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Effect of temperature change on power generation of microbial fuel cell

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Microbial fuel cell (MFC), which can directly generate electricity from biodegradable materials, has been receiving increasing attention. Effects of temperature change on power density, electrode potential, columbic efficiency, chemical oxygen demand removal and internal resistance in two chambers MFCs were examined in this paper. The maximum power density of 7.89 W/m^3 was achieved at 37 °C, with 199% higher at 10 °C (2.64 W/m^3), 24% higher at 30 °C (6.34 W/m^3) and 21% higher at 43 °C, no steady power generation was observed at 55 °C. Low temperature to 10 °C might have a huge effect on anode potential, especially at higher current, but increasing the temperature to 43 °C had a main effect on the cathode performance when the MFCs have been established at 37 °C. The internal resistance of MFC was about 29 Ω at 37 °C, and increased 62% and 303% when MFC switched to 30 °C and 10 °C. Similarly, internal resistance increased 48% at 43 °C. The effect of temperature on MFC performance was expressed by internal resistance, the higher the internal resistance of MFC, the lesser the power density obtained. The Columbic efficiencies were 8.65% at 30 °C, 8.53% at 37 °C, and 13.24% at 43 °C. These results demonstrate that MFCs can effectively be operated over a wide range of temperatures.

Keywords: temperature; microbial fuel cell; power generation

1. Introduction

In the recent years, microbial fuel cell (MFC), a new bioelectrochemical device to generate electricity from biodegradable materials, has attracted wide-ranging interest.[1,2] Similar to the conventional fuel cells, MFCs are basically composed of an anode, on which microorganisms are used as the catalyst instead of abiotic catalysts such as platinum or palladium, and a cathode is an oxidant reduced by receiving electrons and protons moving from the anode. The electrons move along an external electrical wire for generating power while protons transfer through a proton exchange membrane (PEM) for charge neutralization.[3–5] However, the power density of MFC is still low compared with the conventional fuel cell, further amplifying the power density remains one of the greater challenges for realizing the practical applications of MFC.

As well known, the anode chamber of MFCs have to be operated in anaerobic atmosphere, and are intimately related to anaerobic digestion when its used for wastewater treatment.[6] Hence, the influence of parameters affecting anaerobic digesters should be assessed. Temperature is an important parameter in anaerobic digester and the characteristics of reactor operated in different temperatures have been widely studied and reported.[7–9] Generally, there are two optima for anaerobic digestion: a smooth one at about 32–42 °C for mesophilic microorganisms and a sharp one at 48–55 °C for thermophilic microorganisms. Temperatures in the range of 40–45 °C belong to the inactivated region for both mesophilic and thermophilic microorganisms. Methanogenics are sensitive to rapid changes of temperature. Thermophilic methanogens are more temperature-sensitive than mesophilics. Even small variations in temperature cause a substantial decrease in activity. Therefore, the temperature should be kept exactly within a range of ±2 °C. As conventional anaerobic digesters, MFCs are strongly affected by temperature. However, the possibility that electrogenesis, and some of the microorganisms involved, might be less sensitive to temperature variations than methanogenesis. To some extent, this is an exciting field of study whose results would have potential application in areas with large temperature variations. Some researches have been done to study the effect of temperature on MFC performance (Table 1), but there is no systematic information regarding the influence of temperature change on steady-operation MFCs. Hence, it was of interest for MFC research to analyse the influence of temperature change on their behaviour.

In this study, the performance of MFC was examined as a function of temperature over a range of 10–55 °C, the MFC system was first started up at temperature of 37 °C, then switched to operate at different temperatures(10 °C, 30 °C, 43 °C and 55 °C).

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Table 1. Experimental results of previous work at different temperatures.

T °C	System	Fuel	Inoculum	Material		V_{max} (mV)	R_{int} (Ω)	P_{max} (mV/m^3)	Reference
				Anode	Cathode				
57	Thermophilic MFCs	Glucose	TC60	Graphite		387	9.25 ± 0.15	3.3–4.5^a	[10]
50	S-MFCs	Synthesis gas	sludge	Carbon felt	–	655	45	34	[11]
20	S-MFCs	Acetate	Wastewater	Carbon paper	-	–	200	660	[12]
32						-	-	720	
10	S-MFCs	Acetate	Sludge	Carbon cloth	-	530–554	72–112	3.02–4.84	[13]
20						561–563	68–115	3.18–4.29	
35						630–611	151–198	2.14–3014	
56	T-MFC	Acetate	Sludge	-	-	-	470	37	[14]
23	New S-MFCs	-	Model leachate	Carbon cloth		300	-	606 ± 57.5	[15]
35						290		479.6 ± 23.1	
23	S-MFCs					220		90.5 ± 23.1	
35						100		55.6 ± 4.7	
15	T-MFC	Acetate	Wastewater	Carbon paper		25	No successful operation		[16]
22						497 ± 6	1000	46^a	
30						537 ± 8	430	70^a	
4	S-MFCs	Acetate	Solution from an MFC	Graphite fibre brush	Carbon cloth	No successful operation			[17]
10									
15						512 ± 2	-	709 ± 10^a	
20						545 ± 3		940 ± 6^a	
30						563 ± 6		1260 ± 10^a	
15	S-MFCs	Sodium acetate	Sludge	Carbon fibre brush	Carbon cloth	500	362	260^a	[18]
25						540	212	591^a	

