

The overshoot phenomenon as a function of internal resistance in microbial fuel cells

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Keywords: Microbial fuel cell, Overshoot, Polarisation, Conductivity, Power curve

Abstract

A method for assessing the performance of microbial fuel cells (MFCs) is the polarisation sweep where different external resistances are applied at set intervals (sample rates). The resulting power curves often exhibit an overshoot where both power and current decrease concomitantly. To investigate these phenomena, small-scale (1 mL volume) MFCs operated in continuous flow were subjected to polarisation sweeps under various conditions. At shorter sample rates the overshoot was more exaggerated and power generation was overestimated; sampling at 30 s produced 23% higher maximum power than at 3 min. MFCs with an immature anodic biofilm (5 days) exhibited a double overshoot effect, which disappeared after a sufficient adjustment period (5 weeks). Mature MFCs were subject to overshoot when the anode was fed weak (1 mM acetate) feedstock with low conductivity ($<100 \mu\text{S}$) but not when fed with a higher concentration (20 mM acetate) feedstock with high conductivity ($>1500 \mu\text{S}$). MFCs developed in a pH neutral environment produced overshoot after the anode had been exposed to acidic (pH 3) conditions for 24 h. In contrast, changes to the cathode both in terms of pH and varying catholyte conductivity, although affecting power output did not result in overshoot, suggesting that this is an anodic phenomenon.

1. Introduction

Secondary wastewater treatment processes currently employ the biological activities of complex microbial biofilms to remove organic pollutants. Microbial fuel cells (MFCs) are able to capture the electrons produced during microbial processes to generate electricity and therefore offer the promise of a new sustainable source of energy, particularly for the wastewater industry. Despite significant advances in the understanding and performance of MFCs in recent years, there are still unanswered questions before the technology can be scaled up. One tool for assessing such confines is the polarisation sweep where different external resistances are applied to the MFC at set intervals (sample rates). As the applied

external resistance becomes lower (i.e. the load gets ‘heavier’) there is a greater electron demand requiring that the microbial consortium increase metabolic activity thus improving power and treatment efficiency. As long as this is approximately at the point of maximum power transfer (MPT) it will also be sustainable. If however the performance is pushed beyond this critical parameter then power output becomes non-sustainable.

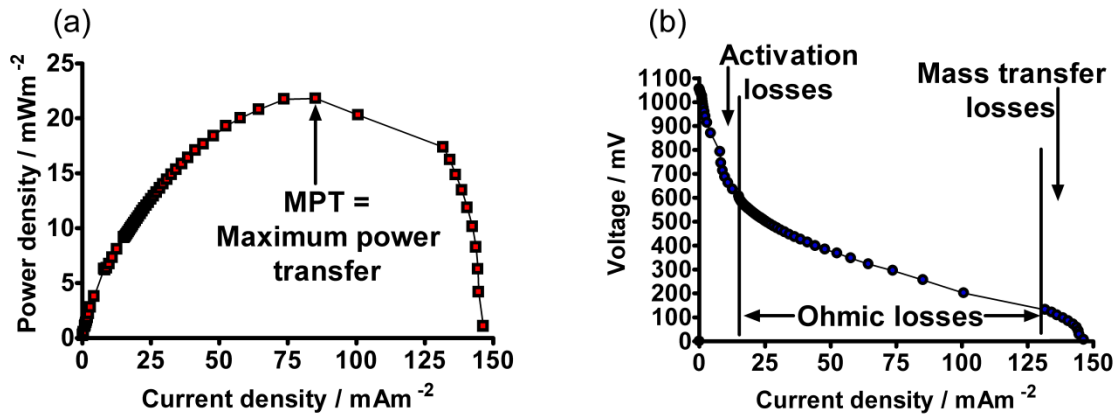


Fig. 1. Polarisation data is used to produce (a) power density curve; indicating the power producing capabilities where MPT is the point of maximum power density and (b) polarisation curve; relating to the losses that occur in a fuel cell; 1. Activation losses, 2. ohmic losses and 3. mass transfer losses.

Power curves produced from polarisation data can indicate the MPT point as illustrated in Fig. 1a. As well as highlighting the power producing capabilities, polarisation data can be used to examine the internal resistance of the reactor using polarisation curves (Fig. 1b). The shape of these curves gives an insight into where the losses (internal resistance) are occurring and in the case of conventional fuel cells, can be broken down into three general areas; activation, ohmic and mass transfer losses [1,2]. The biological nature of MFCs can introduce further losses, such as, limited performance at high current densities due to the metabolic rate. Even in open circuit the MFC is prone to losses through microbial side reactions such as biomass build-up and incomplete redox reactions [3]. Generally when a fuel cell reaches its limiting current density any further decline in voltage should not result in a subsequent drop in current [4] as illustrated by the almost vertical drop towards zero power density in Fig. 1a that is indicative of a ‘healthy’ MFC. However, often in MFC research these curves are accompanied by an overshoot phenomenon where both power and current decrease concomitantly. This is illustrated by a bending inwards of the curve and signals a system limitation. The shape and position on the curve of the overshoot can vary across MFC

