

Fuel cell power generation from marine sediments: Investigation of cathode materials

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Abstract

BACKGROUND: Marine sediment microbial fuel cells (MFC) utilise oxidisable carbon compounds and other components present in sediments on ocean floors and similar environments to produce power in conjunction with, principally, oxygen reduction at the cathode in the overlying water. The aim of the work was to investigate a range of cathode materials for sediment MFC, to achieve relatively high levels of power.

RESULTS: Cell potential and power density performance data are reported for sediment MFC using cathodes of: carbon sponge, cloth and paper, graphite and reticulated vitreous carbon (RVC), Co and Fe-Co tetramethoxyphenyl porphyrin (FeCoTMPP) and platinised carbon and titanium. The anode was graphite cloth. After a period of stabilisation, open circuit voltages of 700 mV and maximum power densities of 62 mW m⁻² were obtained, using FeCoTMPP. Relatively low cost carbon cathodes gave power densities of around 30 mW m⁻².

CONCLUSIONS: The study has shown that low level power can be produced from marine sediments using MFC without separators between the fuel and seawater containing dissolved oxygen. Cathode performance was an important factor determining the power output. Electrocatalyst at the cathode improved performance: FeCoTMPP gave power densities of 60 mW m⁻² which was twice that achieved with the best un-modified carbon.
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Keywords: biological; microbial fuel cell; sediment; carbon cathodes; porphyrin; TMPP

NOTATION

a_s	active area of the electrode per unit cross sectional area of the electrode
b	Tafel slope (mV ⁻¹)
C_{O_2}	concentration of dissolved oxygen (mol m ⁻³)
F	Faradays constant (C mol ⁻¹)
j	current density (mA m ⁻²)
j_{lim}	mass transport limiting current density (A m ⁻²)
j_0	exchange current density (A m ⁻²)
k_1	mass transfer coefficient (m s ⁻¹)
n	number of electrons
R	gas constant
T	temperature (K)
α	transfer coefficient
η	overpotential (V)
DO	dissolved oxygen
OCP	open circuit potential
PTFE	polytetrafluoroethylene
RVC	reticulated vitreous carbon
TMPP	tetramethoxyphenyl porphyrin

INTRODUCTION

Oxidisable carbon deposits are present in vast quantities on the ocean floors and in other water environments, providing an abundant supply of low level power. It has been estimated that sediments containing around 2% organic matter, have energy density capabilities of approximately 17 Wh dm⁻³.¹ Furthermore, micro-organisms, limited by oxygen supply by overlying seawater, can create potential drops of up to 0.8 V over a few millimetres of sediment.² With such vast supplies of fuel, possibilities abound for applications requiring low levels of power using microbial fuel cells (MFCs).

Although the concept of a microbial and bio-fuel cells is not new, many of the studies to date have concentrated on organic matter in waste water,^{3–5} carbohydrates,^{6,7} or biomass as a source of hydrogen.⁸ While the latter forms rely on supplying the cell with an external fuel source, waste waters containing members of the *Geobacteraceae* have been shown to produce electricity by reducing Fe(III).⁹ This type serves mainly as a waste water treatment, while

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producing power as a useful by-product. Also, fuel cells of this type generally utilise a solid polymer electrolyte membrane (PEM), such as Nafion[®] to aid proton transfer. Liu¹⁰ demonstrated, however, that a wastewater MFC increased in performance from 28 mW m⁻² to 146 mW m⁻² when the PEM was removed, substantially reducing oxygen starvation in the cathode chamber.

Aiming specifically at low-level power for marine instrumentation, a collaboration of several research groups^{2,11–13} have reported maximum current and power densities up to 135 mA m⁻² and 32 mW m⁻², respectively, using a membrane-less MFC. Bond *et al.*¹² performed a microbial analysis of the anoxic sediment and found a pronounced enrichment of the δ -proteobacteria sub-group at energy-producing anodes. Furthermore, 70% of the increase was due to an organism of the anaerobic family Geobacteraceae, which are known to exist in redox cycles, coupling the oxidation of organic compounds to the reduction of such electron acceptors as Fe(III) and Mn(IV), the quantity of which will largely depend on location.