Notes: S-MFCs, single-chamber MFC; T-MFCs, two-chamber MFC; -, no reported.
[a]the units is mV/m^2.

2. Materials and methods

2.1. MFC construction

MFCs were two-chamber, rectangle-shaped reactors having equal volume and dimension (500 mL; 5.0 × 1.0 × 1.0 cm) as previously described.[19] Each compartment contained one piece of graphite plate (66 cm^2) as electrodes. The anode and cathode chambers were separated by a PEM (Nafion 117, Dupond, 10 × 10 cm). The membrane was pretreated by boiling in H_2O_2 (3%) and deionized water followed by 3–5% H_2SO_4 and deionized water, each for 2 h, and then stored in water prior to use. Titanium wires (0.5 mm diameter) were utilized as leads for both compartment electrodes. The wires were connected to an external resistance of 510 Ω during the MFC operation.

The sludge from river mud was used as an inoculum in the anode compartment of the MFC. Acetate (4 g/L) was used as an energy source in a medium amended with inorganic salt solution (12.8 g/L Na_2HPO_4, 3 g/L KH_2PO_4, 1.0 g/L NH_4Cl, 0.5 g/L NaCl). Potassium ferricyanide (50 mmol/L) was added into acthodeic compartment as the electron acceptor, and the same inorganic salt solution was used as the buffer solution (pH = 7.09).

2.2. MFC operation

All MFCs systems were operated in the fed-batch mode, 20% (V/V) of sludge was inoculated and 80% (V/V) influent solution was added. The MFCs were first operated at 37 °C for 96 d before being tested at lower temperature. When the stable operation was obtained, the operation temperatures were then switched to 10 °C, 30 °C, 43 °C and 55 °C. The temperature was increased from 43–55 °C with stepwise increments of 2 °C per day as done in the process of anaerobic digestion. Reactors were refilled each time when the voltage decreased to less than 100 mV, forming a complete cycle of operation.

2.3. Analytics and calculations

Cell voltages were measured across the external circuit containing a resistor using a multimeter. Current (I) was calculated as $I = U/R$, where $R(\Omega)$ is the external circuit resistance. Power (P) was calculated as $P = U^2/R$. The volumetric power density (W/m^3) was calculated based on the volume of chamber (500 mL). Polarization curves were obtained by changing the external resistor after leaving the reactor under open circuit potential for two hours, with each measurement taken under maximum power output conditions. The internal resistance, r, was calculated from the slope of the voltage–current graph according to $U = E - Ir$, where $E$was the electromotive force of the cell. Columbic efficiency (CE, the number of electron recovered as current in the reactor to the total electron stored in biomass) was calculated based on COD removal as previously described.[20] Ag/AgCl reference electrodes were placed into the anode and cathode compartments to determine individual electrode potentials. COD was determined by HACA-DR2700.

3. Results

3.1. Voltage of MFC under different temperatures

When MFCs were initially operated at 37 °C, and then switched to 10 °C, 30 °C and 43 °C, stable power generation was obtained at these temperatures (Figures 1 and 2). The maximum voltage of 660 ± 4 mV was obtained at 10 °C, 687 ± 22 mV at 30 °C, 672 ± 11 mV at 37 °C, and 665 ± 6 mV was produced at 43 °C. When the temperature of MFCs was increased to 55 °C, no appreciable voltage was obtained. Similar results were reported in previous studies. It was found that the MFCs started up at the temperatures of 4 °C and 10 °C did not produce appreciable power even after very long operation times, but if reactors were first operated at a higher temperature of 30 °C, and

