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ORIGINAL PAPER

A tubular microbial fuel cell

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Abstract Cell potential and power performance for tubular microbial fuel cells utilising manure as fuel are reported. The microbial fuel cells do not use a mediator, catalysts or a proton exchange membrane. The cell design has been scaled up to a size of 1.8 m in length using electrodes of 0.4 m^2 in area. The cell does not require a strictly controlled anaerobic environment and has potential practical applications when adapted into the form of a helix allowing fuel to flow through it. The cell could be used for power generation in remote applications. The peak power density of the cell is over 3 μW cm^{-2} (30 mW m^{-2}). The performance can be improved by a more effective design of the interface between the anode and cathode chambers.

Keywords Fuel cell · Microbial fuel cell · Tubular · Carbohydrate · Waste · Manure

1 Introduction

Microbial fuel cells (MFC) can convert readily available carbon (and electron) rich substrates into electrical energy. Microbial fuel cells offer a new source of electricity from waste and other carbohydrate sources. The use of microorganisms eliminates the isolation of individual enzymes, thereby providing cheaper substrates for biological fuel cells. In MFC, that do not use mediators, metal-reducing bacteria e.g. *Geobacteraceae* family and *Shewanella* genus are the most used species. These organisms can reduce many substrates, such as Fe(III) [1, 2]. However, the range of electron donors that these organisms can use is limited to simple organic acids such as acetate. Bond [3] has shown that *Geobacter sulfurreducens* provide a 3,000-fold increase in electron activity in comparison to other organisms such as *Shewanella putrefaciens*. This latter organism can also operate in mediator-less fuel cells as well as in cells with mediators and can utilise waste water [4].

Microbial fuel cells that use *S. putrefaciens* are more established than those that use organisms of the *Geobacteraceae* family. The Korean Institute of Science and Technology (KIST), has constructed microbial fuel cells that use *S. putrefaciens*. Like the *Geobacteraceae* family, *S. putrefaciens* can reduce a wide range of substrates including Fe(III) [4]. Fe(III) reduction is important as Fe(III) acts as an electron acceptor in anaerobic respiration, in particular with regard to c-type cytochromes, which are surface active and responsible for electron transfer to the anode [5]. Other organisms are also capable of Fe(III) reduction with surface active cytochromes, e.g. *Clostridium beijerinckii, Clostridium butyricium, Desulfotomacum reducens, Rhodobacter capsultatus, Thiobacillus ferroxidans*, and can be used in mediator-less fuel cells, for example using starch waste water [6, 7].

Tender et al. [8] have created a simple MFC using different sediments on the sea floor, based on two carbon electrodes placed in two different environments: one in the anoxic sediment and the other in the seawater immediately above the sediment. The peak power density of the sediment fuel cell is around 30 mW m^{-2} at a current density of around 75 mA m^{-2} and a voltage of 400 mV.

Mediator-less fuel cells have advantages over those with mediators in terms of lower cost as well as the absence of undesirable toxic mediators. Successful MFC have been

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constructed without expensive selective membranes and using mixed communities and, most recently, electricity has been generated using complex energy sources; including wastewater. The power output of MFCs is generally low and variable. With complex substrates the reported power densities are in the range 10–146 mW m^{-2} whilst, with defined media, the reported range is rather greater: 0.3–3,600 mW m^{-2}. For example Jang et al. [9] fed artificial wastewater to sewage sludge in a novel membrane-less, mediator-less flow-through reactor and observed the current to increase 20 fold over 30 days, presumably reflecting the selection of favourable organisms- though the ultimate power density was just 1.3 mW m^{-2}. However, Rabaey et al. [10] achieved a power density of 3,600 mW m^{-2} and 90% coulombic efficiency by passing sludge from an anaerobic digester through a series of five glucose fed batch reactors.

