Scale-up of membrane-free single-chamber microbial fuel cells

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Abstract

Scale-up of microbial fuel cells (MFCs) will require a better understanding of the effects of reactor architecture and operation mode on volumetric power densities. We compared the performance of a smaller MFC (SMFC, 28 mL) with a larger MFC (LMFC, 520 mL) in fed-batch mode. The SMFC produced 14 W m⁻³, consistent with previous reports for this reactor with an electrode spacing of 4 cm. The LMFC produced 16 W m⁻³, resulting from the lower average electrode spacing (2.6 cm) and the higher anode surface area per volume (150 m² m⁻³ vs. 25 m² m⁻³ for the SMFC). The effect of the larger anode surface area on power was shown to be relatively insignificant by adding graphite granules or using graphite fiber brushes in the LMFC anode chamber. Although the granules and graphite brushes increased the surface area by factors of 6 and 56, respectively, the maximum power density in the LMFC was only increased by 8% and 4%. In contrast, increasing the ionic strength of the LMFC from 100 to 300 mM using NaCl increased the power density by 25% to 20 W m⁻³. When the LMFC was operated in continuous flow mode, a maximum power density of 22 W m⁻³ was generated at a hydraulic retention time of 11.3 h. Although a thick biofilm was developed on the cathode surface in this reactor, the cathode potentials were not significantly affected at current densities <1.0 mA cm⁻². These results demonstrate that power output can be maintained during reactor scale-up; increasing the anode surface area and biofilm formation on the cathode do not greatly affect reactor performance, and that electrode spacing is a key design factor in maximizing power generation.

Keywords: Microbial fuel cell; Scale-up; Single chamber; Membrane free

1. Introduction

Microbial fuel cells (MFCs) use microorganisms as catalysts to directly generate electricity from organic matter. MFCs have great potential as a method of wastewater treatment and as power sources for autonomous sensors [1–5]. Extensive recent studies have led to a better understanding of the electron transfer mechanisms between cells and surfaces [6–8], and have shown several factors that can affect MFC performance, including: electrode materials [9–11], solution chemistry [12,13] and reactor configuration [14–17].

Scale-up is an important issue for the application of MFCs, especially in the field of wastewater treatment, but there is little information available on the effects of scaling on power output. There have been a few tests of power generation with relatively large, two-chamber systems (~1 L) and a ferricyanide catholyte [16,17], but such systems are not sustainable due to the need to chemically regenerate ferricyanide. Air-cathode MFCs hold a greater promise for practical applications due to their simple configuration, sustainable operation, and relatively high power densities [1,14]. The liquid volumes of many air-cathode MFCs, however, have been relatively small (tens of mL). Although an air-cathode MFC of 1.5 L was developed [18], the maximum volumetric power density of 2 W m⁻³ was up to three orders of magnitude lower than smaller air-cathode MFCs [15,19,20]. MFCs can be stacked together in series or in parallel to achieve higher voltage or current [21–23]. However, stacking multiple MFCs together in series can result in problems, such as voltage reversal, contact voltage losses, and erratic operation [21]. Producing larger MFCs can alter electrode spacing, and thus affect power density through changes in the area-specific internal resistance. In small air-cathode MFCs, electrode
spacing and anode surface area have been shown to affect power output [24]. More information is needed on how these key design factors affect reactor performance as reactor size is increased.

In this study, we constructed and operated a larger MFC (LMFC) with a relatively higher anode surface area and reduced electrode spacing, and compared its performance to a similar but smaller MFC (SMFC). To better understand the effects of anode spacing and surface area on performance, we altered the electrode orientation and examined the effect of additional surface area by adding graphite granules or using graphite fiber brushes as the anode.