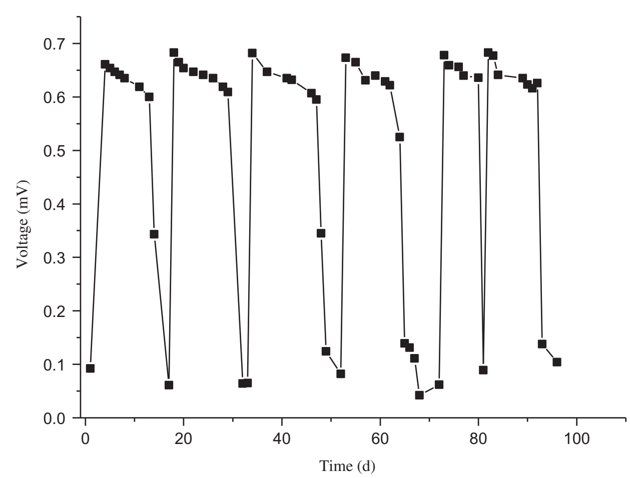

Figure 1. Volrage of MFCs at 37 °C.

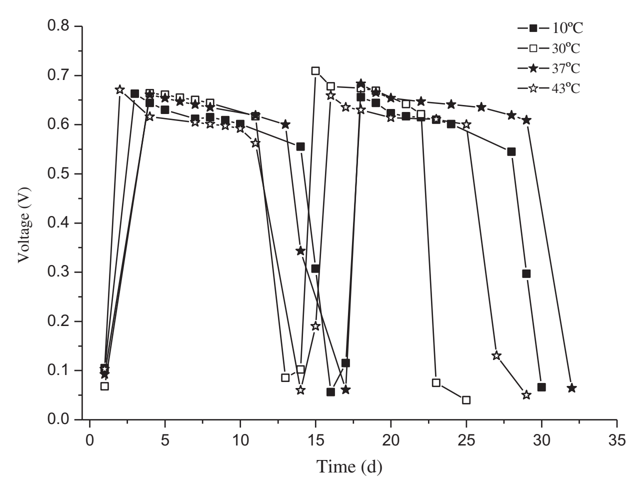

Figure 2. Variation of voltage with time under different temperature change.

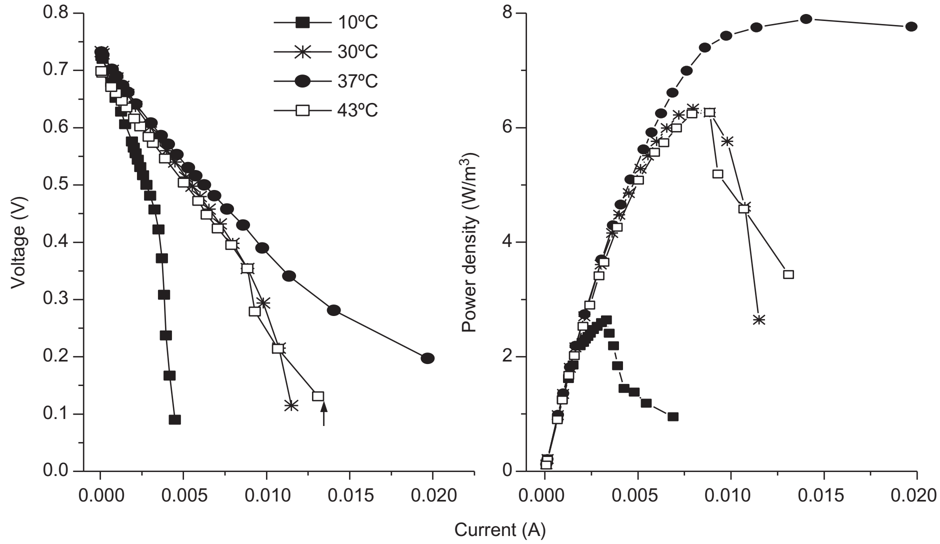

Figure 3. Voltage and Power density as a function of current under different temperature conditions.

then switched to these lower temperatures, the maximum voltages of 425 ± 2 mV (4 °C) and 484 ± 3 mV (10 °C) were obtained, respectively.[17] But the amount of maximum voltage is larger here than Cheng's observation. This difference could be due to the different construction of MFCs and electron acceptor. Previous studies found that using ferricyanide shows much greater power generation than those with oxygen due to the fact that there is little polarization of the cathode; therefore, the achieved cathode potential is quite close to that calculated for standard conditions, while oxygen is predicted to have a higher cathode potential than ferricyanide, in practice the potentials achieved using oxygen are much lower than theoretical values.[21,22] In two-chamber MFCs tests, Oh et al. [23] found that replacing the aqueous cathode using oxygen with ferricyanide increased the power output.