A number of different cell designs have been tested to increase cell power density or enable continuous treatment of wastewaters. Most small systems are based on simple plate electrodes in standard fuel cell configurations. Other cells have been designed with an outer cylindrical reactor with a concentric inner tube cathode [11, 12]. Cells with an inner cylindrical reactor (anode consisting of granular media) with the cathode on the outside have also been tested [13]. One design used a fixed bed biofilm reactor with up-flow of fuel through the anode chamber, separated from the cathode chamber by a membrane [14].

In this paper we report the performance of tubular MFC with carbon cloth electrodes and manure as the fuel. The cell is readily scaled up.

2 Experimental

The fuel used was dried blended farm manure (William–Sinclair). The average nutrient content of the manure was; 0.6% N:0.3% P:0.65% K:0.25% S:0.15% Mg (manufacturers data). The measured calorific value of the manure was 82 kJ g^{-1}. This fuel was selected on the basis that it was not sterilised but only dried and therefore could be reactivated by hydration. In operation 250 g of dried manure was hydrated with 200 ml of water to form a thick slurry. To re-activate the manure a porous nylon cloth was placed on top of the slurry and sealed to the edge with silicone sealant. An air tight plastic sheet was sealed on top of the nylon cloth. Space was left between the plastic sheet and the nylon cloth to allow biogas formation under the sealed layer. The build up of biogas from carbohydrate digestion could be seen after two to three days of incubation. The manure was left incubating for one week.

2.1 Reactor design

The following fuel cells designs were constructed using Ballard Avcarb 1071HCB woven carbon cloth as the anode and cathode materials. Characteristics of this electrode material are given in Table 1.

2.2 Tubular fuel cell

Figure 1 shows a schematic of the tubular fuel cell which was made from transparent Nylon; 1,000 mm in length, 50 mm outer diameter and 46 mm inner diameter, which functioned as the fuel cell anode chamber. Another smaller non-porous Nylon tube; 16 mm outer diameter and 14 mm inner diameter and 1,200 mm long, was used to form the cathode chamber. The interface between the anode and cathode to allow ion transport was formed using a series of 1 mm holes, 10 mm apart along the length of the tube and 3 mm apart around the circumference of the tube. This clearly is an un-optimised means of linking the anode and cathode compartments of the cell, where ideally a porous barrier would be preferable. However the arrangement was suitable in terms of confining the slurry to the anode chamber, although there would be interchange of species between the liquids in the anode and cathode chambers. In addition there may be issues relating to non-uniform current distributions and thus to under utilisation of the electrodes regarding microbial activity. However, due to the very low current densities achieved and the use of seawater in the cathode chamber, to assist in ionic conductivity, these would not be too severe. The quantity of sea water used in the cathode chamber was 180 cm^3.

The carbon cloth cathode (140 mm × 20 mm) was threaded through the cathode tube/separator. The cathode tube was inserted into the outer tube and the anode was threaded through the anode chamber formed between the outer and inner tubes. The cell was operated with a 250 g batch of fuel in the anode chamber. Anti-fouling electrodes were not used as it was desired to encourage biofilm formation. Also as the final fuel cell is intended to have flow of substrate over the electrode, natural sloughing-off of biofilm will occur. The anode was sealed into the cell with silicone. Once microbial activity was seen in the Nylon tube (i.e. by gas formation), which typically took around 1 week, air was pumped through the cathode at 1.0 dm^3 min^{-1}.

The tubular fuel cell was scaled up to test its suitability in ex-situ locations. Figure 2 shows the large scale tubular fuel cell. Because the length of the cell was increased significantly, the cell was coiled in a helical formation. The cross section of the cell remained the same as shown in Fig. 1. The fuel capacity for the scaled up cell was 10 kg of manure; mixed as a slurry with 3 dm^3 of water and incubated as described above. Once the active slurry was

