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Short communication

Energy accumulation and improved performance in microbial fuel cells

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Abstract

The mechanisms for electron transfer from the microorganisms found in anaerobic sludge to the anode electrode in microbial fuel cells (MFCs) have been investigated. In doing so, both the energy accumulation and improved performance were observed as a result of the addition of exogenous Na_2SO_4. Treatment of anaerobic sludge by centrifugation and washing can provide samples devoid of sulphide/sulphate. Addition of exogenous sulphate can give matched samples of S-deplete and S-replete suspensions. When these are compared in an experimental MFC, the power output of the S-deplete is only 20% that of the S-replete system. Moreover, repeat washing of the anodic chamber to remove suspended cells (leaving only cells attached to the electrode) and addition of buffer substrate gives MFC that produce an output between 10 and 20% that of control. We conclude that anaerobic sludge MFCs are a hybrid incorporating both natural mediator and anodophillic properties. We have also shown that disconnected MFC (open circuit) continue to produce sulphide and when reconnected gives an initial burst of power output demonstrating accumulator-type activity.

Keywords: Microbial fuel cell; Energy accumulation; H_2S^-/SO_4; Redox-reaction; Anodophiles

1. Introduction

Renewable energy sources are at the centre of attention globally as an alternative to conventional methods of producing electricity from fossil fuels. Energy-generating systems based on the fossil fuels impose a burden of greenhouse gases on the environment and are thus problematic. Therefore, an effort should be made to develop greenhouse gas-neutral systems such as fuel cells, wind-generators, wave-generators, breakwater-generators and solar panels.

Chemical fuel cells are electrochemical transducers that convert chemical energy contained in hydrogen or methane into electricity. Depending on the electrolytes, electrodes, catalysts and fuels used, they may offer a clean and environmental friendly way of producing energy for a wide range of applications. The most commonly used fuel is hydrogen (H_2) extracted from hydrocarbons (gasoline, methane and diesel) which results in CO_2 greenhouse gas emissions. This technology can only be described as eco-friendly if the source of methane or H_2 is biological, from carbohydrates or from water via electrolysis, the energy for which must come from hydroelectric, solar or nuclear power.

Microbial fuel cells (MFCs) also belong to the fuel cell category. MFCs work by abstracting metabolic energy (reducing power/electrons) from microorganisms around the anode [1]. Bacteria in an MFC form an ecosystem which can be viable for prolonged periods. Electron transfer from the bacterial cells to the electrode surface can take place directly or indirectly with the use of soluble redox mediators [2,3]. These mediators can be either synthetic (neutral

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red, methylene blue and thionine) [2,4–6] or natural (sulphate/sulphide) [7] depending on the species of microbes used. Direct electron transfer from bacterial cells to the anode has also been described using anodophillic species such as *Geobacter sulfurreducens* [8] or *Rhodoferax ferrireducens* [9]. These species attach themselves directly onto the electrode surface and use it as their end terminal electron acceptor. Since MFCs can utilise renewable biomass-derived substrates as their feedstock (thus working within the immediate carbon cycle), they offer the prospect of long-term eco-friendly energy generation. Providing the microbes are continuously fed, they will continuously generate electricity. Although at their present state of development, the energy density ($\sim$0.15 mA cm^{-2}) [6] is small compared to MFCs whose electrodes have been periodically poised resulting in energy densities of 1.5 mA cm^{-2} [10] and other systems, they operate at normal temperature and pressure and can be made to work in continuous mode. Therefore, these represent a novel energy system for driving low-power applications.

MFCs using synthetic mediators give low-power output and in continuous mode produce a waste-stream containing mediator which is environmentally toxic, hence, disposal is a problem. The sulphate/sulphide MFCs have the advantage of producing a waste-stream that is less toxic than synthetic mediators. Also, when operated under similar conditions can produce much higher power output. MFCs based on anodophiles can utilise fuels such as acetate, glucose, sucrose and xylose with the added advantage of no toxic waste. Acetate polluted areas may provide a continuous feed for these types to produce continuous power. Recently, MFCs have been described using anaerobic sludge as a microcosm-catalyst in the anode [5,7,11–13]. Although it is certain that this MFC cannot be classified as one based on the synthetic mediators, it is still to be determined which type it actually is, one based on sulphate/sulphide or one based on anodophiles.

In our comparative studies of MFC, we have previously observed that when sulphate/sulphide types of MFC were disconnected from the electrical circuit for a period of a few hours, power generation was higher upon re-connection. Therefore, one of the objectives of the present study was to investigate this phenomenon of power accumulation. The second objective of this work was to investigate the properties of an anaerobic sludge MFC and identify whether its operation is based on either natural mediators, anodophillic bacteria or a combination of the two.