configurations depending on size, shape and whether individually operated or as part of a stack. The overshoot is not limited to the MFC field and has been observed in studies of conventional fuel cells. For example, Kulikovskiy et al. [5] produced the phenomenon when focussing on the energy efficiency of polymer electrolyte fuel cells (PEMFC) and attributed it to starvation as a result of limited reactant; they successfully produced a simple model mimicking the experimental data. Although the phenomenon appears fairly frequently in published MFC accounts [6], its presence is not fully understood. Aelterman et al. (2006) [7] suggested that these occurrences were the result of mass transfer limitations, a theory that was revisited by Min et al. (2008) [8] who were unable to verify the hypothesis through further experimentation. A theory recently proposed is that these underperformances result from ionic and electrical depletion at the lower resistance values [6]. Another suggestion is that it is the result of an insufficient sample rate such that the microbial contingent are not given enough time to adjust to each new resistance value [9], resulting in a rapidly declining voltage that is still dropping when the next new resistance is introduced. Much advancement has been made in recent years suggesting that the scale-up of MFC technology could be achievable. However, it is important to understand system limitations, particularly when a major obstacle to scale-up is the cost-effectiveness of materials. The overshoot indicates a mode of underperformance in MFCs and its frequent appearance demands that the trend be given some attention. To investigate the phenomenon, small-scale (1 mL volume) MFCs operated in continuous flow were subjected to polarisation sweeps under various conditions. Anodic biofilm maturity, feedstock composition, catholyte composition and sample time were varied to investigate the global reactor response in terms of power curve shape and more specifically the overshoot phenomenon.

2. Material and methods

2.1. MFC construction and inoculation

The MFC design used in this study is as previously described [10]. A 0.5 cm × 0.5 cm square window was cut towards the bottom of a 1 mL pipette tip in the narrowing region. Cation exchange membrane (CEM) (VWR, Leicestershire, UK) (2 cm × 1 cm) was adhered over the window using double-sided adhesive (SPI Supplies, West Chester, USA). The anode was constructed from carbon veil (total surface area: 10 cm²) folded in half and rolled to create a porous cylindrical 3D structure (projected surface area: 1.96 cm²). A piece of nickel chrome wire (8 cm) was used to make a connection point with the electrode. The end of the wire was pulled through the narrow end of the pipette tip so that the anode was held firmly against the

CEM window. Two pieces of silicon tubing (5 cm long with 4 mm internal diameter) were pulled over each end, making a water-tight seal against the pipette tip. A section was cut over the CEM window before the cathode (4 × 10 cm piece of carbon veil) was wrapped around. It was held in place by double-sided adhesive before a piece of nickel chrome wire (8 cm) was threaded through. Two pieces of parafilm were wrapped around to hold the cathode firmly against the CEM window and keep the wire secured. A plastic Y-connector was slotted into the bottom tube with the anode wire coming out through one of its channels before aquarium sealant (Wet Water Sticky Stuff, Barry Read Supplies, Ivybridge, UK) was used to seal and block. The tubing at the top acted as the influent entry point and the unsealed Y-connector channel at the bottom was the effluent exit point. MFCs were inoculated individually using 1 L of primary effluent (Wessex Water, Saltford, UK) enriched with 10 g tryptone and 5 g yeast extract. This was recirculated at 1.5 mL/h using a 16-channel peristaltic pump (Watson Marlow 205U) and the cathode was hydrated with tap water at the same flow-rate. After 3 days running under open circuit conditions, an 8.2 K Ω load was connected to each MFC. A fresh batch of inoculum was fed after 14 days and by the end of the fourth week the MFCs demonstrated good performance, verified by polarisation experiments.

2.2. Anolyte and catholyte composition and flow-rate

Feedstock used during experimentation was fed in continuous flow at 30 mL/h; a TYE solution (pH 7 or adjusted to pH 3 using HCl) was prepared by adding tryptone and yeast extract to 1 L deionised water (concentrations of 1% and 0.5% respectively) resulting in a conductivity of approximately 4800 μ S. Acetate feedstock was prepared by adding into 1 L deionised water either 1 mM or 20 mM sodium acetate (resulting in conductivities of approximately 90 μ S and 1500 μ S respectively). Tap water (pH 7) was used in all experiments to hydrate the cathode at a flow rate of 270 mL/h, however for the catholyte pH experiment specifically, the tap water was adjusted to pH 3 using HCl or pH 11 using NaOH. Furthermore, for the catholyte conductivity experiment either deionised water (0 μ S) or deionised water with added NaCl (2000 μ S) were used. Conductivity was measured with a multi-range conductivity meter (HANNA Instruments HI 9033).