Table 1 Carbon Cloth Specifications

Specification of ballard 1071 HCB carbon cloth	
Diameter/μm	7.5
Cross section	Round
Density/g cm^{-3}	1.75–1.77
Surface area/gcm^{-3}	0.62
Tensile Strength/kN cm^{-2}	192.5
Tensile Modulus/N m cm^{-2}	26.6
Elongation @ break/%	0.72
Electrical Resistance/ohm cm	1.1×10^{-3}
Thermal Oxidative Stability/wt. loss/h @ 500°C in air	<1.0
Carbon Content/%	99.5
Weave construction	Plain
Weight per unit length/g m^{-1}	105–125
Thickness/μm	280–432

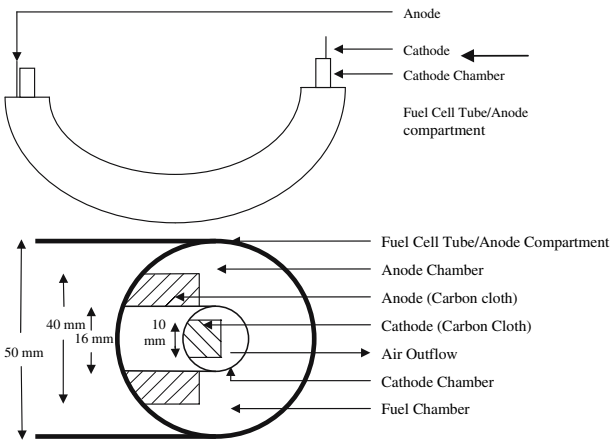

Fig. 1 Schematic diagram of the tubular fuel cell

placed inside the cell, it was not sealed and the anode was left exposed to air. Nylon tubing, 1,800 mm long, was used for the inner tube. The cathode cloth was 2,000 mm by 50 mm and the anode was 2,000 mm by 200 mm. The cell was constructed using either aluminium tubing or polyethylene tubing for the outer tube; both 1,700 mm in length. After the cathode was fed into the outer tube (the anode), the cell was then coiled. Air was pumped through the cathode at 1.0 dm^3 min^{-1} for all tests.

Polarisation and power density curves were generated after steady open cell potentials were achieved. Fig. 3 shows the length of time taken to run a polarisation curve (data taken from Figure 6). Each data point shows the time at which the current was increased. The space between the points is the time taken for the cell to recover from a change in load and achieve a steady voltage. The pH of the cell remained approximately constant at 7.0 throughout the tests.

To measure electrode potentials a silver chloride reference electrode was connected to the cathode side of the cell using a luggin capillary probe and a KCl salt bridge.

3 Results and discussion

3.1 Tubular fuel cell

After the fuel cells were set up and allowed to stabilise, they typically gave open circuit potentials of 510 mV. This open circuit potential is typical for many microbial fuel cells which use waste or other substrates [15–19]. Such potentials are significantly below thermodynamic calculated values based on the consumption of the fuel substrate, combined with oxygen reduction, due to several factors including bacterial metabolic losses and mixed potentials. The involvement of inorganic species, such as sulphate and manganese and iron oxides, which can be microbially reduced to form S^{2-}, Mn^{2+} and Fe^{2+} respectively, may have an influence on the measured open circuit potentials [20].

