



# Analysis of polarization methods for elimination of power overshoot in microbial fuel cells

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## ABSTRACT

Polarization curves from microbial fuel cells (MFCs) often show an unexpectedly large drop in voltage with increased current densities, leading to a phenomenon in the power density curve referred to as “power overshoot”. Linear sweep voltammetry (LSV,  $1 \text{ mV s}^{-1}$ ) and variable external resistances (at fixed intervals of 20 min) over a single fed-batch cycle in an MFC both resulted in power overshoot in power density curves due to anode potentials. Increasing the anode enrichment time from 30 days to 100 days did not eliminate overshoot, suggesting that insufficient enrichment of the anode biofilm was not the primary cause. Running the reactor at a fixed resistance for a full fed-batch cycle (~1 to 2 days), however, completely eliminated the overshoot in the power density curve. These results show that long times at a fixed resistance are needed to stabilize current generation by bacteria in MFCs, and that even relatively slow LSV scan rates and long times between switching circuit loads during a fed-batch cycle may produce inaccurate polarization and power density results for these biological systems.

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## 1. Introduction

Much of the research involving the use of microbial fuel cells (MFC) for combined electricity production and wastewater treatment is focused on producing the most power through improved reactor designs [1]. However, estimates of the amount of power that can be produced in an MFC are a function of the technique used to obtain polarization data. Linear sweep voltammetry (LSV) is commonly used in MFC studies to obtain polarization data, but high scan rates can overestimate power production [2]. An alternate approach is to vary the circuit resistance at fixed time intervals, ranging from 10 s to 24 h [3,4]. There have been few studies comparing the different techniques, but in one study it was found that power production with scan rates higher than  $0.1 \text{ mV s}^{-1}$  produced higher power densities than those where the circuit resistance was varied [2].

A common problem often encountered when evaluating polarization curves is “power overshoot” [2,5–7]. Power overshoot refers to the response of the system at high current densities (past the maximum power) in a power density curve where the cell voltage and current drop very quickly resulting in a doubling back of the power density curve, producing lower power than previously measured for the lower current densities [7]. One hypothesis on the cause of this power overshoot is that as the current resistance is decreased the bacteria on the anode are unable to produce sufficient current at

lower voltages [7]. However, there does not seem to be a correlation in the literature between the magnitude of current density and power curve shape.

Accurate methods are needed to ensure that power densities reported by different researchers reflect the true performance of the MFC. So far there has been no study on how different polarization techniques might affect the development of power overshoot or methods to eliminate it. We therefore examined MFCs that exhibited power overshoot when analyzed using common LSV and fixed resistances methods, and showed that power overshoot could be eliminated by allowing sufficient time for the biofilm to adjust to a change in resistance by using a single fixed resistance for each separate fed-batch cycle.

## 2. Experimental procedures

### 2.1. MFC reactor construction and operation

Cube-shaped MFCs with a cylindrical chamber (28 mL,  $7 \text{ cm}^2$  cross section) were constructed without a membrane as previously described [8]. The brush anode was constructed from carbon fibers (PANEX®33 160 K, ZOLTEK) wound into a titanium wire core (2.5 cm diameter, 2.5 cm length,  $0.22 \text{ m}^2$  surface area) which was heat treated at  $450 \text{ }^\circ\text{C}$  [9] and placed horizontally in the center of the chamber. Air cathodes (projected surface area of  $7 \text{ cm}^2$ ) were made from carbon cloth (30 wt.% wet proofing polymer, #B1B30WP, BASF Corp.) with four PTFE diffusion layers and  $0.5 \text{ mg-Pt cm}^{-2}$  [10]. The electrode spacing was 2.5 cm (center of the anode to the face of the cathode).