In the first of two papers, Reimers *et al.*² employed platinum mesh electrodes to produce current from both salt-marsh and estuarine sediments. The results showed a maximum current density of 7.4 mA m⁻², and a maximum power density 1.4 mW m⁻². It was suggested that in the estuarine sediment the anode reaction involves the oxidation of a microbe-produced reductant, which promotes additional oxidation of sediment organic matter. Significantly improved current and power densities (130 mA m⁻², 32 mW m⁻²) were achieved during a field study, employing perforated graphite disc electrodes. Tender *et al.*¹¹ 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 was around 30 mW m⁻² at a current density of 75 mA m⁻² and voltage of 400 mV. The work also confirmed that power was generated by at least two anode reactions: oxidation of sediment sulphide (a by-product of microbial oxidation of sedimentary organic carbon) and oxidation of sedimentary organic carbon catalysed by micro-organisms populating the anode.

Logan *et al.* studied the application of microbial fuel cells to marine environments in a two-chamber MFC, using sediment from the North Sea, and a cysteine substrate¹⁴ as an oxygen scavenger. Power densities ranged from 19 to 39 mW m⁻², depending on the concentration of cysteine and the presence of platinum catalyst at the cathode. Clone libraries indicated that the predominant bacteria were closely related to *Shewanella affinis*, though others were identified. It is clear that the reaction chemistry is complex and largely dependent on the location of the fuel cell. This in turn will dictate essential factors such as organic carbon availability, mineral type and

content, temperature, pH, oxygen content, and the type of bacteria present. As the microbes consume the oxidisable carbon, transferring electrons to the anode surface, redox coupling takes place, with a variety of combinations possible depending on the nature of the surroundings. Fe(III) and Mn(IV) reduction are well documented,^{12,13} as is the reduction of sulphate and nitrate.^{2,11}

Various studies of microbial fuel cells have investigated aspects of cathode electrode materials and design. Cheng *et al.*¹⁵ investigated the influence of binder of polytetrafluoroethylene (PTFE) and Nafion on platinised carbon electrodes and Co tetramethoxyphenyl porphyrin (CoTMMP) electrodes. Cells used gas fed cathodes and the study showed that alternative catalysts to Pt can be effectively used and that Nafion was a more effective binder than PTFE for the electrodes. Graphite electrodes have frequently been used in MFC.¹⁶ Air cathodes in conjunction with graphite fibre brush electrodes have been shown to produce improved power performance in MFCs compared with planar or tubular electrode configurations.¹⁷

Rotation of the electrode has also been used to enhance MFC power.¹⁸ The application of a rotating cathode increased the oxygen availability to the cathode, and therefore improved the cathode reaction rate, resulting in a higher power production (49 mW m⁻²) compared to a non-rotating Pt coated RVC cathode (29 mW m⁻²).

Biffinger¹⁹ used a biofilm enhanced carbon felt electrode in a miniature MFC and obtained a power density of 70 mW m⁻². By platinising the electrode they were able to increase the power density by an order of magnitude.

In addition to modifying the cathode other workers have also used modified anodes. For example Lowy *et al.*²⁰ evaluated include graphite modified by adsorption of anthraquinone-1,6-disulfonic acid (AQDS) or 1,4-naphthoquinone (NQ), a graphite-ceramic composite containing Mn²⁺ and Ni²⁺, and graphite modified with a graphite paste containing Fe₃O₄ or Fe₃O₄ and Ni²⁺. The MFCs generated a 2 to 5-fold greater current density than a previously characterised fuel cell equipped with a plain graphite anode, and operated at the same site.

Overall; although there has been several studies of different cathode materials for MFCs; of which reviews have captured more recent information;^{21,22} much of the data has not been conducted with sea sediment/sea water fuel cell systems. The aim of this study was to investigate the effect of a wide range of cathode materials on the production of power from marine sediment based MFC. An objective was to explore the use of relatively low cost materials, using high surface area carbons and the use of porphyrin catalysts, for cathodes as alternatives to solid graphite and platinised materials. All cathodes were operated with aqueous solution with dissolved oxygen (from air). In this study we use two sediment sources; one