2.3. Polarisation experiments (sweeps)

Polarisation and power curves were generated using a variable resistor (Centrad Boite A Decades De Resistances DR07). Data were produced by sweeping 69 resistor values starting

at 5 megaohm and gradually decreasing to 50 Ω . The time interval between resistance changes was 1 min except for the case of the sample rate experiment where 30 s and 3 min were used. All experiments were carried out at room temperature (24 ± 2 $^{\circ}\text{C}$). Experiments were repeated at least twice both for the 'healthy' curves and those exhibiting overshoot. Despite the reproducibility of the overshoot phenomenon the pattern did vary (e.g. compare Fig. 4a with Fig. 5a) and so the presented figures show the results of single polarisation experiments in order to clearly illustrate curve shape.

2.4. Calculations of power output

The current (I) in amperes (A) was calculated using Ohm's law, $I = V/R$, where V is the measured voltage in volts (V) and R is the known value of the external load resistor in ohms (Ω). Power (P) in watts (W) was calculated by multiplying voltage with current; $P = I \times V$. Current density (mA/m^2) and power density (mW/m^2) were calculated in terms of electrode surface area; $\text{PD} = P/\alpha$, where α is the electrode total surface area in square-meters (m^2).

3. Results and discussion

3.1. Sample rate

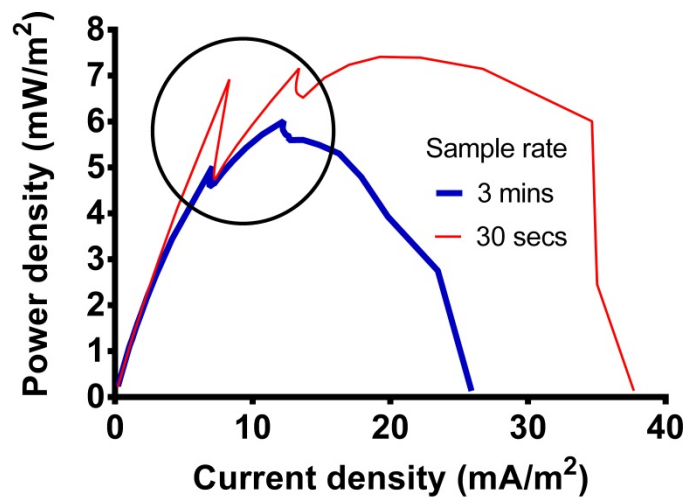


Fig. 2. The effect of sample rate on the exaggeration of power density and overshoot. Comparison of power curves produced at sample rates of 30 s and 3 min. Circled area highlights overshoot peaks.

The sample rate is an important parameter during a polarisation sweep because it is the time the microbes are given to adjust to each new resistance value. As previously mentioned, an insufficient sample rate has been reported as a cause of overshoot. To further explore this hypothesis, an underperforming MFC and such resistance values were selected to encourage overshoot. The same MFC was then subjected to two polarisation sweeps under identical conditions but at two sample rates. Fig. 2 shows that the circled overshoot peaks are more exaggerated at a shorter sample rate of 30 s than at a longer sample rate of 3 min. Further to this the shorter sample rate produced a higher MPT value where power was 23% higher at 30 s than at 3 min. This is in accordance with previous studies where maximum power densities were overestimated using potentiostats at high scan-rates (equivalent of fast sample rates) [11,12]. The occurrence of both the overshoot phenomenon and the overestimation of power density at fast sample rates can be attributed to the microbes' inability to adjust to each new and more demanding resistance value. Therefore the voltage is still decaying when the next resistance value is prematurely introduced and thus the value recorded at that particular resistance is inflated. The overshoot shape is produced when the deterioration of the voltage begins to slow down (as might occur when the size of resistance change is reduced, e.g. when decrements of 100 Ω become decrements of 10 Ω) and eventually stabilisation results in the correct voltage value for the corresponding resistive load. The presence of the overshoot can therefore indicate that the length of sample time is insufficient and that the maximum power produced in that curve might not be accurate. Consequently, even the presence of the less profound overshoot peaks in Fig. 2 suggests that 3 min is still an insufficient sample rate for that particular MFC and its anodic community. In conjunction with this, there are various published accounts showing overshoot at longer sample rates such as 20 min (e.g. [9,12]) and there are many more instances where the sample rate is not provided. Another method for verifying the suitability of a sample rate is to perform two polarisation sweeps; the first starting at open circuit and decreasing in a step-wise manner down to zero, the second performed by increasing the resistance values from zero back up to open circuit. If the voltage behaviour from these two runs over time matches, then the sample rate can be deemed sufficient. In previous experiments this method has shown that when the voltage behaviour of the two polarisation sweeps does not match, the resulting power curve exhibits an overshoot but when the curves of voltage behaviour do match, a healthy power curve is produced (data not shown). When a MFC is run in continuous flow under a single resistive load the biofilm theoretically is operating in a steady state. This steady state can be disrupted on three levels: (i) metabolic, (ii) cell growth and physiological expression and (iii)