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Seven MFCs were inoculated using effluent from another MFC operated under similar conditions (50% v/v inoculum and medium) [3] at 30 °C in a controlled-climate room, and were covered to exclude light. The medium was a 100 mM phosphate buffer solution (PBS) containing ( $\text{g L}^{-1}$ ): 9.125  $\text{Na}_2\text{HPO}_4$ , 4.904  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , 0.31  $\text{NH}_4\text{Cl}$ , and 0.13  $\text{KCl}$ ; pH 7, vitamins and minerals [11]; and  $1 \text{ g L}^{-1}$  sodium acetate. The electrodes were connected through a  $1000 \Omega$  resistor, except as noted. Once an MFC produced  $\geq 100 \text{ mV}$  at  $1000 \Omega$ , no additional inoculum was added to the medium over subsequent fed-batch cycles. MFCs were considered enriched and ready for testing once they achieved the same maximum voltage for three consecutive batch cycles [3].

## 2.2. Analysis

The voltage across the resistor was recorded every 30 min using a multimeter data acquisition system (model 2700 Keithley Instruments, Cleveland, OH). Polarization was performed once the voltage stabilized after the MFC was fed. Polarization curves were obtained by three different methods. In the first method (single-cycle), conducted on days 30 and 100, various external resistances (OCV, 1000, 500, 250, 100, 75, 50, and  $25 \Omega$ , except where noted) were connected across the MFC, with each resistance being connected for 20 min and the voltage recorded using a digital multimeter (Model 83 III, Fluke) over a single batch cycle [12]. For the second method (multiple-cycle), conducted after 100 days, the maximum sustainable voltage over the cycle (typically sustained for 7 to 30 h depending on the total length of the cycle) was recorded using a single resistor over a complete fed-batch cycle [12]. Each resistance was tested for three consecutive cycles to ensure that the voltage response was unchanged with successive cycles. The third method, linear sweep voltammetry (LSV), was run after the multiple-cycle method. LSVs were run three times at the recommended scan rate of  $1 \text{ mV s}^{-1}$  over a range of 0.5 V starting from the measured open circuit voltage [13]. For the applied resistance methods, current density was calculated from  $I = E/R$ , where  $I$  is the current,  $E$  the measured voltage, and  $R$  the external resistance, and normalized to the projected cathode surface area. Power densities were calculated using  $P = IE$ , and normalized by the projected cathode surface area [13].

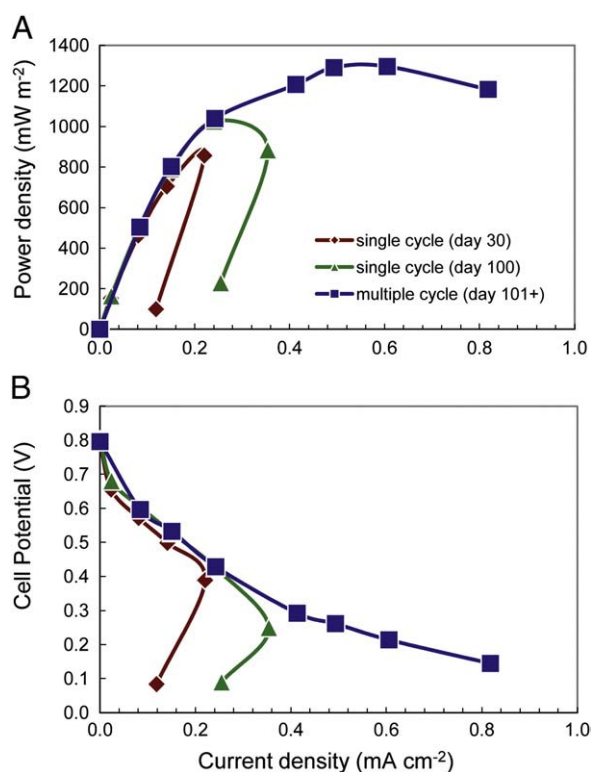
## 3. Results

### 3.1. Polarization by varied resistance, single-cycle method

Polarization curves obtained using the single-cycle method (20 min intervals) exhibited a steep drop in voltage at higher current densities resulting in power overshoot occurrences in power density curves. In an example power density curve (Fig. 1), for the 30 day test the MFC produced a maximum power of  $856 \text{ mW m}^{-2}$  ( $0.22 \text{ mA cm}^{-2}$ ) before the power rapidly decreased. The measured electrode potentials indicate that the anode potential was responsible for power overshoot. At the point of overshoot, the anode potential rapidly became more positive (from  $-0.354 \text{ V}$  to  $+0.022 \text{ V}$ ) and the current decreased while the cathode potential returned to a value consistent with that previously measured at that current (Fig. 2). Not all reactors tested exhibited power overshoot, and therefore additional tests were conducted to further investigate this phenomenon.