2. Materials and methods

2.1. Larger MFCs

The LMFC was constructed from Plexiglas (15 cm × 15 cm × 7 cm). This MFC contained five equally spaced baffles (12.7 cm × 4.3 cm × 0.6 cm) glued to the bottom of the reactor, forming six channels. Each baffle had a slot (0.25 cm × 14.5 cm, 0.25 cm from the top edge) and a hole (d = 1 cm, 1 cm to the side edge) to allow the anode and water to go through the reactor. The anode was a single piece of carbon cloth (non-wet-proofing; Type A, E-Tek, USA) with a total surface area of 757 cm² (146 m² m⁻³). The cloth was placed onto one side of the chamber wall, across the bottom of each channel and around each baffle (through the slots to avoid the contact with cathode), and then held to the surface using small plastic screws (Fig. 1). The carbon cloth cathode (161 cm², 0.35 mg cm⁻² Pt; 30% wet-proofing, E-Tek) was coated with four diffusion layers to reduce water loss as previously described [9]. The cathode was covered with a thick plate of Plexiglas containing holes (1.3 cm diameter) to allow oxygen diffusion to its surface and to hold the cathode against the chamber. The average electrode spacing was 2.6 cm (range of 0.5–4.3 cm). Strips of anode and cathode carbon cloth were left to extend outside the reactor to allow connection of the electrode to the circuit using alligator clips.

To further investigate the effect of surface area, graphite granules (300 g) were added to the anode chamber of the LMFC. The addition of graphite granules with particle diameters of 2–6 mm (Graphite Sales, Inc., Chagrin Falls, OH) increased the total anode surface area to 4500 cm² (870 m² m⁻³), assuming specific surface area $A = \frac{6 \theta d}{d}$ [25] for $d = 4$ mm, and $\theta = 0.53$, but decreased the liquid volume to 280 mL. Cloth (Pledge cloth; S.C. Johnson & Son, Inc., USA) was placed between the granules and the cathode to avoid short-circuiting of the electrodes. In another set of test, the baffles were removed and four graphite fiber brushes (5 cm in diameter and 7 cm long) with an average fiber diameter of 7.2 μm (PANEX33 160K, Zoltek) were used as the anode, increasing the total anode surface area to 42,200 cm² (7680 m² m⁻³) [26]. The brushes were placed horizontally in the chamber, with the titanium core protruding through a hole on the reactor side. The four electrodes were connected with titanium wire. The electrode spacing, defined as that from the brush center to the side of the cathode, was 3.3 cm.

2.2. Smaller MFCs

Single-chamber SMFCs were constructed as previously reported with a 28 mL liquid volume and a 4 cm electrode spacing of the two electrodes oriented in parallel to each other [14]. The anode surface area per volume, $A_s$, was 25 m² m⁻³. The effect of anode orientation was examined by placing the anode perpendicular to that of the cathode, at a distance of 1–4 cm from the cathode, producing an average electrode spacing of 2.5 cm. Since the carbon cloth was too soft to be fixed in a perpendicular orientation to the cathode in an SMFC, we conducted our perpendicular anode tests using carbon paper anodes (plain toray carbon paper, 7 cm², no wet-proofing; E-Tek, USA). Cathodes were made of carbon cloth (7 cm²; 0.5 mg cm⁻² Pt; 10% of Pt/C catalyst; 30% wet-proofing; E-Tek, USA).

2.3. MFC operation

The MFCs were inoculated using domestic wastewater and a nutrient medium amended with sodium acetate (1 g L⁻¹) as previously reported [4]. After replacing this solution twice over 2 days, the system was then operated using only the nutrient medium and acetate (ionic strength, IS = 100 mM). The system was considered to be operating under steady conditions when the voltage output was reproducible after refilling the reactor with medium at least two times. Stable power output was normally achieved in 2–3 batches (about 1–2 days per batch). Polarization curves were obtained by measuring the stable power generated.
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at various external resistances. For each resistance, the fuel cells ran for at least two complete batch cycles to guarantee a stable and sustainable voltage. In some tests using the LMFC, the IS was increased to 300 mM using NaCl.

The LMFC was also operated in continuous flow mode at a flow rate of 35–130 mL h\(^{-1}\) using a feed containing 800 mg L\(^{-1}\) acetate in nutrient medium. The theoretical retention time was calculated from the volume of the medium and the flow rate into the reactor. The actual hydraulic retention time (HRT) was determined by spiking the feed line with a KCl solution, and measuring the conductivity of the reactor effluent, as previously described [27,28].

2.4. Analysis and calculations

Voltage (\(V\)) was measured using a multimeter with a data acquisition system (2700, Keithley, USA), and used to calculate the power (\(P\)) according to \(P = IV\). Power was normalized by the cross-sectional area (projected) of the cathode or reactor volume. The internal resistance of the cell, \(R_{\text{int}}\), was calculated from the slope of plots of \(V\) and \(I\) using

\[
V = E_{\text{cell}} - IR
\]

where \(E_{\text{cell}}\) is the electromotive force of the cell [1].