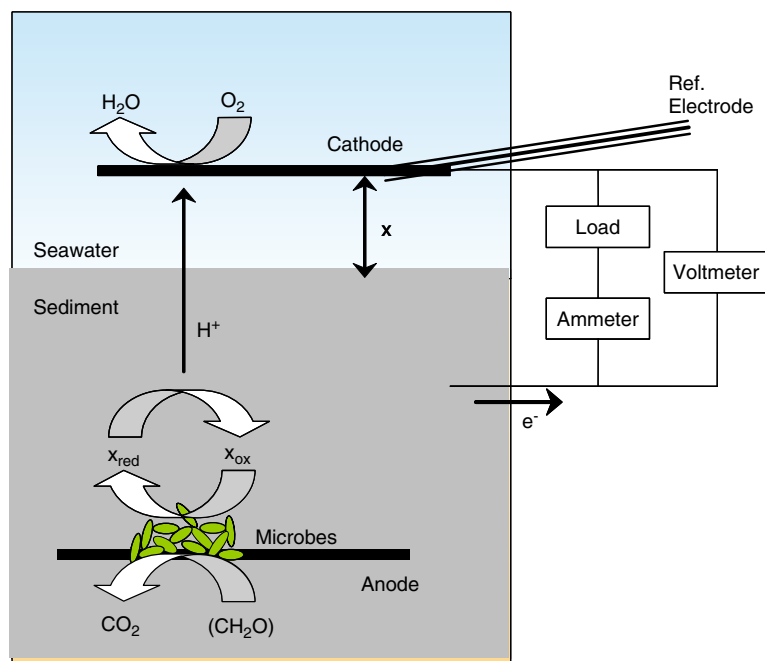


Figure 1. Marine sediment fuel cell schematic.

from the coastal shoreline and the other from a depth of 62 m in the North Sea.

EXPERIMENTAL

Fuel cell

Figure 1 shows a schematic of the MFC, which consisted of an inert cylindrical container, 16 cm in diameter and 16 cm high. The anode was carbon cloth, 11 cm in diameter, which was buried 3 cm below and parallel to the surface of the sediment. The cathode, 15 cm in diameter, was positioned in the seawater, 3 cm above and parallel to the sediment surface. The seawater layer above the cathode was 5 cm in depth. No separator was used in the cell. The anode and cathode were supported by plastic rings to maintain their horizontal positions. The fuel cells were maintained at room temperature except when the effect of temperature was investigated. All cells were tested simultaneously, using the same sources of sediment and seawater, over the period of the study, which for some cells was 9 months.

Silver chloride references electrodes were connected to the cells, via luggin capillary probes, to measure electrode potentials.

Marine sediment and seawater were collected from two locations; off the north-east coast of England at a depth of 62 m and at the waters edge at low tide from Tynemouth beach (55°01'08"N, 1°25'11"W). The materials were transported at low temperature to restrict microbial growth, to nearby laboratory facilities.

Electrode materials

Two types of cathodes were used in this study; catalysed and un-catalysed. The un-catalysed materials

were; carbon cloth (Avcarb 1209 HC, Ballard, Japan), carbon paper (Toray Carbon Paper TGP60 0WP, Canada), carbon sponge, graphite (5 mm thick disk) and reticulated vitreous carbon (RVC). The RVC was 1.2 cm thick 100 ppi (nominal pores per linear inch) grade. RVC is a very porous, rigid material of low density with an open structure and has good electrical conductivity. Electrodes were pre-treated by washing in acetone for 15 min, followed by boiling in 1.0 mol dm⁻³ (M) HCl for 15 min and then rinsing in de-ionised water.

The catalysed materials were Co and Fe–Co tetramethoxyphenyl porphyrin (TMPP) and platinised carbon and platinised titanium.

The platinised carbon electrode consisted of carbon paper (Toray Carbon Paper, TGP60 0WP) with a carbon-supported platinum layer. This electrode was prepared by spraying a suspension of carbon particles (Ketjen Black EC-300, Akzo Chemicals Ltd, AE Amersfoort, Netherlands) onto the surface of the carbon paper, to form a microporous layer (MPL), onto which a catalyst layer was sprayed as an ink. 5 wt% of PTFE in suspension was added to the MPL to bind the carbon particles. The catalyst ink was 60% carbon-supported platinum (E-TEK, Division of De Nora NA, Inc., NJ, USA) in 2-propanol (Sigma-Aldrich Co. Ltd Gillingham, Dorset, England) with 5 wt % Nafion® (Sigma-Aldrich Co. Ltd. Gillingham, Dorset, England). The platinum loading was 0.3 mg cm⁻².