ecological. Short scan rates (e.g. 1 min) would impact on the metabolic steady state, such that the microbial contingent is exposed to rapid environmental changes, resulting in a pressure to maintain each increased demand for electrons. In this scenario the polarisation sweep would reveal the electrochemical capabilities of the biofilm that started the experiment. Any resulting losses (previously described as ‘turnover overpotential’ [3]) would be reflected in the high current density region of the power/polarisation curve. Should the length of the scan rate be increased (e.g. to several hours per resistance value) the physiological steady state could be affected resulting in growth and development [13] producing a bio-electrochemical system perhaps different to that which started the polarisation sweep. Extending the sample rate even further, so that each resistance value was held for a number of days, could affect the ecological steady state. In this instance the anodic microcosm as a whole might differ from one ohmic value to the next. The use of long scan rates could reveal further insights into biofilm dynamics and evolution however; in terms of comparability it might be more edifying for the MFC community to use shorter scan rates. Furthermore, a valid way of evaluating MFC performance is by connecting the resistance value that produced the MPT during a polarisation run for an extended period of time (days/weeks). Only if the same peak power is produced during this extended testing period, can it then be concluded that the scan rate was appropriate. Therefore, it might be more beneficial to employ short scan rates and then to evaluate whether the MFC performance is sustainable, as previously shown [14].

The MFC used in Fig. 2 was specifically selected because it was an underperforming reactor and polarisation experiments using other MFCs of the same design consistently produced healthy curves (e.g. Fig. 1). Under optimal conditions at a sample rate of 1 min, these MFCs exhibited fast stabilisation without the steep voltage drops responsible for overshoot or exaggerated power output. To verify this Fig. 3 shows the voltage behaviour over the polarisation sweep that produced the curves in Fig. 1 using a sample rate of 1 min. At each new resistance value, following the initial drop, the voltage can clearly be seen to stabilise as exemplified by the magnified area showing the step-like decline at the higher current densities. This highlights the suitability of 1 min as a sample rate for this design of MFC under optimal conditions. These results suggest that while faster sample rates can exaggerate the overshoot in underperforming MFCs, it might actually be that suboptimal operating conditions affecting internal resistance are ultimately the reason for the presence of this phenomenon. The MFC design used in the present study produced good power curves at 1 min sample rates when operating under optimal conditions; experiments were therefore

performed under various sub-optimal conditions to investigate those that might be responsible for inducing overshoot.

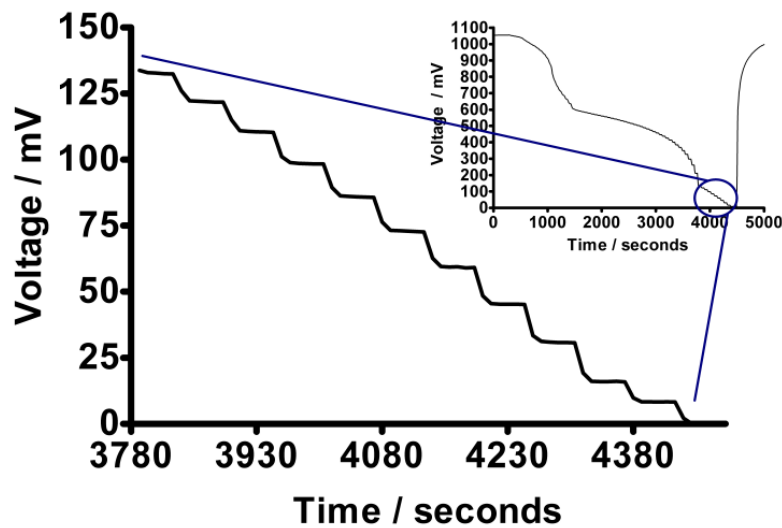


Fig. 3. Voltage behaviour in response to declining external resistances (range shown is 1 K Ω down to 50 Ω) using 1 min sample rate. Inset shows raw data for entire polarisation sweep (5 M Ω –50 Ω).

3.2. Biofilm maturity

The inoculation period is an important process designed to select for a healthy electroactive microbial community. When a MFC just 5 days old was subjected to a polarisation sweep, a double overshoot effect was observed (Fig. 4a). In effect, the sparsely populated anodic community were unable to maintain the increasing electron demand. The two points of overshoot occurred when the size of resistance drop changed, e.g. point 1 in Fig. 4a indicates where drops in 100 K Ω steps changed to 10 K Ω steps and at point 2 the 10 K Ω drops became 1 K Ω decrements. The rapid decrease in voltage was able to slow at these points as the microbes were subject to a less intense demand for electrons per resistance change. Eventually recovery following the overshoot was observed as the inflated voltage value stabilised and settled to become the more accurate value for that resistance. Often in published examples of the overshoot, such a recovery is not recorded/observed (e.g. [15]) especially when this happens towards the end of the polarisation sweep at high current densities where recovery is more difficult to take place. The same MFC after 5 weeks (Fig. 4b) produced a better and more powerful curve with no evidence of overshoot even at the points of resistance step change (points 1 and 2) confirming that a successful inoculation and establishment of anodic biofilm had taken place.