2. Experimental

2.1. Anaerobic sludge

Anaerobic activated sewage sludge was provided by the Wessex Water Scientific Laboratory, Saltford, UK. The samples were pre-processed, prior to the supply, in a series of activation processes to remove pathogenic viruses. Samples were kept in their original sludge–water based suspension, at 4 °C, up to 3 weeks following nitrogen flushing to keep them anaerobic. The measured pH was found to be 7.3.

For experiments comparing power output in S-deplete and S-replete conditions, activated sewage sludge was centrifuged at 6000 rpm for 30 min (HS18 centrifuge, MSE Scientific Instruments, Crawley, UK). The cell-sediment pellet was washed by re-suspension in 0.1 M di-potassium hydrogen phosphate (Sigma, Dorset, UK) buffered saline (PBS) adjusted to pH 7.3 as re-suspension buffer. The centrifugation and washing procedure was repeated twice and cells were finally re-suspended in phosphate buffer or phosphate buffer plus sodium sulphate (2.5%, w/v, final concentration) to give S-depleted or S-repleted samples, respectively, at an optical density at 660 nm wavelength (OD_{660}) value of 15. The MFCs were connected to a 1.3 kΩ load across the terminals and the decrease of power output followed down to baseline to ensure that endogenous substrate was depleted before being fed with 0.1% (w/v) final concentration sucrose.

For some experiments, the effects of washing out the anodic chamber in situ were studied. Cell suspension in the anodic chamber was removed by suction pipette and replaced by PBS and briefly agitated. This procedure of removal/replacement was repeated three times in total. The chamber fluid was finally replaced with phosphate buffer plus sucrose (0.1%, w/v) as a substrate.

2.2. Estimation of biomass

Samples (0.25 mL) of re-suspended cells were serially diluted (1:1000) until within the linear range of optical density readings of a spectrophotometer (Shimadzu UV-1202) at a wavelength of 660 nm. An OD of 1 was considered to be equivalent to 1200 μg dry weight cells per mL [14]. The 660 nm wavelength was chosen to allow comparison with previous work [6].

2.3. MFC design and operation

The MFCs comprised two (anode and cathode) 25 mL perspex chambers with dimensions $h = 6$ cm, $w = 5$ cm, $l = 1.5$ cm, open on one side and with two holes on top as described by Bennetto [1]. They were assembled using 5 mm stainless steel studding, washers and nuts and physically separated by a Nafion® proton exchange membrane (Merch Ltd., Lutterworth, UK) with a 30 cm^2 surface area. Each chamber contained a folded sheet of carbon fibre veil (20 m^2 g^{-1}) as the electrode, pierced with a 5 cm long nickel–chrome wire coming out of one of the two top holes to provide the connection points for the external circuit. The electrode conformation was such that 180 cm^2 surface area of carbon veil was 'folded down' to 5 cm^2 in order to reduce the resistance of the material and hence reduce the internal resistance of the fuel cell. The analytical form of a MFC is shown below in Fig. 1.

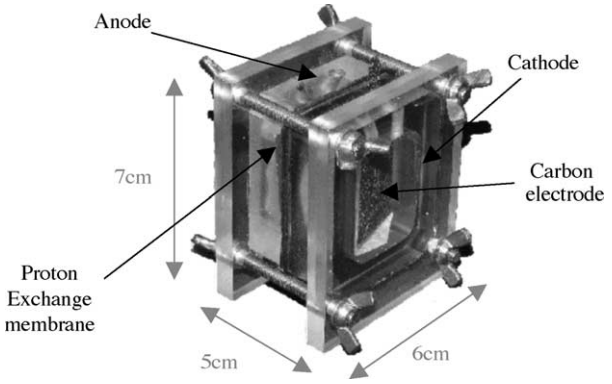

Fig. 1. Analytical form of MFC used in these comparative experiments.

2.4. Catholyte composition

The catholyte consisted of $K_3Fe[CN]_6$ (III) (32.88 g L^{-1}) mixed with K_2HPO_4 (87.09 g L^{-1}), with the pH adjusted to 7.5. For the purpose of this investigation, the catholyte composition was the same for all the experiments.

2.5. Data capture

Electrode output was measured in millivolts (mV) against time. This was achieved by linking the MFCs to the serial communications port of a desktop pc via an 8-channel RS232 interface connected to an ADC-16 A-D converter (Pico Technology Ltd., Cambridgeshire, UK). Two such systems were configured for the experiments involving more than eight MFCs.

Real time data was recorded using PicoLog® v. 5.09.4 recorder software and retrieval of the data was performed using the PicoLog® v. 5.09.4 player software (Pico Technology).

