Design of a Microbial fuel cell for Continuous electricity production using manure sludge waste

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Abstract:

The cell voltage and power performance of a microbial fuel cell utilizing waste carbohydrate as a fuel, that does not use a mediator, catalysts or a proton exchange membrane, is reported. Tests were conducted with the cell operated essentially as a battery using manure sludge as fuel and with oxygen reduction in an aqueous solution. Using carbon cloth as anode and cathode, the cell produced peak power of the order of 5mWm⁻². The cell performance was not greatly influenced by the quantity of fuel used and required a suitable separation between the cathode, anode and sludge/water interface. Agitation of the sludge did not adversely affect the cell performance, indicating that a continuous fuel cell system could be operated using the manure sludge. Using a platinised carbon cathode doubled the power density to over 10mWm⁻². The use of nickel as an alternative cathode catalyst was not found to be effective under the conditions of operation of the cell. The cell power performance was found to be consistent and stable over the 3month duration of the tests, after which point over 95% consumption of carbohydrate was achieved. Examination of the carbon anodes after the tests showed consistent formation of a biofilm on the surface of the fibers. A cell stack design based on multiple pocket anodes containing the fuel sludge has also been demonstrated.

Keywords: Microbial fuel cell, Waste energy, Manure sludge utilization

Introduction

Microbial fuel cells (MFCs) offer a new source of electricity from waste and other carbohydrate sources. MFCs have been demonstrated by several groups both with and without the use of mediators to facilitate electron transfer to the anode.¹ Micro-organisms that require a mediator do not have electrochemically active surface proteins to transfer electrons to the anode. In MFCs that do not use mediators, metal reducing bacteria such as those of the Geobacteraceae family can reduce many substrates, e.g. iron(III).²⁻⁴ Bond et al.⁵ have shown that Geobacter
*sulfurreducens* gives a 3000-fold increase in electron activity in comparison with other organisms such as *Shewanella putrefaciens*. This latter organism can also operate in both mediatorless and mediated fuel cells and can utilise wastewater.

The Korean Institute of Science and Technology has constructed MFCs that use *S. putrefaciens*. Like the Geobacteraceae family, *S. putrefaciens* can reduce a wide range of substrates, including iron(III). Other organisms are also capable of iron(III) reduction with surface-active cytochromes; for example, *Clostridium beijerinckii, Clostridium butyricum, Desulfotomacum reducens, Rhodobacter capsulatus* and *Thiobacillus ferroxidans* are all suitable for use in mediatorless fuel cells, e.g. in cells using starch wastewater.

The mediatorless fuel cell has an advantage over those with mediators in terms of cost and the absence of undesirable toxic mediators. Successful systems have been constructed without expensive selective membranes, mixed communities have been successfully exploited in a number of MFCs and, more recently, electricity has been generated using complex energy sources, including wastewater. With complex substrates the reported power of MFCs is in the range 10–146 mW m$^{-2}$, whilst with defined media the reported range is rather greater, 0.3–3600 mW m$^{-2}$. For example, Jang *et al.* fed artificial wastewater to sewage sludge in a novel membraneless, mediatorless flow-through reactor and observed the current to increase 20-fold over a 30 day period, presumably reflecting the selection of favourable organisms, though the ultimate power density was only 1.3 mW m$^{-2}$. However, Rabaey *et al.* using a simple electrode, achieved a power density of 3600 mW m$^{-2}$ and 90% coulombic efficiency by passing sludge from an anaerobic digester through a series of five glucose-fed batch reactors.