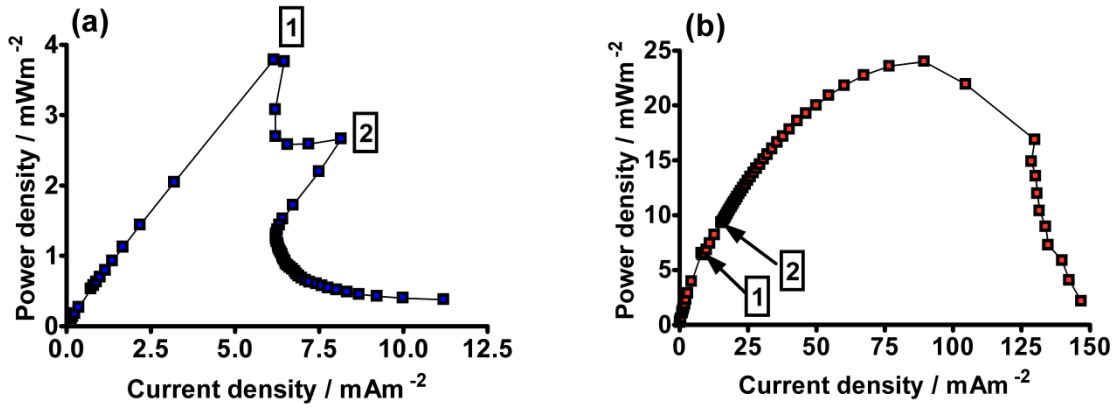


Fig. 4. Power curves produced from the same MFC after (a) 5 days inoculation and (b) 5 weeks inoculation. Point 1 indicates where resistance drops changed from 100 K Ω decrements to 10 K Ω decrements and point 2 indicates where 10 K Ω decrements became 1 K Ω decrements.

This healthy microbial community was able to efficiently maintain the increasing electron demand as the resistive load became heavier (low ohmic values). During the inoculation process, as the electrode surface is colonised by the anodophilic microbial community, the anode potential becomes gradually more negative [16] and the introduction of microbial biocatalysts reduces the polarisation resistance of the anode [17] resulting in a lower internal resistance. Time, in this instance, works in favour of the MFC establishment as a robust system such that power overshoot disappears following an adequate inoculation period. This is consistent with previous work [7] where the evolution of an already healthy biofilm appeared to result in the disappearance of the overshoot.

3.3. Feedstock composition

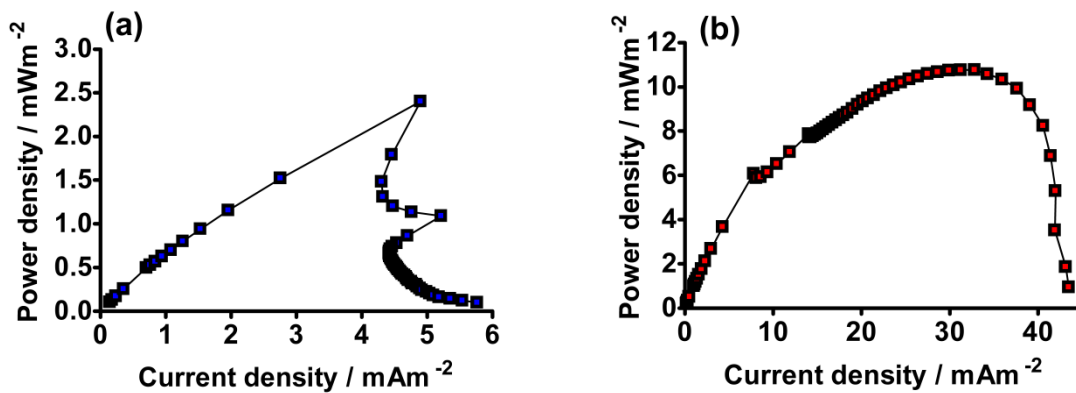


Fig. 5. Power curves produced from MFC with a mature, healthy biofilm when feedstock was either (a) 1 mM acetate or (b) 20 mM acetate.

A healthy electro-active microbial community requires sufficient fuel both in terms of carbon energy source and the conductivity of that solution. Fig. 5a shows the effect an insufficient feedstock had on an established healthy MFC (>5 weeks old) where again a double overshoot is observed. The same concentration of acetate (1 mM) in synthetic wastewater with a conductivity of approximately 950 μS did not induce an overshoot (data not shown) suggesting that in the present study it was perhaps the low conductivity of the solution (<100 μS) responsible for the overshoot. However, previous research investigating organic loading has produced the phenomenon at low carbon energy source concentrations (e.g. [18]). In the current study the steep voltage drops responsible for the overshoot pattern could be taking place when the weak anolyte is drained of electrons and ions [6]. Recovery is again observed and made possible not only by the reduction in size of resistance drop but by the continuous delivery of fresh substrate. When fed deionised water with 20 mM acetate (>1500 μS) a better curve was produced with no evidence of overshoot (Fig. 5b). High ionic conductivity of electrolyte (anolyte or catholyte) reduces the ohmic overpotential of the system [19] and so the presence of the overshoot can again be linked to the MFC's internal resistance.