3.2. *Overall performance of MFC under different temperatures*

To evaluate the influence of temperature on performance of MFCs, the voltage and power densities as a function of current were examined by varying external resistance from 9000 to 10 Ω (Figure 3). The maximum power density of MFCs at 10 °C, 30 °C, 37 °C, and 43 °C were 2.64, 6.34, 7.89 and 6.26 W/m^3. Compared with 37 °C, power density of 30 °C reduced 24%, and continued decreasing by 199% at 10 °C. Likewise, power density of 43 °C reduced 21%. It was demonstrated that power density of MFCs was seriously affected by operation temperatures. The MFCs first established at 37 °C and then switched to 10 °C, a stable power generation was obtained, which was consistent with other studies. This showed that the bacteria were capable of functioning at different temperatures when the biofilm formed, and some of the bacteria involved might have higher tolerance to lower temperature.[6] Lower power density was obtained when the temperature was increased to 43 °C, this result was in disagreement with the findings of Behera et al.,[24] who found that maximum power density of 34.38 mW/m^2 was achieved at an operating temperature of 40 °C. There was no stable power generation observed when the MFC switched to 55 °C, this could be due to the composition of bacterial communities being different in mesophilic and thermophilic conditions. The dominant bacteria in the anode compartment of thermophilic MFCs was phylogenetically close to an uncultured clone.[25] *Shewanella putrefaciens*, *Geobacter sulfurreducens* and *Rhodoferax ferrireducens* were usually presented in MFCs operated in mesophilic condition.[25,26]

During the generation of the polarization curves, the values of the anode and cathode potential versus a standard Ag/AgCl reference electrode were also recorded (Figure 4). Decreasing the temperature from 43 °C to −30 °C, the

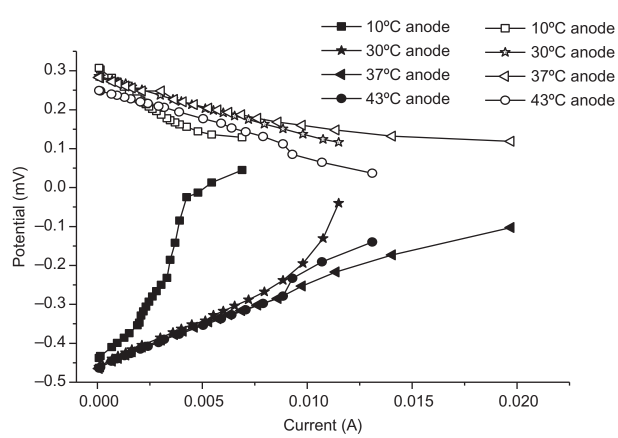

Figure 4. Anode and cathode potentials as function of current density at different temperature.

anode potential showed almost the same value over a current range of 0.076–7.2 mA, but at higher current (>7.2 mA) the higher anode potential was obtained at 30 °C. The cathode working potential of MFC operated at 30 °C was also comparable to that operated at 37 °C for current in the range of 0.076–11.5 mA. but the higher cathode potential was obtained at 37 °C at higher current (>11.5 mA). Further decreasing the temperature to 10 °C, both anode and cathode were affected, and led to a decrease in maximum power density. For example, at a current of 0.003 A, reducing the operating temperature from 37 ° to −10 °C reduced anode performance as shown by an increase in the anode potential by 36.22% (from −392 to −250 mV) and the cathode potential decreased by 16.66% (from 246 to 187 mV). And the higher anode potential was obtained at higher current, for example, at a current of 0.00392 A, anode potential increased by 76.96% (from −369 to −85 mV) and the cathode potential decreased by 26.36% (from 220 to 162 mV) when the operating temperature switched from 37 °C to −10 °C. It can be seen that lower temperature might have a huge effect on anode potential, especially at higher current. The anode open circuit voltages (OCV_{an}) of MFC at the temperature of 30 °C, 37 °C and 43 °C were similar to, but the OCV_{an} at 10 °C was only 447 mV. This suggested that the activity of microbial was partly inhibited, this is consistent with other studies,[27] it was the strategy of anodic community to acclimatize itself to environmental change and to gain more energy for vital activity under lower temperature. Lower cathode potential was found when the operated temperature switched to 43 °C. For example, at a current of 0.003 A, anode potential reduced by 0.51% (from −392 to −398 mV) and the cathode potential decreased by 15.73% (from 248 to 209 mV). Thus, increasing temperature to 43 °C had a main effect on the cathode performance.