Cathode potentials, either new or containing a biofilm (i.e. from an MFC operated for 3 months), were measured at different current densities by chronopotentiometry using a PC4/750 potentiostat (Gamry Instruments) and a three-chambered electrochemical cell [9]. One chamber of the three-chambered cell was used for the reference electrode, while the other two chambers housed the counter (anode) and working (cathode) electrodes. The catalyst-coated side of the cathode was placed facing the solution with the other side exposed directly to air [9]. All reported potentials were therefore given as measured (based on Ag/AgCl; +198 mV vs. standard hydrogen electrode).

The current–potential characteristics of cathode (with biofilm and without biofilm) were fitted using

\[
E = A \ln i + B
\]

where \(E\) (mV) is the cathode potential, \(i\) (mA cm\(^{-2}\)) is the current density of the cathode, \(A\) is the slope of the line, and \(B\) (mV) is the cathode potential at 1 mA cm\(^{-2}\). This equation is a variation of the Tafel equation, which is commonly used in describing the overvoltage at the electrode surface in chemical fuel cells [29].

3. Results

3.1. LMFC performance

The maximum power density generated by the LMFC containing a cloth electrode was 16 W m\(^{-3}\) (520 mW m\(^{-2}\)-cathode area) at a current density of 0.18 mA cm\(^{-2}\), which was slightly higher than that (14 W m\(^{-3}\)) of the SMFC (Fig. 2). Based on the slope of the polarization curve, the larger system had an internal resistance of \(R_{\text{int}} = 9.4 \Omega\) (Fig. 3). The Coulombic efficiency of the LMFC ranged from 38 to 52%, with an overall energy recovery of 8–12%. A low Coulombic efficiency is consistent with that found in previous studies, and could be due to bacterial growth, loss of substrate sustained by aerobic growth using oxygen that diffused through the cathode, and other non-electricity generating processes such as methanogenesis, denitrification and sulfate reduction [14].

3.2. Effect of anode surface area on power generation

To investigate that if increasing the anode surface area would affect power generation, we added graphite granules or used graphite brushes as the anode which increased the overall surface areas by factors of 6 and 56, respectively. A maximum power density of 17 W m\(^{-3}\) (560 mW m\(^{-2}\)) was obtained with granules and 15 W m\(^{-3}\) (490 mW m\(^{-2}\)) with brushes when the MFCs were operated in batch mode. Both are similar to the 16 W m\(^{-3}\) obtained with only the carbon cloth anode (Fig. 2). This demonstrated that further increasing anode surface area had a negligible effect on power generation, and that the cathode was the limiting electrode as a result of its significantly smaller surface area in the LMFC.
3.3. Effect of solution ionic strength

The performance was improved to 20 W m\(^{-3}\) (630 mW m\(^{-2}\)) (Fig. 2) at current density of 0.26 mA cm\(^{-2}\) when the solution IS was increased from 100 to 300 mM as a result of the decreased internal resistance \((R_{\text{int}} = 7.3 \Omega)\) (Fig. 3). Thus, ionic strength had a greater impact on power generation than anode surface area.

3.4. Effect of anode orientation on power generation of the SMFC

The LMFC had part of the anode oriented perpendicular to that of the cathode, and part oriented parallel. To investigate whether the relative anode orientation would affect the power output, we examined power output using the SMFC with anodes oriented in parallel and perpendicular to the cathode. The maximum power density of the SMFC with electrodes placed parallel to each other was 14 W m\(^{-3}\). When the electrode was placed perpendicular to the cathode, the power increased by 36% to 19 W m\(^{-3}\) mainly due to the reduced electrode spacing (4 cm vs. 2.5 cm) (Fig. 4). Future research is needed to investigate how the electrode orientation affects the power output with the same electrode spacing.