3.4. Hostile environment

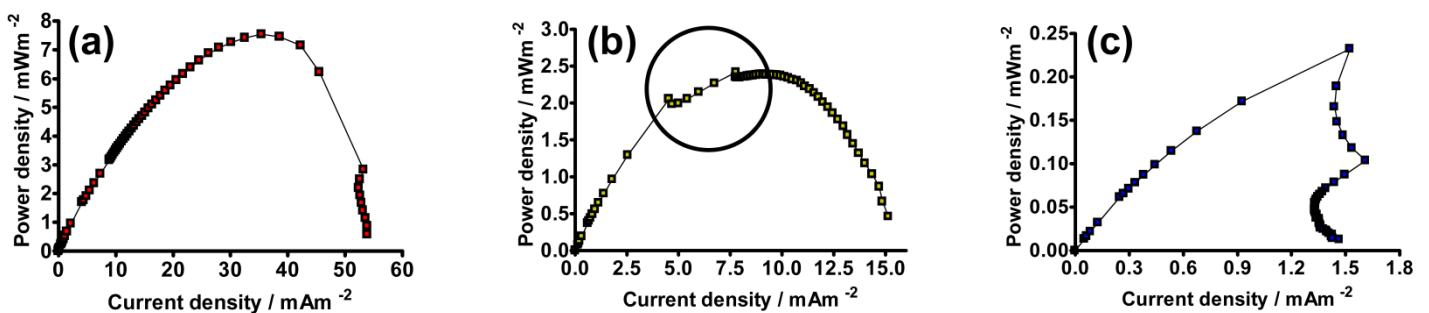


Fig. 6. Performance of a MFC that had been inoculated and operated in pH neutral conditions. Power curves produced when (a) feedstock at pH 7, (b) after 1 h exposure to acidic feedstock (pH 3), circled region indicates emergence of double overshoot, and (c) after 24 h exposure to acidic feedstock (pH 3).

Fig. 6 shows the deterioration in performance when a MFC was subjected to unfavourable, “hostile” conditions. The MFC housing an anodic biofilm adapted to pH neutral conditions, produced a clean curve when the feedstock was pH 7 (Fig. 6a). When this was lowered to pH 3, the power output was detrimentally affected as shown by the power curve produced after 1 h exposure to the acidic conditions (Fig. 6b). The emergence of an overshoot can be seen in

the circled region. After 24 h a double overshoot is again observed with a concomitant power decrease. Clearly, the environment was unsuitable for the microbial community to operate in and the electron demand could not be maintained. These conditions proved to be toxic for the experimental MFCs and a full recovery was not observed for several weeks. Therefore, a user knowing their system limitations could use a reduction in power in conjunction with a perturbation in curve shape to flag the presence of possible pollutants or toxic elements. As previously discussed the development of a healthy anodophilic microbial community can reduce the internal resistance and eliminate any power overshoot. Inversely, the destruction or inhibition of a healthy biofilm will result in an increase in internal resistance, which will in effect deteriorate the performance and reproduce overshoot.

3.5. Cathode effects

The three previous examples of overshoot-inducing environments were the result of anode exposure to varying conditions, where the biofilm was directly affected and all could be linked to factors affecting the internal resistance of the MFC. During those experiments, the cathode was continuously hydrated with tap water (pH 7). To further the understanding of the overshoot occurrence, the cathodic environment was altered while the anode operated under optimal conditions i.e. healthy mature biofilm fed with a rich feedstock at neutral pH.

3.5.1. Catholyte conductivity

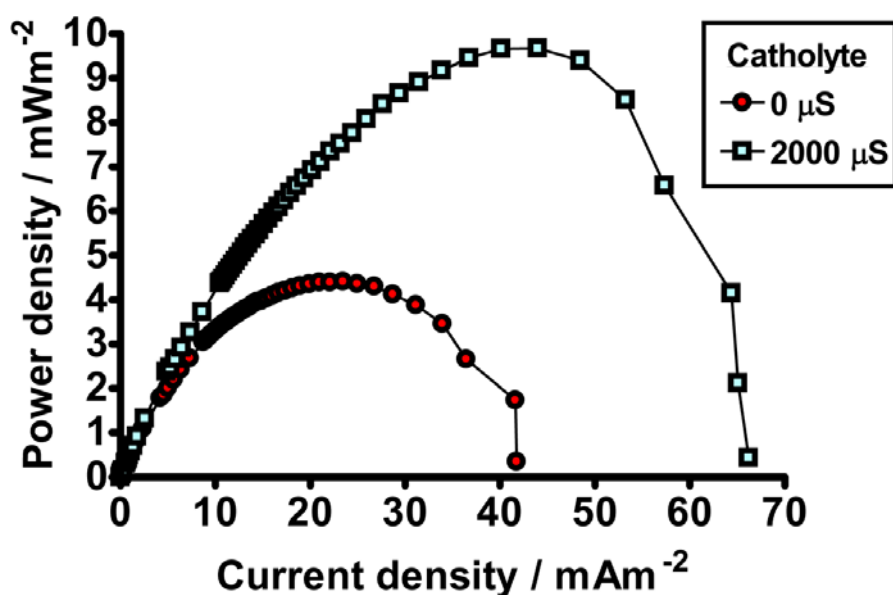


Fig. 7. Power curves produced from MFC with a mature, healthy biofilm. Catholyte either conductive (2000 μS) or non-conductive (0 μS).