The internal resistances of MFC were about 117 Ω at 10 °C, 47 Ω at 30 °C, 29 Ω at 37 °C and 43 Ω at 43 °C, respectively (Figure 5). Internal resistances determined by linear regression were associated with high values of coefficient of determination in the range 0.989-0.996, i.e. the regressions were significant. Compared with 37 °C, internal resistance of 30 °C increased to 62%, and continued to increase by 303% at 10 °C. Similar result was found at 43 °C with the internal resistance increased to 48%. This implied that the effect of temperature on MFC performance was expressed by the internal resistance of the cell, the higher the internal resistance of MFC, the less the power density obtained. As shown in Figure 4, the relevance between operating temperature and the maximum power density could be well fitted by: $Y = -1.66825 + 0.49581X - 0.00704X^2 (R^2 = 0.922)$. Cheng et al. found that power production increased linearly in the range of 4–30 °C. This difference could be due to the operating was temperature, 10 °C, 30 °C, 37 °C, 43, and 55 °C used in these experiments, while it was 4–30 °C for Cheng et al.

The CEs and COD removal rate at the different temperature was calculated and listed in Figure 6. In all experiments, the COD removals were 94–99%. The CEs were 8.65% at 30 °C, 8.53% at 37 °C, and 13.24% at 43 °C. Similar results were reported by previous studies. Liu et al. [12] found that CE decreased from 25% to 17% when the temperature was decreased from 32 °C to 20 °C, and Cheng et al. [17] reported a decrease from 17% to 15%. Higher COD removal rate was accompanied by lower coulombic efficiencies, similar results were reported by other researchers. These results could be explained by several effects. First, the open-style chamber was used for cathode, and oxygen diffusion through the PEM was mostly caused by part of PEM directly contacted with air. Feng et al. [28] thought that the low CEs result in part due to substrate depletion by aerobic bacteria sustained by oxygen transfer through the cathode. Second, due to the consumption of the easily degradable carbon source by co-existent methanogenic and anodophilic microorganisms.[29]

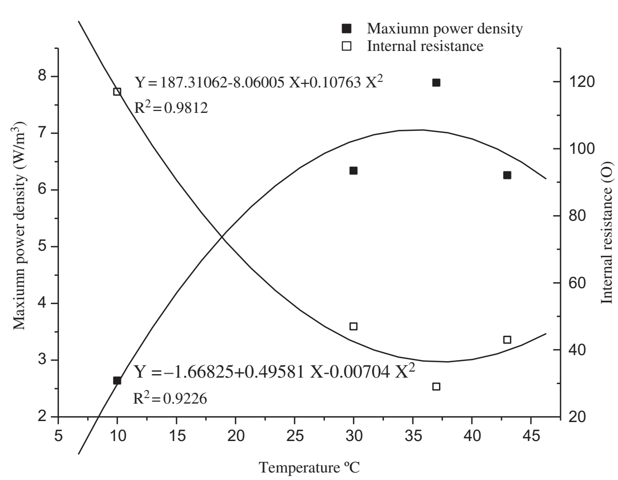

Figure 5. Maximum power density and internal resistance as a function of operating temperature.

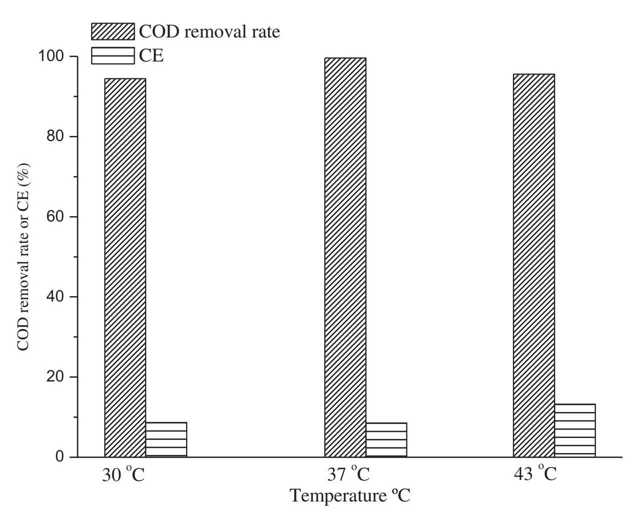

Figure 6. variety of COD removal rate and coulombic efficiency with different temperature.

4. Conclusion

It was shown that power generation of MFC was greatly influenced by the operating temperature. Electricity can be generated by MFC in temperature ranges from 10 °C to 43 °C, but no steady power generation was observed at 55 °C. When the temperature increased from 10 °C to 33 °C, the power density increased from 2.64 to 6.34 W/m^3 accordingly. Further raising temperature to 43 °C, the power density decreased to 6.26 W/m^3. The effect of temperature on MFC performance was expressed by the internal resistance of the cell, the higher the internal resistance of MFC, the lesser the power density obtained.

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