There have been a number of different cell designs that have been tested to increase power density or provide for continuous treatment of wastewaters. Most small systems have been 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 that is the cathode. Cells with an inner cylindrical reactor (anode consisting of granular media) with the cathode on the outside have also been tested. A variation in design is the upflow fixed bed biofilm reactor, in which the fuel fluid flows continuously through a porous anode with a membrane separating the anode from the cathode chamber. Tendler *et al.* have created a simple microbial fuel cell 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$^{-2}$ with a current density of about 75mA m$^{-2}$ and a voltage of 400 mV. Recent work has shown that, by using modified anodes incorporating anthraquinone, quinone and manganese and iron oxide species, up to a 2.2-fold increase in power density can be achieved in a marine sediment cell.$^{18}$

Various researchers have conducted MFC research by studying a variety of cathode and anode materials and reaction configurations. The field and methodology have recently been reviewed by Logan et al.$^{19}$ Materials ranging from non-corrosive stainless steel$^{20}$ to versatile carbons have been used as anodes in various forms and shapes.$^{19}$ In order to enhance the anode performance, various chemical and physical strategies have been developed by different researchers. Park and Zeikus$^{21}$ incorporated manganese(IV) and iron(III) and used covalently linked neutral red to mediate the electron transfer to the anode. Electrocatalytic materials such as polyaniline/platinum composites have also been shown to improve the current generation by assisting the direct oxidation of microbial metabolites.$^{10,18,22}$ These electrodes were biocompatible and the presence of polymer on the anode surface slowed down the anode deactivation caused by interference from bacterial metabolic products as well as by-products of the electrocatalytic oxidation process.

Using a physical strategy, Cheng et al.$^{23}$ found that, by directing the anode fluid flow through the carbon cloth towards the anode and decreasing the electrode spacing from 2 to 1 cm, increased power densities were achieved using an air cathode MFC. The flow-through anode has also been employed in reactors using exogenous mediators.$^{24}$ In the same way, in order to minimise MFC operational costs, researchers have either reduced the platinum loading in the cathode to as low as 0.1mg cm$^{-2}$, or developed open air cathode systems.$^{14,24}$ More recently, noble metal-free catalysts such as pyrolysed iron(II) phthalocyanine and CoTMPP (cobalt tetra(p-methoxyphenyl) porphyrin) have been proposed as potential MFC cathodes.$^{25,26}$ However, the presently available technology has not provided sufficient power densities, so considerable work remains to be done in the combined disciplines of microbiology, electrochemistry and chemical engineering to develop MFCs as an alternative, economical and reliable technology. In this paper we report data of the performance of MFCs operated as a batch battery system using simple carbon cloth as the electrodes.
Experimental

Cell feed

The fuel for the cell used was dried blended farm manure, supplied as commercial garden fertilizer and selected on the basis that it was not sterilised but only dried and therefore could be reactivated by hydration and incubation. The average nutrient content of the manure was 6mg N, 3mg P, 6.5mg K, 2.5mg S and 1.5mg Mg g$^{-1}$ (manufacturer’s data). The measured calorific value of the manure was 82 kJ g$^{-1}$. The amount of dried manure in the majority of cells was 3 kg and it was hydrated with deionised water until a thick slurry was obtained. The volume of solid to water used was 20% by weight. A nylon cloth separation layer was placed on top of the slurry and sealed to the edge with silicone sealant. An airtight plastic sheet was sealed on top of the nylon layer (once the previous silicone layer had cured) with silicone.

Space was left between the plastic sheeting and the nylon separator to allow biogas formation under the sealed layer. Prior to testing as a fuel cell, the reactor was placed in an incubator at 37ºC for 1 week to allow the formation of an anaerobic environment in the anode. The build-up of biogas from carbohydrate digestion could be seen after 2–3 days of incubation. The cell was left incubating for 1 week to allow for a complete anaerobic environment to form.

Cell reactor design

The fuel cell reactor was tested initially as a batch system, similar to a battery. The reactor was constructed from a modified 7 dm3 laboratory sharps’ cylindrical incineration bin manufactured from ABS plastic. The fuel cell contained horizontally positioned electrodes as shown in Fig. 1.

Fig.1 Schematic of Reactor
The manure slurry was placed on the bottom of the reactor, in which was located the anode. The cathode was placed in water above the manure. The reactor also contained gas spargers for the supply of gases (air, nitrogen, carbon dioxide). The spargers were constructed from hard plastic tubing, with four 1mm holes around the tube drilled at 1cm intervals. Also incorporated into the cell were luggin capillaries connected to a reference electrode via a KCl salt bridge to measure individual electrode potentials.

**Electrode structure**

The electrodes were made from Ballard Avcarb 1071HCB woven carbon cloth cut into circular pieces. Characteristics of the cloth are shown in Table 1.