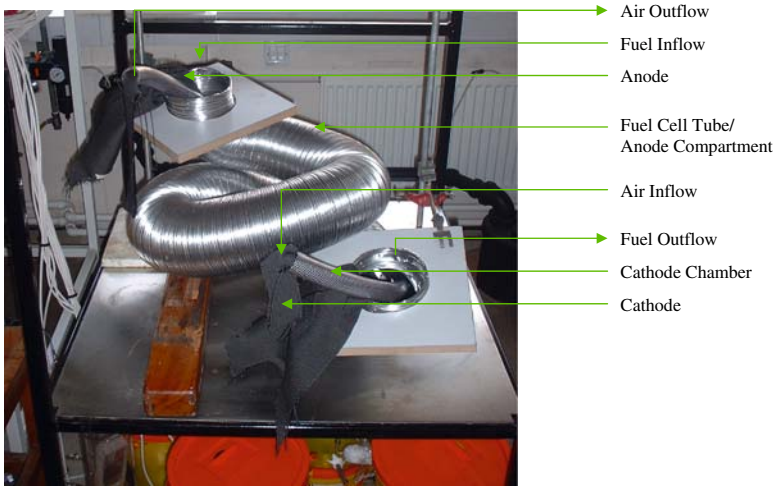

Fig. 2 Large scale coiled fuel cell

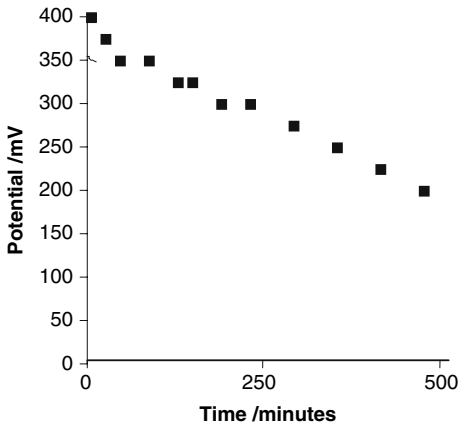

Fig. 3 Time taken for coiled cell steady state polarisation to be achieved

The cell voltage, current density behaviour of the tubular fuel cell, with a sealed anode, is shown in Fig. 4. The cell potential fell from an open circuit value of approximately 530 mV until a maximum current density of approximately 4 μA cm^{-2} (40 mA m^{-2}) was reached at zero voltage. Current densities are based on the anode cross sectional area. The cell gave a peak power output of 0.25 μW cm^{-2} (2.5 mW m^{-2}) at a current density of 0.8 μA cm^{-2} (8 mA m^{-2}). During the tests, the cell potential fell relatively suddenly, by approximately 100 mV, between 8 and 9 mA m^{-2}. After this current density the cell voltage fell gradually with increase in current density.

The cell polarisation behaviour, at around 8 mA cm^{-2}, would normally suggest some type of mass transport limitation, but this did not continue at higher current densities. The behaviour cannot be readily explained, but may be due to changes in the oxidisable substrate (fuel) in the manure or a coupling of several oxidation/reduction redox processes associated with the microbial activity.

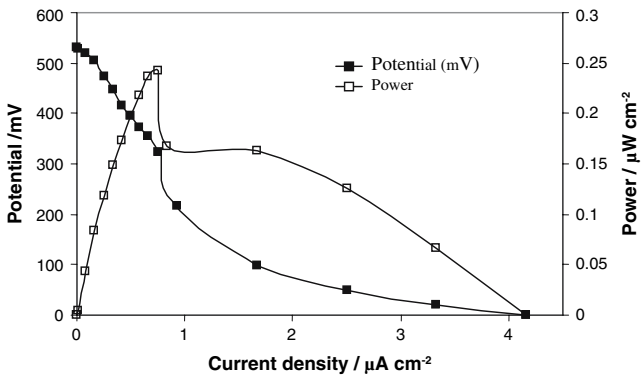

Fig. 4 Cell potential and power density behaviour with a sealed anode. Room temperature

The power densities obtained with the tubular cell were significantly lower than those for microbial fuel cells using wastewater or sediment [20]. The reason for this is the composition of the manure and the resultant sludge formed. The sludge and the water layer above it is a complex composition of carbohydrate with nutrients such as Mn, Fe, N, S and P. In general, microbes in the sludge potentially reduce O_2 as part of the oxidation of organic matter and MnO_2, Fe_2O_3 and SO_4^{2-} can be reduced producing a series of reductants: Mn^{2+}, Fe^{2+}, and S^{2-}. The reductants act to generate the voltage of the cell in combination with the anode reactions. The anode reactions may include oxidation of S^{2-} to S [20]. Thus oxidation of manure sludge organic matter is coupled to reduction of, for example, Fe(III) and Mn(IV) oxides and is catalysed by a consortia of microorganisms which break down the organic matter to produce fermentation products, such as acetate and aromatic compounds and long-chain fatty acids, which are potential electron donors. Then, for example, *Geobacteraceae* can oxidise these compounds coupled to the reduction of Fe(III) and Mn(IV) [21].

