Controlling the occurrence of power overshoot by adapting microbial fuel cells to high anode potentials

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**Abstract**

Power density curves for microbial fuel cells (MFCs) often show power overshoot, resulting in inaccurate estimation of MFC performance at high current densities. The reasons for power overshoot are not well understood, but biofilm acclimation and development are known factors. In order to better explore the reasons for power overshoot, exoelectrogenic biofilms were developed at four different anode potentials (−0.46 V, −0.24 V, 0 V, and 0.50 V vs. Ag/AgCl), and then the properties of the biofilms were examined using polarization tests and cyclic voltammetry (CV). The maximum power density of the MFCs was 1200 ± 100 mW/m². Power overshoot was observed in MFCs incubated at −0.46 V, but not those acclimated at more positive potentials, indicating that bacterial activity was significantly influenced by the anode acclimation potential. CV results further indicated that power overshoot of MFCs incubated at the lowest anode potential was associated with a decreasing electroactivity of the anodic biofilm in the high potential region, which resulted from a lack of sufficient electron transfer components to shuttle electrons at rates needed for these more positive potentials.

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1. Introduction

Microbial fuel cells (MFCs), that use bacteria to convert organic matter into electrical current, are being investigated for energy recovery from wastewaters and waste biomass sources. The amount of power that can be produced in a MFC is typically estimated from polarization data obtained under non-steady conditions using linear sweep voltammetry, or by using different resistances in the circuit for specification data obtained under non-steady conditions using linear sweep

could be eliminated [11,12]. It was suggested that the main reason was an increase of the anode potential to values outside the range of the midpoint potentials of respiratory enzymes. However, this could not definitively be proven using the approach of changing resistances because this method simultaneously affects both current and anode potential. Consequently, power overshoot could have been due to the inability of the biofilm to produce higher current densities, or to an inability of a biofilm to respond to the elevated anode potentials.

In order to more effectively operate MFCs, the importance of the current density versus the potential for producing power overshoot needs to be more conclusively established. This can be done by direct potentiostatic control of electrode potentials. The anode potential affects biofilm development, and this approach of varying the anode potentials has been used to optimize power generation in many different types of bioelectrochemical systems [13]. Microorganisms can obtain different amounts of energy from respiration using alternative electron acceptors, and can respond differently to changes in set anode potentials [13–18]. For example, *Geobacter sulfurreducens* can express different outer membrane cytochromes at anode potentials of 0.1 V and 0.6 V vs. Ag/AgCl [19].

To better understand the reasons for power overshoot in MFCs, the influences of anode potentials on the electroactivity of anodic biofilm were investigated in this study. MFCs were operated at four different set anode potentials (−0.46 V, −0.24 V, 0 V, 0.50 V vs. Ag/AgCl), and then were examined using polarization tests and cyclic voltammetry in order to determine the factors that contributed to power overshoot.

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2. Experimental

2.1. MFC reactor construction and operation

Many different types of MFCs have been developed, but here the MFCs consisted of a cylindrical chamber 4 cm long by 3 cm in diameter (empty bed volume of 28 mL), constructed from a solid cube of Lexan, and they did not contain a membrane. The anode was a carbon fiber brush (2.5 cm diameter, 2.5 cm length, 4.9 cm² projected area relative to the cathode, and 0.22 m² total fiber surface area) which was heat treated at 450 °C for 30 min before use [20]. The air cathode (projected surface area of 7 cm²) was made from carbon cloth with four PTFE diffusion layers and a 0.5 mg·Pt·cm⁻² catalyst layer [21]. The brush anode was placed horizontally in the center of the chamber, and the air cathode was placed vertically in the same chamber with the catalyst coating facing the solution. The center of the anode to the surface of the cathode was 2.5 cm, and the distance between the tip of the fiber brush anode and the cathode was 1.25 cm. An Ag/AgCl electrode (BASI), located between the anode and the cathode (1 cm to cathode and ~0.5 cm to anode), was used as the reference electrode. All potentials were reported here vs. Ag/AgCl electrode (+210 mV vs. a standard hydrogen electrode).

MFCs were inoculated using 14 mL of primary clarifier effluent collected from the Pennsylvania State University wastewater treatment plant, and 14 mL of growth medium. The growth medium contained (per L): 1 g sodium acetate (except as indicated), 4.28 g Na₂HPO₄, 2.45 g NaH₂PO₄·H₂O, 0.31 g NH₄Cl, 0.13 g KCl, 12.5 mL minerals, and 5 mL vitamins [22]. Then, the MFCs were acclimated at different anode potentials (−0.46 V, −0.24 V, 0 V, and 0.5 V vs. Ag/AgCl) set using a potentiostat (BioLogic, VMP3) in a temperature controlled room (30 °C). Currents were recorded using EC-Lab V10.02 software at 10 minute intervals. Once current was generated in the reactor, only growth medium (28 mL) was used to feed the reactors, with the medium refreshed every day (dechlorinated). Currents for clarity.