The Co and FeCoTMPP catalysts were prepared by adsorbing the TMPP onto Ketjen black carbon. The process involved dissolving the macrocycle in acetone, then mixing with Ketjen black carbon powder, and agitating the mixture in an ultrasonic bath for 30 min.

The catalyst was filtered, dried in an oven and heat-treated at 750 °C for 2 h, under a continuous flow of nitrogen to avoid oxide formation, and then allowed to cool under flowing nitrogen. The electrodes were prepared by spraying a catalyst ink, made from the catalyst (FeCoTMPP or CoTMPP) and Nafion^R (10 wt% solution from DuPont) in isopropanol, onto the non-wet-proofed Toray 90 carbon paper using an automated spray gun. The loading of catalyst was 0.4 mg cm⁻².

The platinised titanium electrode (Pt/Ti) was prepared by thermal decomposition of a platinum precursor salt (chloroplatinic acid) onto a Ti minimesh substrate. The Ti mesh was first pre-treated by washing in acetone and then immersed in oxalic acid to remove any oxide deposits and to etch the surface; thereby forming a surface that could be wetted easily by the catalyst precursor solution. The mesh was dipped into the catalyst precursor solution and dried at 100 °C for 10 min, and this process repeated several times until the desired catalyst loading was achieved. The precursor solution was a mixture of 0.2 mol dm⁻³ H₂PtCl₆·6H₂O in isopropanol. The catalyst-coated mesh was heat treated in air at 430 °C for 1 h. The electrodes prepared in this way were sonicated with water and the amount of catalyst deposited was determined by comparing the substrate weight before and after deposition. The loading of catalyst was 0.3 mg cm⁻².

Cell testing

Cells were tested simultaneously, under two conditions of air supply; either by natural diffusion from the surface of the seawater or with seawater sparged with air, at flow rate of 500 mL min⁻¹, using an aerator fitted with a porous glass frit, to maintain approximate saturation of oxygen.

As part of the test protocol, the cells were initially left to equilibrate, while monitoring the open circuit potential (OCP). A typical OCP, time profile for the sand sediment fuel cell, during the equilibration period is shown in Fig. 2, with operating conditions shown in

Table 1. Once the OCP had stabilised, an external circuit was established, connecting the electrodes through a variable load, consisting of a power supply and variable resistor. Current generated across the cell, of the order of microamps, was measured using a multimeter, while continually monitoring the voltage via a second multimeter. Other parameters that were monitored in the water and in the sediment were electrode potential, temperature, pH, using a glass electrode, and dissolved oxygen (YSI 550A dissolved oxygen meter, Hertfordshire, UK).

Three validation tests were undertaken to determine whether the power from the MFC was a direct result of microbial activity or whether other chemical processes were significant. Each validation test was carried out using carbon cloth anode and the carbon-supported platinum cathode.

The first validation involved sterilising the cell to check for chemical activity. The cell was prepared in the usual manner, covered and sealed, and placed in an autoclave bag. The bag was also sealed, with just the electrode connections protruding. The cell was then autoclaved at 121 °C for 20 min to kill any sediment-based microbes, and left to equilibrate.

The second validation test was to evaluate the contribution of a differential oxygen concentration by eliminating oxygen from the cell. Initially the seawater was boiled, in the presence of oxygen-free

Table 1. Conditions during equilibration

Time (days)	T (°C)	pH	
		Water	Sand
0	18	7.8	7.8
1	18.5	7.1	7.55
2	17	7.5	7.6
5	17	7.75	7.45
7	16	7.83	7.5
13	7	8.0	7.9
21	7	8.0	8.0