To rule out substrate depletion at the end of the polarization cycle as the cause of the power overshoot, each MFC was refilled with fresh medium, left to stabilize at  $1000 \Omega$  (30 min to 1 h) and polarization testing was started at a lower resistance ( $500 \Omega$  instead of OCV). The same rapid increase in anode potential was still observed under these new starting conditions ( $-0.341 \text{ V}$  to  $0.034 \text{ V}$ ) at the same resistances (from  $250 \Omega$  to  $100 \Omega$ ).

In order to see if the overshoot was caused by incomplete enrichment of the anode with biofilm, the MFCs were maintained

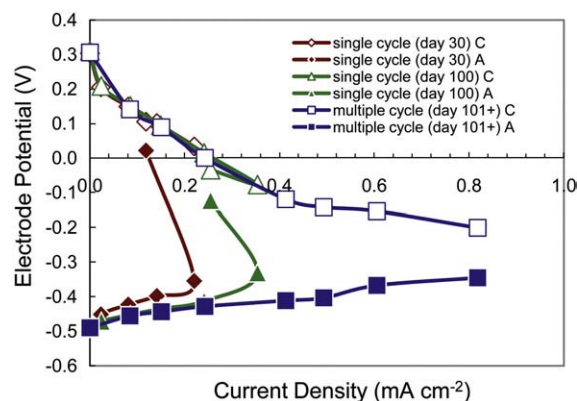


**Fig. 1.** (A) Power density and (B) polarization curves for single-cycle (20 min) resistance changes at 30 days ( $\diamond$ ) and 100 days ( $\triangle$ ) and multiple-cycle resistance changes ( $\square$ ).

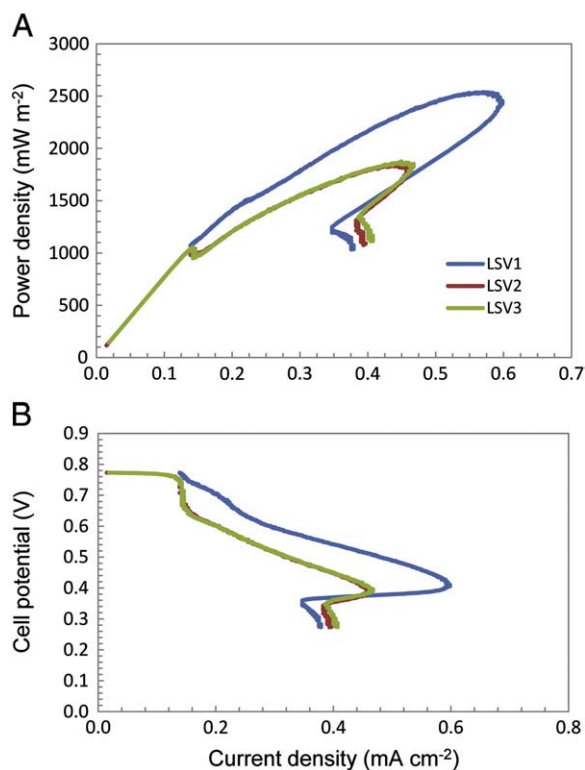
over repeated fed-batch cycles for another 70 days. After 100 days of operation, polarization curves still exhibited power overshoot using the 20 min single-cycle method (Fig. 1) ( $1027 \text{ mW m}^{-2}$ ,  $0.24 \text{ mA cm}^{-2}$ ). As before, the anode potential dropped off when changing resistance from  $250 \Omega$  to  $100 \Omega$  (Fig. 2).

### 3.2. Polarization by varied resistance, multiple-cycle method

Polarization data using the multiple-cycle method (a separate resistor for each fed-batch cycle), conducted after 100 days, produced power density curves without overshoot. At low current densities, the power curve followed that obtained using the single-cycle (20 min) method, but at the point where the other curves dropped off, the multiple-cycle curve extended to a higher power density ( $1296 \text{ mW m}^{-2}$ ) with increased current production ( $0.61 \text{ mA cm}^{-2}$ )



**Fig. 2.** Electrode (A = anode and C = cathode) potential measurements (vs. Ag/AgCl) during cell polarization for single-cycle (20 min) resistance changes at 30 days ( $\diamond$ ) and 100 days ( $\triangle$ ) and multiple-cycle resistance changes ( $\square$ ).