<table>
<thead>
<tr>
<th>Specification of Ballard Avcarb 1071HCB woven carbon cloth</th>
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<tr>
<td>Fibre diameter (μm)</td>
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<tr>
<td>Density (g cm−3)</td>
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<tr>
<td>Surface area (g m−2)</td>
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<tr>
<td>Tensile strength (kN cm−2)</td>
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<tr>
<td>Tensile modulus (N m cm−2)</td>
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<tr>
<td>Elongation @ break (%)</td>
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<tr>
<td>Electrical resistance (Ω cm)</td>
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<tr>
<td>Thermal oxidative stability (weight loss h−1 @500 °C in air)</td>
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<tr>
<td>Carbon content (%)</td>
</tr>
<tr>
<td>Weave construction</td>
</tr>
<tr>
<td>Weight (g m−1)</td>
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<tr>
<td>Thickness (μm)</td>
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All electrodes had a cross-sectional area of 256cm². The carbon electrodes were electrically connected to the load outside of the reactor by means of a hole in the side of the reactor sealed with silicone. Antifouling electrodes were not used, as it was desired to encourage biofilm formation and to allow electrical conductivity between the substrate and electrode due to the electrochemically active nature of biofilms.
Materials other than pure carbon were also used in the cell. A Pt/C cathode and anode were also constructed with a Pt/C loading of 0.5mg cm$^{-2}$ (using 20% Pt in C; E-Tek, USA). The cathode comprised a backing layer, a gas diffusion layer and a catalyst layer. The backing layer consisted of carbon paper (Toray TGHP-090, 20 wt% wetproofed; E-Tek) to which a gas diffusion layer was applied. The gas diffusion layer consisted of ultrasonically mixed carbon black (Ketjen black 300), isopropanol and 100 g/litre polytetrafluoroethylene (PTFE) suspension. Catalyst layers were then applied to the substrates by spraying an ultrasonically mixed ink containing the electrocatalyst, Nafion solution (Aldrich, Poole, UK) and isopropanol. Pure nickel mesh (expanded) was also tested as cathode material. All electrodes had a cross-sectional surface area of 256cm$^2$.

**Cell test procedure**

For the initial testing of a cell the open circuit potential (OCP) was monitored. This potential tended to rise gradually during the tests to values (typically >400 mV) which indicated that the anode had become populated with micro-organisms and electrochemical activity had been established. When a stable OCP was reached and maintained for 48 h, testing on the cell commenced. The potential was measured using a digital multimeter.

To measure the power output of the cell, i.e. to obtain cell polarisation data of potential vs current, a power supply was used to apply load to the fuel cell through a variable resistor. The resulting potential, measured through another multimeter, provided the value of the current. At each change in load the cell was left to recuperate and achieve a steady potential, if left at a set load. After each change in load the cells took around 2 h to recover and achieve steady state.

Once a single fuel cell had been constructed and initial tests carried out with air in the cathode and nitrogen in the anode, a test programme with different variables was executed (Fig. 2).
Carbohydrate utilisation

Each cell was assessed to see if the output from the cell was a direct function of carbohydrate fuel utilisation, using a simple calorimeter. A sample of manure was taken from each cell and a sample of unused manure as a control. Both were dried in an oven at 60 °C to remove all water vapour. 1 g manure sample was used in each test.
**Bacterial colonisation of electrode**

The bacteria in biofilm formation directly transfer electrons to an electrode surface, conducting electrons. An environmental electron microscope, which allows samples to be examined whilst still wet, was used to analyse the surface of the electrodes for bacterial colonisation/biofilm.

**Multiple anode cell**

A fuel cell design created from small pockets of fuel, packaged within the anode material itself, was tested. The anode cloth pockets were surrounded by nylon cloth separator and suspended above the carbon cloth cathode. Figure 3 shows a schematic of the multiple anode stack cell.

![Fig 3. schematic of the multiple anode stack cell.](image-url)

It was attempted to see if increasing the fuel’s contact with the anode would result in higher power output. The anodes were surrounded by nylon separator to give the anode strength and to maintain the interface to the outer layer of the anode, thereby maintaining an anaerobic environment within each anode compartment.