3.5. Continuous flow operation (LMFC)

The performance of the LMFC was further evaluated by switching the reactor from batch feeding to continuous flow mode (IS = 100 mM). The power density and acetate removal were found to be a function of HRT (fixed external resistance of 4 \(\Omega\)) (Fig. 5). Power density increased from 17 W m\(^{-3}\) at 4.1 h, to a maximum 22 W m\(^{-3}\) (695 mW m\(^{-2}\)) at 11.3 h, and then decreased to 20 W m\(^{-3}\) when HRT further increased to 16 h. The lower power density generated at 4.1 h than that at 11.3 h was possibly due to the relatively higher oxygen concentration in the cell because the influent contained dissolved oxygen (\(\approx 8 \text{mg L}^{-1}\) at 30°C). The substrate concentration in this range should not affect the maximum power generation. The decrease in power generation at a longer retention time of 16 h was possibly due to the decrease of substrate concentration and a reduction in cell metabolism since the acetate removal increased from 52% at a HRT = 4.1 h to a maximum of 90% at a HRT of 16 h (Fig. 5). The fouling of the electrodes caused by cell decay or death at a longer HRT might also contribute to a reduction in MFC performance. These results show that power generation can be increased by continuous flow, rather than fed-batch operation, by optimizing HRT.

3.6. Effect of biofilm on cathode performance

During operation of the LMFC, a thick biofilm was developed on the cathode even after only 1 week of operation. To determine if this biofilm affected cathode performance, we compared the current–potential characteristics of a new cathode to that of a biofilm-covered cathode using an electrochemical cell. The cathode potential as a function of current density was well described using Eq. (2) with constants of \(A_c = -94.8 \text{ mV}\) and \(B_c = -176 \text{ mV} (R^2 = 0.9932)\) for the cathode without a biofilm, and \(A_c = -99.6 \text{ mV}\) and \(B_c = -201 \text{ mV} (R^2 = 0.9938)\) for the cathode with a biofilm (Fig. 6). The difference between the values of \(A_c\) for cathodes with/without biofilm is very small, indicating charge transfer kinetics were not significantly affected by the formation of the biofilm. The cathode potentials were not significantly affected by the biofilm over the current density range examined (0–1.0 mA cm\(^{-2}\)), although the potentials for cathode with a biofilm were slightly lowered than those without a biofilm (Fig. 6). Possible reasons for the decreased potential...
in the presence of the biofilm include decreased proton mass transfer to the cathode surface, reduced availability of oxygen at the cathode surface due to oxygen utilization by aerobic bacteria, and possible deactivation of the Pt catalyst by bacteria or chemicals produced by the bacteria.

4. Discussion

The scale-up of MFCs can lead to changes in volumetric power density depending on what factors are kept constant or altered as reactor size is changed [30]. In experiments by others, the power density (10 W m$^{-3}$) of a small MFC (0.025 cm$^3$) was much higher than that (0.6 W m$^{-3}$) of a very similar but larger MFC (5 cm$^3$) [30]. The changes in power density during scale-up result from changes in many important factors, such as electrode spacing and electrode specific surface area (surface area per volume). Power density can be maintained or even increased during scale-up if these factors, especially electrode spacing, are considered and optimized during scale-up. As shown here, the power density increased by $\sim$15% in spite of a $\sim$20× increase in volume.

4.1. Electrode spacing

Electrode spacing and orientation was found here to be the key factor that affected the area-specific internal resistance and power density. Therefore, to maintain the power density during scale-up, the larger reactor architecture must maintain or even reduce the electrode spacing. It was previously shown that power density was increased when the anode and cathode spacing was decreased from 4 to 2 cm [24]. In our study here, the reduction in average electrode spacing (2.6 cm in the LMFC vs. 4 cm in the SMFC) accounted for most of the 15% increase in power density. The importance of electrode spacing on power density was further evidenced by altering the electrode orientations in the SMFC. A 36% increase in power density was obtained when the electrode orientation was altered from parallel to perpendicular, which was mainly due to the reduced electrode spacing (4 cm vs. 2.5 cm). While further decreases in electrode spacing can result in even smaller internal resistance, too close an electrode spacing can limit performance. Cheng et al. [24] reported a 50% decrease in surface power density in air-cathode MFC when the electrode spacing was reduced from 2 to 1 cm due to oxygen diffusion into the anode chamber. However, volumetric power densities can be maintained or even increased by adding a cloth separator and reducing the spacing between the electrodes [15]. Reduced electrode spacing and the use of cloth separators need to be explored further for their relative advantages in larger MFCs.