Microbiological activity has a significant influence on the power density and the relatively low values obtained may be a result of several factors:

1. Interaction of many potential reductants and oxidants causing significant polarisation of anode and cathode.
2. Poor mass transport of redox active species, in the sludge, to the anode, coupled with greater mobility of oxidants in the water environment around the cathode above the sludge interface.
3. Low open circuit potential caused by mixed potentials and indicative of significant electrode polarization.

Tests were undertaken to see if it was necessary to seal the anode as there was a possibility that air could pass from the cathode into the anode. Figure 5 shows the performance of the tubular cell with an "open" anode, where it can be seen that the open circuit potential was unaffected; both cells gave approximately 520 mV. The cell with an open anode gave a peak power of 1.9 mW m^{-2} at 8 mA m^{-2}. Compared to the cell with the anode closed, the peak power was 0.6 mW m^{-2} lower. Thus, although some air would transfer into the anode chamber, and a complete anaerobic environment not produced, the quantity of fuel was sufficient for microbial activity to utilise the oxygen in the air before the system turned aerobic.

3.2 Coiled fuel cell

Data for the tubular cell (Figs. 4 and 5) were obtained in batch operation. To be of use for practical power generation a continuously fed system is required. By coiling the tube into a vertical helix, the cell could be operated con-

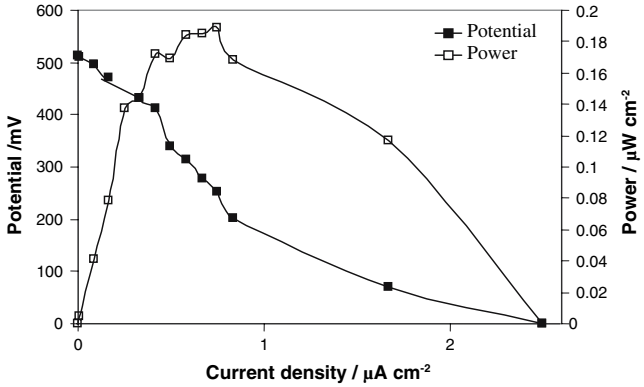

Fig. 5 Cell potential and power densities behaviour of the tubular fuel cell with an open anode. Room temperature

tinuously with fuel flowing from the top to the bottom under the influence of gravity. If the degree of coiling in the helix is regulated, the fuel residence time can be large enough to achieve large extents of microbial digestion.

Figure 6 shows the cell potential and power density performance of the coiled fuel cell. The cell gave an open circuit potential of 470 mV. On polarisation, the cell potential fell steadily with increasing current density and the peak power was approximately 30 mW m^{-2}. The maximum current density achieved was 320 mA m^{-2}. Measurement of the cathode potential (Fig. 7) showed that the cathode was a major cause of power loss at higher current densities; a Tafel slope of approximately 170 mV per decade in the region of 10–100 mA m^{-2}. The anode potential remained approximately constant in that current density region. Cell performance could therefore be improved by using alternative cathodes to carbon cloth, such as metal porphyrins or phthalocyanines, which have recently been reported to give improved performance in MFCs [22, 23]. Of course the additional cost of using catalyst materials is an issue that will affect the overall economics of MFC for power generation and/or waste

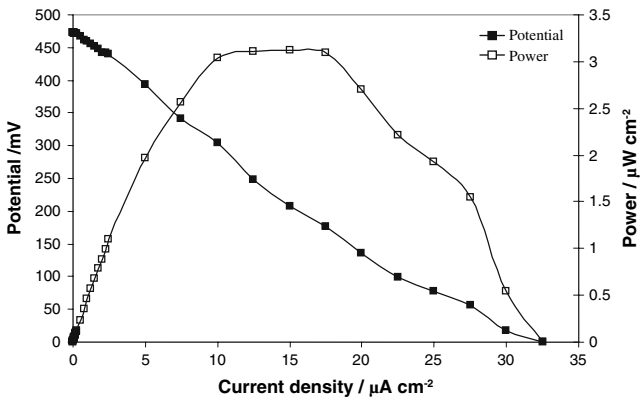

Fig. 6 Cell potential and power density behaviour of the coiled fuel cell: Open cathode. Batch operation