**Results and discussion**

All the experimental results were obtained with cells at laboratory room temperature, normally 20° C, during daytime tests. The cells were subjected to overnight cooling, when heating in the laboratory was switched off. It was impractical to try to maintain the temperature of the cells constant owing to equipment constraints and the fact that cells were tested simultaneously. Furthermore, it was felt appropriate to test the cells under these conditions which would relate more to any potential practical applications of an MFC using waste, i.e. variable temperatures during day and night. The fuel cell was set up as a battery so that power output
could be established without concerns about fuel delivery. The cell described above was tested in various configurations and with different parameters, as shown schematically in Fig. 2.

**Effect of geometric parameters**

An initial series of fuel cell tests was performed to determine the effect of geometric parameters (anode and cathode location) on the power performance. In each anode the dissolved oxygen level dropped to approximately zero, showing that an anoxic environment was present. In tests it was found that bubbling of nitrogen to the anode reduced the power output, because it disturbed the mass transfer of bacteria contacting the anode. The bubble movement over the surface of the anode (also through the woven cloth anode) reduced the contact between the anode and the fuel.

![Figure 4. Fuel cell voltage and power density performance using cell 1.](image)

Figure 4 shows the fuel cell data obtained for cell 1. The OCP was 410 mV, which fell, on applying a load, as a result of electrode polarisation. This value of OCP is lower than that reported in other microbial fuel cell studies, where potentials between 0.6 and 0.7V were found. The maximum current density achieved was just less than 40mA m$^{-2}$ at a cell voltage of zero. There is an apparent sharp fall in potential at about 16mA cm$^{-2}$ (270 mV). This fall in potential was seen in many of the data generated under different test conditions, although at the moment we are not clear as to the cause of this effect. The cell had a peak power performance of
over 4 mW m\(^{-2}\). This power density is significantly lower than that reported for other cells using wastewater or sediments as fuel sources.\(^{18}\)

The reason for the relatively poor cell power performance will be due to the composition of the manure and the resultant sludge formed. The sludge formed in the cell and the water layer above it will be a complex composition of carbohydrate, with many nutrients such as Mn, Fe, N, S, P, etc. In a general case, microbes in the sludge will potentially reduce O\(_2\) in the oxidation of organic matter, and MnO\(_2\), Fe\(_2\)O\(_3\) and SO\(_4^{2-}\) can be reduced in the sludge, consequently 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 reactions at the anode. The reactions at the anode may include oxidation of S\(^{2-}\) to S and micro-organisms colonizing the anode (Geobacteraceae) oxidising e.g. acetate.\(^{28}\) Thus the oxidation of organic matter in the manure sludge is coupled to the reduction of e.g. iron(III) and manganese(IV) oxides. This process is catalysed by a consortium of micro-organisms that break down the organic matter to produce fermentation products such as acetate and aromatic compounds and long-chain fatty acids, which are potential electron donators. Then, for example, Geobacteraceae can oxidise these compounds, coupled to the reduction of iron(III) or manganese(IV).\(^{29}\)

Overall, the factors that influence the relatively low power density are:

- The initial low OCP – peak power occurs at potentials around 0.25V and thus higher OCPs could result in a 50–100% increase in peak power;
- Interaction of many potential reductants and oxidants can cause significant polarisation of the anode and cathode respectively;
- Poor mass transport of redox-active species to the anode within the sludge coupled with greater mobility of oxidants in the water environment around the cathode above the sludge interface.

In previous work we have shown that the geometric position of the anode and cathode has a major effect on the fuel cell. The tests with cell configurations 2–4 (Fig. 2) gave power performances that were inferior to that of the ‘standard’ configuration of cell 1. The principal reason for this is believed to be either the closer proximity of the anode to the oxygen containing water or the influence of a greater exposure of the anode to oxygen-containing solution between the cathode and the sludge/water interface.
Fig 5. Effect of increased fuel load on MFC voltage and power density. The distance between the anode and cathode in cell 5 is the same as the standard cell, but the volume of fuel in the anode is increased to 5 kg (normally 3 kg) whilst keeping the anode 20mm from the bottom of the cell and increasing the overall distance between the anode and the cathode (cathode 170mm from bottom of cell).