2.6. Background current

The power output due to the microbial cells was obtained by subtracting the MFC power recorded in the absence of microbes (background current) from that recorded in the presence of cells.

3. Theory and/or calculation

3.1. Calculation 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). The external load value used for the experiments was 1.3 kΩ. From this, it is possible to calculate the power output P in watts (W) of the MFCs.

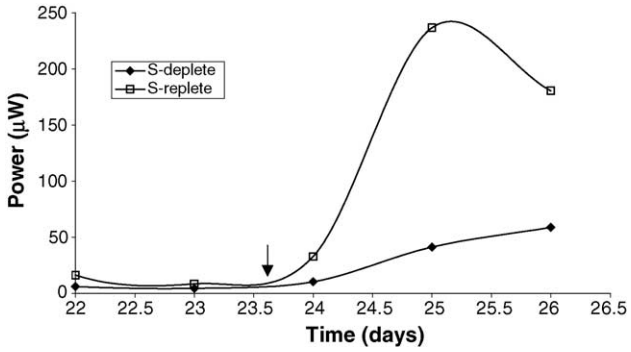

Fig. 2. Power output comparison between S-replete and S-deplete anaerobic sludge MFCs following feeding with sucrose. Arrow indicates point of feed.

4. Results

4.1. Comparison of S-replete and S-deplete MFC

Fig. 2 shows an example of the data recorded for two MFCs using cell suspensions at the same OD, one being S-replete and the other S-deplete following feeding with sucrose. The S-deplete condition resulted in a power output that was approximately 20% the value of the S-replete condition.

For both the S-deplete and S-replete conditions, the power output diminished during electrode washing in situ (Fig. 3). The output following this procedure was approximately 25% the initial values for the S-deplete and 10% the initial value for the S-replete, respectively.

Fig. 4 shows an example of the output profile from an MFC where the electrical load has been periodically switched off and then re-connected. Compared to the control MFC (no switching), the power output can be seen to be significantly greater upon re-connection. The additional power output eventually decays to control values after a period of time. The data in Fig. 5 shows the relationship between the time period of disconnection and the magnitude of the "burst" of power following re-connection up to 100 s. The longer the cell is disconnected, the greater the burst of power output upon re-connection, up to disconnection times of approximately 20 min (data not shown).

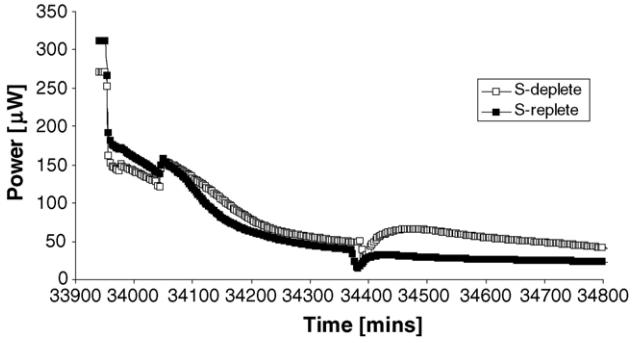

Fig. 3. Power output decrease subsequent to electrode washing from two anaerobic sludge MFCs.

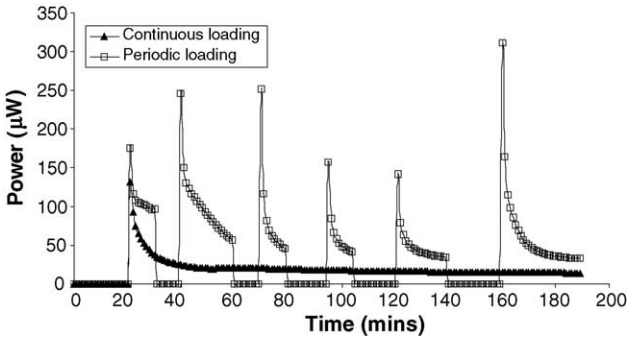

Fig. 4. Energy accumulation phenomenon from the periodically loaded sludge MFC (open symbols) compared to the constant but lower power output from the control MFC (closed symbols).

5. Discussion

A comparison of S-replete and S-deplete MFC shows the dependency of this type of fuel cell on the presence of sulphate/sulphide. Centrifugation and washing of the cells would be expected to remove a high proportion of the initial sulphate/sulphide. In the absence of the addition of exogenous sulphate (S-deplete), the power output was only 60% the S-replete condition. These data suggest that the anaerobic sludge MFC is in general one based on the natural electron redox mediator sulphate/sulphide. However, this may not account for all the power output and it is possible that other mechanisms of electron mediation are occurring. If this is the case, it is unlikely that the other proposed mechanisms involve soluble mediators since these would also have been lost upon centrifugation and washing of the cells. The possibility that direct transfer of electrons from bacterial cells to the electrode surface was occurring was tested by washing cell suspension out of the anodic chamber and replacing with buffer substrate. Power output was monitored throughout this procedure. The power output diminished but was still measurable at about 10% (S-replete) to 25% (S-deplete) the initial values. It is proposed that the anodic chamber washing and substrate buffer replacement procedure removed all the cells and soluble mediators but left attached biofilm cells on the electrode. It seems likely that some of these attached cells were anodophiles. It also seems likely that the microcosm resulting from S-depletion contained a higher proportion of anodophillic types than did the S-replete microcosm since the resultant power output from the S-deplete MFC following the washing/replacement procedure was higher.