After acclimation for 1 month at set potentials, the reactors had reproducible cycles of current generation. Polarization and power densities would be 1860 ± 40 mW/m² (anode projected area) and 42 ± 0.1 mW/m² (anode area). The MFCs acclimated to the most negative anode potential of −0.46 V had slightly higher maximum power densities than the other reactors. This was due to the higher electroactivity of the biofilms at low potentials (from −0.50 V to −0.30 V) over the scanned potential range (−0.50 V to −0.20 V), as indicated by the black box in Fig. 2B). However, power overshoot occurred due to decreasing electroactivity in high potential region (−0.30 V to −0.20 V, indicated by black dashed lines in Fig. 2A and B). Once power overshoot occurred, the power densities produced were much lower than those produced by reactors acclimated to higher anode potentials.

CVs showed that the electroactivity of biofilms at high potentials, based on current, was enhanced by acclimation to higher potentials, with maximum CV currents of 3.54 ± 1.16 mA (−0.46 V), 9.38 ± 0.68 mA (−0.24 V), 11.06 ± 1.56 mA (0 V), and 11.35 ± 1.76 mA (0.50 V) (Fig. 2C). DCVs (Fig. 2D) showed that the anodic biofilms of the MFCs incubated at higher potentials exhibited increasing electroactivity (I’ > 0) over a broader anode potential range, suggesting that bacteria expressed more electron transfer components (ETCs) in order to function at these higher potentials and obtain more energy [16,19]. ETCs are broadly defined here as organic or inorganic compounds used to convey electrons to a perturbation amplitude of 10 mV. The frequency was varied from 10³ to 0.01 Hz.

3. Results and discussion

3.1. Performance of MFCs at different anode potentials

After 1 month of operation, the reactors exhibited reproducible cycles of current generation. The maximum current (I_max) during a single cycle generally increased with set potential, with values of 1.06 ± 0.24 mA (−0.46 V), 7.65 ± 0.48 mA (−0.24 V), 10.34 ± 1.15 mA (0 V), and 10.18 ± 1.32 mA (0.50 V) (Fig. 1). At the two highest potentials, the I_max was similar. The increases in current could be due to more energy captured by the bacteria at the higher potentials. The lack of an increase in current at the highest potential of 0.50 V is consistent with that reported by others [15], who also found no increase in current at 0.40 V vs. SHE.

Power density and polarization curves obtained using LSV (Fig. 2A and B) showed that these MFCs could produce maximum power densities of 1300 ± 25 mW/m² (−0.46 V), 1150 ± 20 mW/m² (−0.24 V), 1220 ± 60 mW/m² (0 V), and 1000 ± 50 mW/m² (0.50 V), relative to the projected cathode area. Power densities are different by a factor of 1.43 when normalized to the anode projected area, and to 0.0032 based on actual anode area (all fibers). For example, for the case of the MFC acclimated to −0.46 V, power densities would be 1860 ± 40 mW/m² (anode projected area) and 42 ± 0.1 mW/m² (anode area). The MFCs acclimated to the most negative anode potential of −0.46 V had slightly higher maximum power densities than the other reactors. This was due to the higher electroactivity of the biofilms at low potentials (from −0.50 V to −0.30 V) over the scanned potential range (−0.50 V to −0.20 V, as indicated by the black box in Fig. 2B). However, power overshoot occurred due to decreasing electroactivity in high potential region (−0.30 V to −0.20 V, indicated by black dashed lines in Fig. 2A and B). Once power overshoot occurred, the power densities produced were much lower than those produced by reactors acclimated to higher anode potentials.

Scans started at an initial anode potential (E) of −0.7 V to a final potential of either +0.1 V or +0.5 V at a rate of 1 mV/s. First derivative CV (DCV) was obtained from CV data by plotting the slope of each CV data point against the anode potential (E). The slope was calculated using a central difference quotient (I = dI/dE, mA/V).

Electrochemical impedance spectroscopy (EIS) was performed while maintaining a direct voltage between the anode of the MFCs and the Ag/AgCl reference electrode (potentiostatic EIS) with a
final electron acceptor, and thus ETCs include components internal or external to the cell, and they can be cell-associated or dispersed in solution. The locations of the ETCs are not critical to our CV analysis, only their ability at rates needed to convey electrons from the oxidation of substrate to the anode.