**Fig. 3.** (A) Power density and (B) polarization curves from LSV at  $1 \text{ mV s}^{-1}$  for three consecutive scans.

(Fig. 1). The anode potential did not undergo a rapid increase during the multiple-cycle method as it did when measuring current after 20 min in the single-cycle method (Fig. 2).

The fed-batch cycle curves resembled those reported previously [8], where the cell voltage increases rapidly (over a few hours) after the reactor is fed, and then stabilizes for most of the cycle. Polarization data were obtained during this stable voltage period. Only one full cycle is needed at each different resistance for the multiple-cycle method. Power production over three consecutive cycles at the same applied resistance did not show any noticeable change in maximum voltage from the first cycle to the third cycle (data not shown).

### 3.3. Polarization by LSV

Power density curves obtained using LSV (following the above multiple-cycle results) also exhibited power overshoot as shown by a doubling back of the power density curve (Fig. 3). The maximum power recorded for cycle 1 ( $2530 \text{ mW m}^{-2}$ ,  $0.56 \text{ mA cm}^{-2}$ ) was higher than for cycle 2 ( $1840 \text{ mW m}^{-2}$ ,  $0.44 \text{ mA cm}^{-2}$ ) and cycle 3 ( $1860 \text{ mW m}^{-2}$ ,  $0.44 \text{ mA cm}^{-2}$ ). In addition, there was another type of power overshoot in that the maximum power densities in three of the LSV curves were much higher than power densities measured by the applied resistance methods. Also, none of the LSV cycles measured power at current densities as high as was those measured using the multiple-cycle method.

## 4. Discussion

Power overshoot was observed in power density curves obtained using the single-cycle (20 min intervals) and LSV ( $1 \text{ mV s}^{-1}$ ) methods even with MFCs enriched for 100 days or more. However, power density curves obtained using the multiple-cycle method did not exhibit overshoot even at current densities up to  $0.82 \text{ mA cm}^{-2}$ .

The overshoot resulted from a rapid increase in the anode potential as resistance to current flow was decreased, indicating electron transfer limitation at the anode. The limitation was most likely related to a slow response from the microbes to adjust to the new resistance [7]. When the biofilm was given sufficient time to adjust to a set resistance by fixing the resistance over an entire cycle (multiple-cycle method), the biofilm produced increased currents at lower voltages. Since the maximum cell potential did not change during 3 cycles at the same resistance, the improved performance using the multiple-cycle method was not a consequence of the long-term enrichment of the anode community. Instead, these results showed that the biofilm needed much more time to adapt to the applied resistance than could be obtained in brief intervals at fixed resistances. Additional data in our laboratory has shown that even 1-hr intervals or slower LSV scan rates do not eliminate overshoot. For fed-batch MFCs, longer time periods are problematic as the series of resistances needed to produce a polarization curve cannot be obtained over the whole cycle due to depletion of the substrate. Thus, it is recommended that the full cycle (or in other cases at least a day or more) be used at a fixed resistance when obtaining polarization data in MFCs that exhibit overshoot.

It was also observed that the maximum power produced in a single-cycle polarization curve was less than that produced in a multiple-cycle curve. Thus, power would be underestimated as a result of reporting data where power overshoot occurs. A full polarization curve should be obtained in order to see if overshoot is present. Maximum power densities obtained by LSV were all higher than that obtained using either of the resistance methods, consistent with previous studies [2].

Our results show that it is important to use a reliable and consistent method for measuring maximum current densities in MFCs in order to obtain valid results concerning maximum power densities. If overshoot occurs, it may not be possible to properly compare maximum power from different MFC studies or different conditions within the same study. For fed-batch MFCs, the use of multiple cycles of data, each at different fixed resistances, offers the best method to obtain polarization data for producing power curves representative of performance during steady operation conditions.

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