Figure 5 shows the effect of increasing the mass/volume of fuel (cell 5) on the cell performance. Increasing the volume of fuel slightly improved the maximum power density of the cell, giving over 5mWm$^{-2}$, compared with that obtained with cell 1, which had a power density of 4.5mWm$^{-2}$ with a fuel load of 3 kg. Increasing the volume of fuel increased the number of organisms and created a more stable anaerobic environment for the micro-organisms. This was largely due to the effect of increasing the distance of the anode from the sludge/water interface. The cathode was kept at the same distance from the sludge/catholyte interface (20 mm).

Fig 6. Effect of reduced fuel load on MFC voltage and power density. The volume of fuel was 1.5 kg. The distance of the cathode was reduced from 120mm from the bottom of the cell to 85mm from the bottom of the cell to keep the cathode the same distance from the interface with the anode section. The anode remained 20mm from the bottom of the cell.
Figure 6 shows that, for cell 10, reducing the volume of sludge in the anode decreased the OCP of the cell, although the peak power density was largely unchanged (nearly 5mWm$^{-2}$) in comparison with cells with higher fuel loads. Overall, reducing the fuel capacity of the cell did not have a great influence on the cell performance.

Increasing the volume of catholyte was not found to improve the cell power density (over 4 mW m$^{-2}$ at under 10mA m$^{-2}$ load) but did decrease the maximum current densities that could be achieved, which may be due to an increased resistance to oxygen diffusion from the liquid surface to the cathode.

In the cell polarisation data there is an apparent limiting current density behaviour, i.e. a sharp fall in current with decreasing voltage. If we consider this to be associated purely with oxygen transport, then an order-of-magnitude estimation of this effect can be made. The typical diffusion coefficient for oxygen in water at 20º C is $2 \times 10^{-9}$ m$^2$ s$^{-1}$. The distance from the cathode to the air/liquid interface of the catholyte side was 25–100mm. This situation would give equivalent mass transport coefficients for oxygen, assuming a stationary liquid between the air/liquid interface and the cathode, of $(2–8) \times 10^{-8}$ ms$^{-1}$. Measured dissolved oxygen concentrations during open circuit operation were typically 7.5mg dm$^{-3}$, i.e. 2.5 mmol dm$^{-3}$. With an oxygen solubility of approximately 2.5 mol m$^{-3}$ this gives an oxygen transport limiting current density of 20–80mA m$^{-2}$. These values are in the range of current densities measured in this study, suggesting that the cell would become transport limited in oxygen. Of course, the cell may also be affected by transport limitations of other species formed by the complex microbial activity in the cell.

Figure 7. Effect of fuel agitation on cell voltage and power density vs current density performance. The fuel was mixed every 24 h to try and create an even anaerobic environment throughout the anode.
To examine the effect of achieving continuous operation of the cell, the effect of mixing the sludge was examined. The data in Fig. 7 (for cell 8) show that mixing the sludge did not greatly affect the peak power density of the cell, 4.3 mW m$^{-2}$ (the same as for cell 1), which was achieved at a current density of approximately 20mA m$^{-2}$. This behaviour indicates that a continuous system should be possible. Agitation did not disturb the bacteria on the surface of the electrode, allowing suitable biofilm formation.

**Electrode materials**

The effect of using a Pt/C cathode instead of a carbon cathode is shown in Fig. 8.

**Figure 8. Cell voltage and power density performance with Pt/C cathode.**

The power performance increased to more than twice that of the control, to a peak power density of 1mWm$^{-2}$, which was achieved at a current density of 35mA m$^{-2}$. The greater activity of the platinum catalyst for oxygen reduction increased the OCP to over 700 mV, improved the cathode polarisation characteristics and consequently allowed the load-bearing capacity of the cell to rise (to 35mA m$^{-2}$). Thus, as may be expected, the cathode can be a limiting factor in determining the performance of the cell. It was also found that bubbling air through/over the cathode did not increase the cell performance. Thus limitations in oxygen solubility and mass transport at the cathode are not important, which, at the low current densities achieved in the cells, is not entirely unexpected.