To investigate the effect of catholyte conductivity on the presence of the overshoot, plain deionised water ($0 \mu\text{S}$, pH 7) was compared to a catholyte composed of deionised water with added NaCl ($2000 \mu\text{S}$, pH7). The conductive catholyte generated power density almost three-fold greater than the non-conductive catholyte (Fig. 7). However, despite the inferior performance of the $0 \mu\text{S}$ catholyte there was no evidence of overshoot.

3.5.2. Catholyte at high and low pH

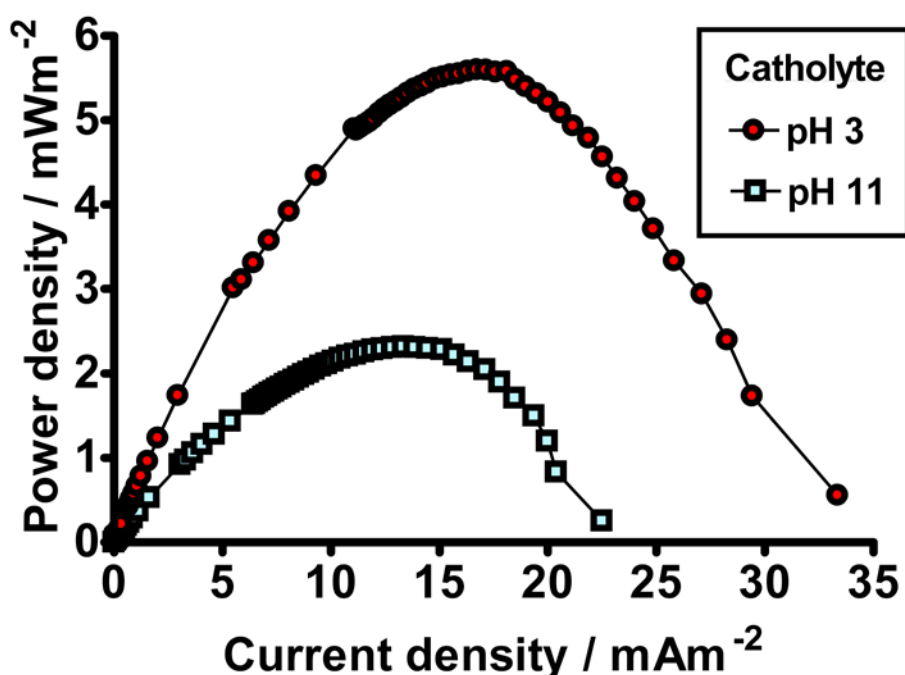


Fig. 8. Power curves produced from MFC with a mature, healthy biofilm. Catholyte modified to be either acidic (pH 3) or alkaline (pH 11).

The pH of the tap water was adjusted to two extremes; acidic (pH 3, conductivity approx. $2000 \mu\text{S}$) and alkaline (pH 11, conductivity approx. $4000 \mu\text{S}$). The low pH catholyte produced a superior performance with a maximum power that was two-fold greater than the high pH catholyte (Fig. 8). Previous work has shown that the passage of protons across the membrane is slower than their rates of production at the anode and consumption at the cathode [20]. To counter this catholytes as low as pH 1 have successfully improved MFC performance [21]. The results here support such previous work; however, the curve produced using the sub-optimal alkaline catholyte, despite the reduced power, showed no evidence of

overshoot. These results suggest that while sub-optimal cathodic conditions (i.e. high pH or low conductivity) might slow the flow of electrons, it is the microbes' ability to supply the electrons that appears to determine the shape of the curve. Therefore, although the overshoot can be directly linked to factors affecting internal resistance, in the present study it was ultimately sub-optimal anodic conditions that determined the presence of the phenomenon. This is an important finding because it suggests that the mode of underperformance signalled by the overshoot can be pinpointed directly to the health of the biofilm. It should be noted that the MFCs in the current study employed perfused but open to air oxygen-cathodes where oxygen availability was unlimited. MFCs using variant cathode configurations utilising oxidisers with limited availability (i.e. ferricyanide) might produce different results. For example, the overshoot phenomena shown by Kulikovskiy et al. [5] using PEMFC was induced when the cathode was starved of oxygen.

4. Conclusions

The incidence of the overshoot phenomenon is not a welcome one because it implies a mode of underperformance; however, its presence could be used to flag that;

- i. The microbial biofilm has not matured to a sufficient level
- ii. The sample rate is too fast for the electroactive capabilities of the anodic microbial community
- iii. Feedstock is insufficient in terms of organic loading or conductivity
- iv. Toxic elements have been introduced into the system

The focus of the current study was to investigate environments responsible for the appearance of the overshoot and experiments were designed to look at the global response of the MFC. Future work focussing on more specific parameters such as individual electrode response and ohmic drop during overshoot events would further enlighten the behaviour of MFCs in sub-optimal conditions.