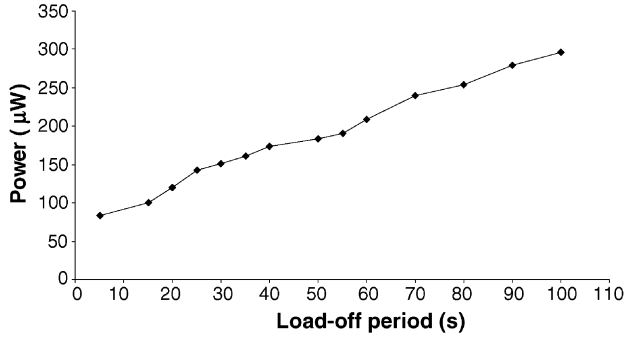

Fig. 5. Average 'burst of' power output (initial 20 (s))vs. the period of time for which the resistor load was disconnected.

The finding that anaerobic sludge MFC can build up power when disconnected for a period of time is a novel observation. The results are compatible with the theory that hydrogen sulphide continues to accumulate when the MFC is switched off (open circuit). When the circuit is switched back on, the high level of hydrogen sulphide produces a higher rate of electro catalytic oxidation at the anode and a higher electrical output until the sulphide level has gone down to the steady state production level. The longer the cell is disconnected, the greater the build up of hydrogen sulphide and the higher the burst of power output upon re-connection. The build up of power when disconnected from the circuit load can be characterised as energy accumulation and may be a useful adjunct to capacitors as a means to store energy for small scale applications.

6. Conclusions

Comparison of S-replete and S-deplete MFC using anaerobic sludge shows that this type of fuel cell is a hybrid between a sulphate/sulphide mediator system and an anodophillic system. Up to ca. 80% of the power output is contributed by sulphate/sulphide and ca. 20% by anodophillic activity.

A sulphate enriched anaerobic sludge MFC can accumulate power when the load is disconnected up to a period of about 20 min. Within this time window, the longer the disconnection, the greater the burst of power upon re-connection.

References

[1] H.P. Bennetto, Biotech. Ed. 1 (1990) 163–168.
[2] S.D. Roller, H.P. Bennetto, G.M. Delaney, J.R. Mason, J.L. Stirling, C.F. Thurston, J. Chem. Technol. Biotechnol. 34B (1984) 3–12.
[3] G.M. Delaney, H.P. Bennetto, J.R. Mason, S.D. Roller, J.L. Stirling, C.F. Thurston, J. Chem. Technol. Biotechnol. 34B (1984) 13–27.
[4] C.F. Thurston, H.P. Bennetto, G.M. Delaney, J.R. Mason, S.D. Roller, J.L. Stirling, J. Gen. Microbiol. 131 (1985) 1393–1401.
[5] D.H. Park, J.G. Zeikus, J. Biotechnol. Bioeng. 81 (2002) 348–355.
[6] D.H. Park, J.G. Zeikus, J. Appl. Environ. Microbiol. 66 (2000) 1292–1297.
[7] W. Habermann, E.-H. Pommer, J. Appl. Microbiol. Biotechnol. 35 (1991) 128–133.
[8] D.R. Bond, D.R. Lovley, J. Appl. Environ. Microbiol. 69 (2003) 1548–1555.
[9] S.K. Chaudhuri, D.R. Lovley, Nat. Biotechnol. 21 (2003) 1229–1232.
[10] U. Schröder, J. Nieβen, F. Scolz, Angew. Chem. 115 (2003) 2986–2989.
[11] K. Rabaey, G. Lissens, S.D. Siciliano, W. Verstraete, Biotechnol. Lett. 25 (2003) 1531–1535.
[12] H. Liu, B.E. Logan, Environ. Sci. Technol. 38 (2004) 2281–2285.
[13] H. Liu, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4040–4046.
[14] F.C. Neidhardt, J.L. Ingraham, M. Schaechter, Physiology of the Bacterial Cell: A Molecular Approach, Sianuer Assoc. Inc., Massachusetts, 1990, pp. 197–203.