For the MFC incubated at $-0.46$ V, the narrow width of the DCV scans suggests that the expressed ETCs functioned optimally over a relatively narrow potential range of about $-0.50$ V to $-0.30$ V. Decreasing electroactivity of anodic biofilm (indicated by black dashed lines in Fig. 2C and D) was observed above $-0.30$ V for the MFC acclimated at $-0.46$ V, in a manner consistent with insufficient levels of ETCs to accommodate an increased rate of electron transfer at higher potentials. MFCs cultivated at $-0.24$ V, 0 V and 0.50 V showed increased currents at the higher potentials over the LSV scan range (about $-0.50$ V to $-0.20$ V, as indicated by the black box in Fig. 2C and D), suggesting these biofilms possessed sufficient ETCs to enable increased current at the higher electrode potentials. Thus, it appears that the power overshoot shown by the MFC acclimated at $-0.46$ V was a result of the insufficient electroactivity of the anodic biofilm at higher potentials, likely due to insufficient ETCs. This lack of sufficient ETCs could be due to low biomass, differences in the microbial communities, or the use of different electron transfer pathways.

3.2. Changes of bacterial electroactivity with anode potentials

In order to further explore the influence of anode potentials on the electroactivity of the anodic biofilm and power overshoot, additional experiments were performed by acclimation of the biofilms at a different potential. For example, the anode potential of the MFC initially acclimated at 0.50 V was changed to a set potential of $-0.46$ V, and then it was returned to 0.50 V and monitored for an additional 7 days (Fig. 3). When the anode potential was lowered to $-0.46$ V, the current immediately decreased from 10.18±1.32 mA to 0.81±0.36 mA. When the anode potential returned to 0.50 V, the current increased initially to 5.10±0.95 mA, and then four more days were needed for it to fully recover to the original current (11.16±0.41 mA). The same effect was observed by switching the other reactors acclimated to one potential to another potential. Thus, these results demonstrated that the electroactivity of anodic biofilm was significantly altered by a change in the anode potentials. A lower anode potential both decreased the current and altered the ability for higher current generation at higher anode potentials.

No power overshoot was observed in power density curves for the MFC incubated at 0.50 V, or after 5 days of acclimation at $-0.46$ V (Fig. 4A and B). However, after 15 or 24 days acclimation at $-0.46$ V, power overshoot was observed. When the MFC was returned to 0.50 V, power overshoot was not observed after just 1 day of acclimation at this higher potential.

The CVs (Fig. 4C) and DCVs (Fig. 4D) clearly indicated the changes in bacterial electroactivity over this 25-day period. The peak current in the CVs gradually decreased from 13.32 mA to 3.05 mA over time.
as the anode became acclimated to $-0.46 \text{ V}$. The range of potentials that showed increasing electroactivity ($I^\prime > 0$) narrowed from $-0.50$ to $-0.17 \text{ V}$ to $-0.50 \text{ V} - 0.27 \text{ V}$ after 24 days at $-0.46 \text{ V}$. These results showed that the bacterial activity changed, and now there was reduced activity of the bacteria at higher potentials. Thus, power overshoot was observed. The potentials where overshoot occurred are shown with a black dashed line in Fig. 4, and a black box is used to show the potential range measured in polarization tests (approximately $-0.50 \text{ V}$ to $-0.2 \text{ V}$). When the MFC was re-acclimated at $0.50 \text{ V}$, rapid restoration in the activity of the biofilm at high potentials was confirmed based on the increase in the CV peak currents from $3.05 \text{ mA}$ to $8.12 \text{ mA}$, and a broader range of increasing electroactivity over potentials of $-0.50 \text{ V} - -0.07 \text{ V}$ after 1 day.

### 3.3. Rate-limiting processes on anodic biofilms

The decrease in bacterial activity when the biofilm acclimated at a lower potential is scanned to higher potentials, could arise from substrate limitations (external factor) or electron transfer limitations (internal factor). EIS was used to study changes in the impedance of the anodic biofilms incubated at $-0.46 \text{ V}$ (Fig. 5A), set temporarily to a range of potentials associated with power overshoot based on CV and polarization data ($-0.3$ to $-0.1 \text{ V}$). Duplicates showed nearly identical results, so only one of the duplicates was shown here for presentation clarity. The data were fitted with an equivalent circuit model ($R_1 + \text{CPE}_1/R_1 + \text{CPE}_2/R_2$, inset in Fig. 5A). $R_1$ represents the solution resistance. $R_1$ and $R_2$ are defined as two charge transfer resistances. Constant phase elements ($\text{CPE}_1$ and $\text{CPE}_2$) were used to model nonideal capacitors. $Z_{\text{CPE}} = 1/\omega^{n}Q/Q_{(\text{soc})}$, where $Q$ has a dimension of $F \cdot s^{-1}$, and $n$ is a dimensionless parameter accounting for non-ideal behavior. The fitting results are listed in Table 1. The charge transfer resistance ($R_1$, based on the size of the first EIS arc) was similar (about 2.5 $\Omega$) at these potentials. Additionally, similar EIS arcs were also observed in control experiments without biofilms (Fig. 5B), which indicated that this process is not associated with electron transfer in biofilms. The second charge transfer resistance ($R_2$, based on the size of the second EIS arc) decreased when set potentials were increased from $-0.3 \text{ V}$ to $-0.25 \text{ V}$, but it then increased with a change in potential from $-0.20 \text{ V}$ to $-0.10 \text{ V}$. This result is in agreement with previous studies [3,7,10] that internal resistance increased in the range of potentials where power overshoot occurred.