As an alternative cathode catalyst to platinum, nickel was examined in the form of a mesh. The cell produced a low OCP (<250 mV) and consequently gave very low power performance in comparison with that obtained with the use of a carbon or a platinised carbon electrode. Even though the nickel electrode was smooth, with therefore a relatively low surface area, the material does not appear to be a suitable catalyst material for oxygen reduction at the
pH and other conditions of the MFC. This was also confirmed with the use of an Ni/C electrode as shown in Fig. 9, where inferior performance to that achieved with carbon alone is seen.

Figure 9. Comparison of cell voltage and power density vs current density performance with nickel and Ni/C cathodes and Pt/C anode with that with carbon electrodes.

As an alternative to carbon at the anode, the use of Pt/C was examined. As shown in Fig. 9, the OCP was low at 70mV and the cell power was greatly reduced; the peak power density was only 0.65mW m$^{-2}$. It has been shown that, under certain conditions, anodic polarisation stops bacterial cell adsorption to platinum electrodes, so this cell did not benefit from having platinum in the anode.$^{21}$

Cell performance after 3months

Figures 10 and 11 show comparisons of the MFC voltage and power density performance for all the cell configurations tested.
These data were collected in the first month of each of the cell tests. The overall duration of each cell test was 3 months, during which cell polarisations were performed on a frequent basis. In these tests, no significant change in cell performance was experienced for each individual cell.
Figure 12. Power density vs current density performance of cells 1–10 after 3 months of operation.

Figure 12 shows the comparative cell data after the 3 month test period, before the cells were examined for bacterial growth. The relative cell performances were very similar to those achieved in the early stages of the cell tests, although individual cell performances were slightly lower. This may have been a result of the utilisation of the carbohydrate, which for most cells was of the order of 90%, as measured by simple calorimetry.

After the cell tests were completed, samples (3 cm$^2$) were cut from the anodes, with great care not to disturb biological material from the carbon cloth, to examine bacterial colonisation of the electrodes and biofilm formation with a scanning electronmicroscope (SEM). Figure 13 shows the typical formation of biofilm on the surface of the carbon fibres.
Figure 13. SEM image from cell 6, the best performing cell. All fibres shown here have a visible biofilm of bacteria.

Multiple anode cell

The multiple anode cell was an attempt to use a relatively simple concept to achieve a stack design that made efficient use of the carbon cloth anode in a relatively compact unit.

Figure 14. Cell voltage and power density vs current density performance of multiple fuel cell stack.

The performance achieved in this cell, shown in Fig. 14, was a peak power density of 2.3 mW m\(^{-2}\) at 9mA m\(^{-2}\). The data clearly demonstrate the feasibility of the concept, although the power density performance was lower than that achieved with the previous batch cell tests. The
reason for this lower performance may well be due to the close proximity of the anode to the catholyte water containing oxygen. Improvements in performance are expected by using cathodes which are not located at the bottom of the cell but are located in between the anode pockets.

CONCLUSIONS

The cell performance data have shown that a microbial cell can be operated with a low-cost fuel material, i.e. manure in the form of sludge, without the use of mediators, single culture organisms or precious metal catalysts. The cell can be operated essentially as a battery using manure sludge as fuel and oxygen (from air) reduction in an aqueous solution. Agitation of the sludge did not adversely affect the cell performance, indicating that a continuous fuel cell system could be operated using the manure sludge. A cell stack design based on multiple pocket anodes containing the fuel sludge has also been demonstrated. The cell does not need to have a strictly controlled anaerobic environment. The cell power performance was found to be consistent and stable over the 3month duration of the tests. Using carbon cloth as both anode and cathode material, the cells produced peak power of the order of 5mW cm\(^{-2}\). The cell performance was not found to be greatly influenced by the quantity of fuel used, provided that a suitable separation between the cathode, anode and sludge/water interface was used. Using a platinised carbon cathode doubled the power density to over 10 mW m\(^{-2}\).

REFERENCES