4.2. Specific electrode surface area

Specific electrode surface area can also be an important factor in reactor performance. It has been found in one study that increasing the anode surface area relative to the cathode can increase power [26]. Increasing the anode surface area here from 25 m$^2$ m$^{-3}$ (SMFC) to 150 m$^2$ m$^{-3}$ (LMFC), however, only resulted in a slight increase in power density from 14 to 16 W m$^{-3}$. The power density increased by only an additional 6% when the specific anode surface area was increased to 870 m$^2$ m$^{-3}$ by adding graphite granules, indicating that the anode surface area did not limit the performance of the LMFC at high anode/cathode surface area ratios. On the other hand, increasing the specific cathode surface area can greatly improve the MFC performance [31]. Future research is needed to reduce cathode limitations on power output through enlarging the cathode surface area, such as using tubular systems [32] and/or developing new catalysts and cathode structures.

4.3. Ionic strength

The power was increased by 25% when the IS was increased from 100 to 300 mM. This increase is not as large as that found in our previous tests (66%) possibly due to the different architectures of the two MFCs and the fact that the LMFC had a smaller average electrode spacing and lower area-specific internal resistance. We previously found that there was little improvement in power generation when the IS was increased from 100 to 400 mM if the internal resistance was reduced by decreasing the electrode spacing from 4 to 2 cm [24]. The reduced electrode spacing from 4 to 2.6 cm in this study decreased the electrolyte internal resistance, lessening the importance of IS to the total internal resistance.

4.4. Other factors limiting the LMFC performance

Compared to power densities generated in other membrane-free air-cathode MFCs, the maximum power generated in this LMFC is 22 W m$^{-3}$, which is 69% higher than the 13 W m$^{-3}$ previously obtained using an SMFC containing equally sized carbon paper anode and cathodes with an electrode spacing of 4 cm [12]. However, it is lower than the 30 W m$^{-3}$ obtained using an SMFC (14 mL) with an electrode spacing of 2 cm [12], and 51 W m$^{-3}$ produced by advective flow through the anode of an SMFC (14 mL) with a 1 cm electrode spacing [24]. There are several factors that contribute to the lower power generation in the larger system tested here than in these other studies. First, the increased electrode surface area in the larger MFC increased the distance electrons travel from the point of generation on the anode to the location that they exit to the external circuit (i.e. where the wire connects to the anode). This distance is not a significant factor in the performance of an SMFC with a surface area of 7 cm$^2$ since the electrode resistance is negligible in comparison to the external resistance (100–200 $\Omega$) for maximum power. However, in the LMFC, the maximum power output occurred at an external resistance smaller than 10 $\Omega$, and therefore a small increase in electrode resistance could greatly increase power loss. Second, contact resistance between the current collecting points (electrode strips) and clips (connected to the external circuit) may have become significant due to the increased current output in the LMFC. Considering the low internal resistance (<10 $\Omega$) of the LMFC, the voltage drop caused by the contact resistance cannot be neglected. Third, while the cover on the cathode had holes drilled to allow oxygen trans-
fer to the electrode, some of the surface area was obscured by the cover plate, perhaps limiting cathode performance. It will be necessary to continue to address these design factors in future scale-up designs. For example, a collector plate could be used to reduce the electron travel distance and contact resistance.

5. Conclusions

The performance of a SMFC (28 mL) was compared with a newly designed LMFC (520 mL) in fed-batch mode. The power density increased by about 15% from 14 W m$^{-3}$ (SMFC) to 16 W m$^{-3}$ (LMFC) in spite of the increase in volume by a factor of nearly 20, mainly as a result of the lower average electrode spacing and higher anode surface area per volume of the LMFC. The effect of the larger anode surface area on power was shown to be relatively insignificant by adding graphite granules or graphite fiber brushes to the LMFC anode chamber. Thus, it was concluded that the cathode was the electrode limiting power generation as a result of its significantly smaller surface area.

Increasing the ionic strength of the LMFC from 100 to 300 mM increased the power density to 20 W m$^{-3}$. When the LMFC was operated at continuous mode, a maximum power density of 22 W m$^{-3}$ was generated at an HRT of 11.3 h. Although a thick biofilm was developed on the cathode surface in this reactor, the cathode potentials were not significantly affected at current densities <1.0 mA cm$^{-2}$. These results demonstrate that power output can be maintained or even increased during reactor scale-up if these factors, especially electrode spacing, are considered and optimized during scale-up.

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