References

- [1] B.E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Microbial fuel cells: methodology and technology, *Environ. Sci. Technol.* 40 (2006) 5181–5192.
- [2] P. Clauwaert, P. Aelterman, T.H. Pham, L. DeSchampelaire, M. Carballa, K. Rabaey, W. Verstraete, Minimizing losses in bio-electrochemical systems: the road to applications, *Appl. Microbiol. Biotechnol.* 79 (2008) 901–913.

- [3] F. Harnisch, U. Schröder, From MFC to MXC: chemical and biological cathodes and their potential for microbial bioelectrochemical systems, *Chem. Soc. Rev.* (2010) 4433–4448.
- [4] J. Ge, H. Liu, Experimental studies of a direct methanol fuel cell, *J. Power Sources* 142 (2005) 56–69.
- [5] A.A. Kulikovskiy, A. Kucernak, A.A. Kornyshev, Feeding PEM fuel cells, *Electrochim. Acta* 50 (2005) 1323–1333.
- [6] I. Ieropoulos, J. Winfield, J. Greenman, Effects of flow-rate, inoculum and time on the internal resistance of microbial fuel cells, *Bioresour. Technol.* 101 (2010) 3520–3525.
- [7] P. Aelterman, K. Rabaey, H.T. Pham, N. Boon, W. Verstraete, Continuous electricity generation at high voltages and currents using stacked microbial fuel cells, *Environ. Sci. Technol.* 40 (2006) 3388–3394.
- [8] B. Min, O.B. Roman, I. Angelidaki, Importance of temperature and anodic medium composition on microbial fuel cell (MFC) performance, *Biotechnol. Lett.* 30 (2008) 1213–1218.
- [9] J. Nam, H. Kim, K. Lim, H. Shin, B.E. Logan, Variation of power generation at different buffer types and conductivities in single chamber microbial fuel cells, *Biosens. Bioelectron.* 25 (2010) 1155–1159.
- [10] J. Winfield, I. Ieropoulos, J. Greenman, Investigating the effects of fluidic connection between microbial fuel cells, *Bioprocess Biosyst Eng.* (2008). doi: 10.1007/s00449-010-0491-x.
- [11] J. Menicucci, H. Beyenal, E. Marsili, R.A. Veluchamy, G. Demir, Z. Lewandowski, Procedure for determining maximum sustainable power generated by microbial fuel cells, *Environ. Sci. Technol.* 40 (2006) 1062–1068.
- [12] S.B. Velasquez-Orta, T.P. Curtis, B.E. Logan, Energy from algae using microbial fuel cells, *Biotechnol. Bioeng.* 103 (2009) 1068–1076.
- [13] K.Y. Cheng, R. Cord-Ruwisch, G. Ho, A new approach for in situ cyclic voltammetry of a microbial fuel cell biofilm without using a potentiostat, *Bioelectrochemistry* 74 (2009) 227–231.
- [14] I. Ieropoulos, J. Greenman, C. Melhuish, Microbial fuel cells based on carbon veil electrodes: Stack configuration and scalability, *Int. J. Energ. Res.* 32 (2008) 1228–1240.

- [15] P.D. Kiely, D.F. Call, M.D. Yates, J.M. Regan, B.E. Logan, Anodic biofilms in microbial fuel cells harbor low numbers of higher power producing bacteria than abundant genera, *Appl. Microbiol. Biotechnol.* 88 (2010) 371–380.
- [16] R.P. Pinto, B. Srinivasan, M. Manuel, B. Tartakovsky, A two-population bioelectrochemical model of a microbial fuel cell, *Bioresour. Technol.* 101 (2010) 5256–5265.
- [17] A.K. Manohar, F. Mansfeld, The internal resistance of a microbial fuel cell and its dependence on cell design and operating conditions, *Electrochim. Acta* 54 (2009) 1664–1670.
- [18] E. Martin, O. Savadogo, S.R. Guiot, B. Tartakovsky, The influence of operational conditions on the performance of a microbial fuel cell seeded with mesophilic anaerobic sludge, *Biochem. Eng. J.* 51 (2010) 132–139.
- [19] H. Liu, S.A. Cheng, B.E. Logan, Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration, *Environ. Sci. Technol.* 39 (2005) 5488–5493.
- [20] G.C. Gil, I.S. Chang, B.H. Kim, M. Kim, J.K. Jang, H.S. Park, H.J. Kim, Operational parameters affecting the performance of a mediator-less microbial fuel cell, *Biosens. Bioelectron.* 18 (2003) 327–334.
- [21] B. Erable, L. Etcheverry, A. Bergel, Increased power from a two-chamber microbial fuel cell with a low pH air-cathode compartment, *Electrochem. Commun.* 11 (2009) 619–622.