In order to investigate if substrate concentrations were too low to maintain current at the higher current densities, the characteristics of the anodic biofilms incubated at $-0.46 \text{ V}$ were examined using CV by changing the sodium acetate concentration (Fig. 6A). When the sodium acetate concentration was below 2.44 mM, the CV peak current increased with increasing substrate concentration, which indicated that substrate concentration could affect current generation only at acetate concentrations below 2.44 mM. At higher acetate concentrations (above 2.44 mM), the CV peak current did not increase with substrate concentration, consistent with prior studies [23–25] that also showed a saturation in current at around 1.22 to 2.44 mM acetate. These results suggested that substrate concentration would not limit current generation at acetate concentrations of 12.19 mM that were used in this study.

In order to test whether the current generation was limited by electron transfer in the biofilms, we examined whether measured peak currents using CV ($I_p$) were consistent with Michaelis–Menten kinetics (Eq. (1)):

$$I_p = \frac{I_{\text{max}}[\text{NaAc}]}{K_m + [\text{NaAc}]}$$

where $[\text{NaAc}]$ is the substrate (sodium acetate) concentration, $I_{\text{max}}$ is the maximum current generated, and $K_m$ is the substrate concentration at which the current is half of $I_{\text{max}}$. The good agreement between the data and this model (Fig. 6B) supports our above findings that electron transfer in the biofilm, due to lack of sufficient ETCs, limited the current generation at high potentials when the acetate...
concentration was high as 12.19 mM. From these results, we infer that biofilms acclimated to higher potentials expressed more ETCs to enable higher current densities at higher potential. The limited currents at high potentials produced by biofilms incubated at lower potentials were therefore due to an insufficient pool of ETCs to accommodate the higher rates of electron transfer as the potential was increased. As internal resistance increased due to a lack of necessary ETCs at the higher potentials, power overshoot occurred.

4. Conclusions

Bacterial activity was significantly influenced by acclimation anode potentials. The current of MFCs increased from 0.82 mA to 11.5 mA with set anode potential from $-0.46$ V to $0$ V, and no further increase was observed at 0.50 V. The maximum power densities of the MFCs ranged from 1000 to 1300 mW/m². The MFCs incubated at $-0.46$ V had a higher maximum power density than those acclimated to more positive potentials due to the higher electroactivity at low potentials, but they exhibited increasing electroactivity over a narrow potential range from about $-0.50$ V to $-0.30$ V, which resulted in decreased current densities and power overshoot at higher potentials. It is concluded that power overshoot occurs at higher potentials due to a lack of necessary ETCs (both internal and external), but these limitations at higher current densities can be overcome through proper acclimation of the biofilm to higher potentials.

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Table 1

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<th>Potentials vs. Ag/AgCl (V)</th>
<th>$R_s$ (Ω)</th>
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<th>$n_1$</th>
<th>$R_1$ (Ω)</th>
<th>$Q_2$ (F s⁻¹)</th>
<th>$n_2$</th>
<th>$R_2$ (Ω)</th>
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Fig. 5. Electrochemical impedance spectroscopy of (A) reactors acclimated to $-0.46$ V, and (B) a control reactor without a biofilm, in the frequency range of $10^3$ Hz to 0.01 Hz, with anode potentials temporarily set at potentials of (a) $-0.30$ V, (b) $-0.25$ V, (c) $-0.20$ V, (d) $-0.15$ V, and (e) $-0.10$ V. Insets are the equivalent circuit, and the black frame shows an expanded region of the spectra.

Fig. 6. (A) Cyclic voltammograms of MFC incubated at $-0.46$ V at sodium acetate concentrations of (a) 0 mM, (b) 0.61 mM, (c) 1.22 mM, (d) 2.44 mM, (e) 6.10 mM, and (f) 12.19 mM, and (B) CV peak current $I_p$/mA is presented as a function of sodium acetate concentration [NaAc]/mM. Solid circles are the experimental results, and the solid line is the best fitting results: $I_p = 5.5[\text{NaAc}]/(0.6 + [\text{NaAc}])$. 

References