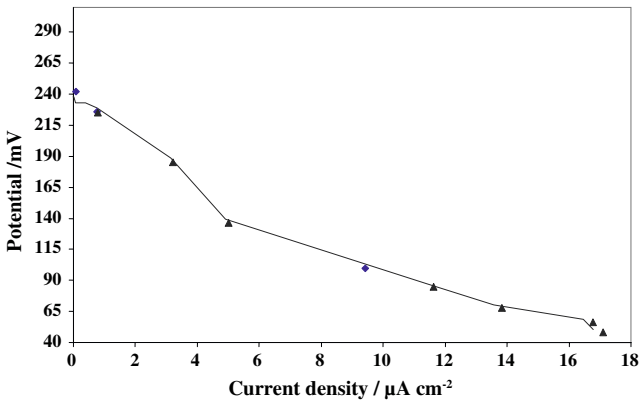

Fig. 7 Cathode polarisation behaviour for the coiled tubular fuel cell

treatment. The notable feature of the cell performance was that power density increased by an order of magnitude compared to that achieved in the small tubular cell design. This factor is due to a greater cathode to anode area and better supply of air.

The choice of aluminium in the coiled cell was for convenience in cell construction, particularly in the coiled configuration. As a test to ensure that the aluminium was not a significant contributor to cell power performance, the coiled cell was operated without manure. In this test only sea water was used in the anode chamber. Figure 8 shows the "cell" polarisation performance without the manure present. The data were obtained with the same anode and cathode used for the manure fuel cell tests. The electrode materials and aluminium tube were cleaned and sterilised using an autoclave prior to use. The cell polarisation gave an open circuit potential of 240 mV and very low current densities, with a peak power density of 0.0028 mW m^{-2}. The data show that power from the coiled cell was due to microbial activity with the manure.

Another factor that would have caused the low power performance was the use of a series of relatively small holes to form the interface between the cathode and anode chambers. With such a design the path for movement of ions between electrodes is restricted and causes an increase in the effective internal cell resistance and a poor distribution of

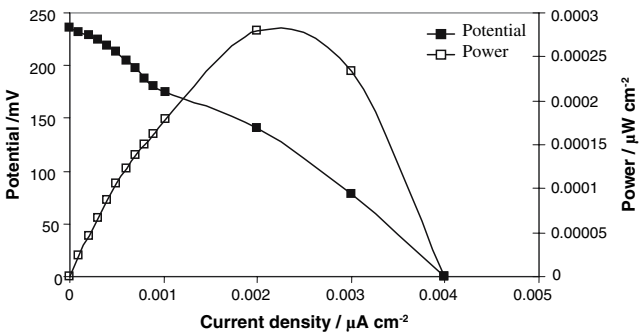

Fig. 8 The coiled cell polarisation behaviour without manure feed

potential and current over the electrodes- both factors would decrease the cell power. The replacement of the tube separator, containing a relatively small number of holes, with a uniformly porous tube separator is expected to significantly improve power performance. We are evaluating a number of materials, initially based on polyethylene, for this purpose.

4 Conclusions

The generation of electrical power from tubular microbial fuel cells fed with manure has been demonstrated. The fuel cells do not need to have strictly controlled anaerobic environments and can cope with air seepage from the cathode, which does not significantly hinder digestion of the fuel. The tubular fuel cell is a concept that has practical applications when operated in the form of a helix, allowing digestion of the fuel to be controlled by the degree of coiling. To improve MFC performance research is required to identify suitable low cost cathode catalysts and more effective anode materials. The cell is relatively low cost, requiring minimal maintenance, and is environmentally friendly as wastes that would otherwise require treatment are used as fuel. The tubular cell has potential for power generation in remote applications.

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