for reactors started up at 4 °C and 10 °C requires further study. Additional studies are needed to explore how initial temperatures might affect microbial community composition in these systems.

5. Conclusions

It was shown here that power generation by an MFC was greatly influenced by the set operating temperature. MFCs achieved reproducible power generation when initially operated at temperatures of 15 °C or higher, but the startup time to reach reproducible voltage output was significantly increased at lower temperatures. MFCs started at lower temperatures (4 °C or 10 °C) did not produce appreciable power unless they were first operated at 30 °C before being switched to the lower temperatures. For the MFCs that produced power at each temperature, the amount of power was proportional to the temperature, and the CE was inversely proportional to temperature. These results suggest that warm startup temperatures are a key factor in MFC performance.

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