Dissolved oxygen concentration at 100% = 9.2 mg dm⁻³

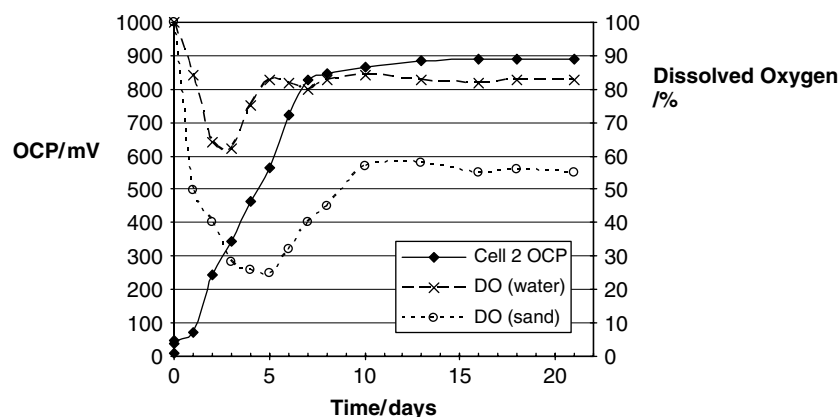


Figure 2. Variation of open circuit potential and dissolved oxygen content with time. Graphite cloth anode, carbon supported platinum on graphite cloth cathode (loading 0.3 mg cm⁻¹ 60% Pt on C). (◆): open circuit potentials. (×): dissolved oxygen concentration in seawater, (○): dissolved oxygen concentration in sand.

nitrogen, within a glove box. While maintaining the supply of nitrogen in the glove box, the materials were transferred to the cell. Mineral oil, also pre-boiled under nitrogen, was added to the cell as a blanket to prevent oxygen diffusion, and equilibration was commenced with a continual supply of nitrogen into the glove box. When the voltage had reached equilibrium, the glove box was opened, the nitrogen supply removed, oxygen sparged into the overlying seawater, and the response of the cell recorded.

With the possibility of trace amounts of dissolved hydrogen present in the seawater, the third validation test involved assembling the cell without sediment, to assess if power was obtained from only seawater. This was shown not to be the case and we do not report data on this aspect.

RESULTS AND DISCUSSION

Sand sediment studies

The MFC were tested with sand sediment collected from the north-east shoreline. Figure 2 shows the variation in OCP with time for the initial cell stabilisation period for the MFC with a platinised carbon cathode. The voltage was initially 40 mV and rose almost linearly after the first day to reach a potential of 830 mV after 7 days. For the following 10 days the potential rose to 890 mV and remained at that value until the end of the tests. The dissolved oxygen (DO) concentrations in sand and water are also shown in Fig. 2, as a percentage of the measured saturation values achieved on exposure to atmospheric air. The DO levels in both sand and water fell gradually in the first 3 to 5 days and then rose to almost constant values of 83% and 56% for water and sand respectively. These DO concentrations were measured away from the electrodes so as to not impede cell behaviour. Consequently near the vicinity of the electrodes dissolved oxygen concentrations would be lower, particularly around the anode where anaerobic conditions would be preferred. Clearly the MFC was operating under partial aerobic conditions.

An initial 24 h activation period was performed on the Pt/C-cathode cell, applying a current density of 1.7 mA m^{-2} . A preliminary steady-state polarisation was performed, taking readings every few minutes over current density intervals of 1.7 mA m^{-2} . At 4.2 mA m^{-2} the potential had dropped to 540 mV. Consequently, at 4.2 mA m^{-2} the system was left to settle overnight at the same load resistance. The following morning the current density had increased to 9.9 mA m^{-2} , and the corresponding cell potential to 760 mV. It was clear that the increase in load current created too great a shift in equilibrium to allow sufficient recovery by diffusion alone over relatively short time periods. Consequently polarisation was continued steadily over 2 weeks (Fig. 3), and the cell was subsequently left for a further 2 weeks at 30 mA m^{-2} , without loss of potential (0.55 V). The cell polarisation exhibited the characteristic variation of an initial sharp fall in potential, due apparently to some type of activation polarisation, at low current densities followed by a gradual fall in potential with increasing current density. Above 40 mA m^{-2} the potential fell rapidly, due to apparent mass transport limitations, until a limiting current of approximately 56 mA m^{-2} was reached. The peak power density of the cell was 20 mW m^{-2} .

Figure 3 shows the cell polarisation behaviour for the MFC with the RVC cathode. The OCP was 640 mV, approximately 250 mV lower than achieved with the Pt/C cathode. The Pt/C cathode as expected showed better oxygen reduction activity with lower activation losses. The cell potential fell steadily with increasing current density and did not exhibit any apparent mass transport limitation down to a potential of 50 mV. Sea water has a relatively high electrical conductivity and thus voltage losses were not due to ohmic losses to any significant extent as the currents obtained were very low. Activation losses were the most dominant factor for the fall in voltage performance for RVC. The RVC-cell gave a higher maximum current of 90 mA m^{-2} (at 0.0 V) compared with 56 mA m^{-2} for the Pt/C-coated cloth. The peak power density of the cell was 15 mW m^{-2} .

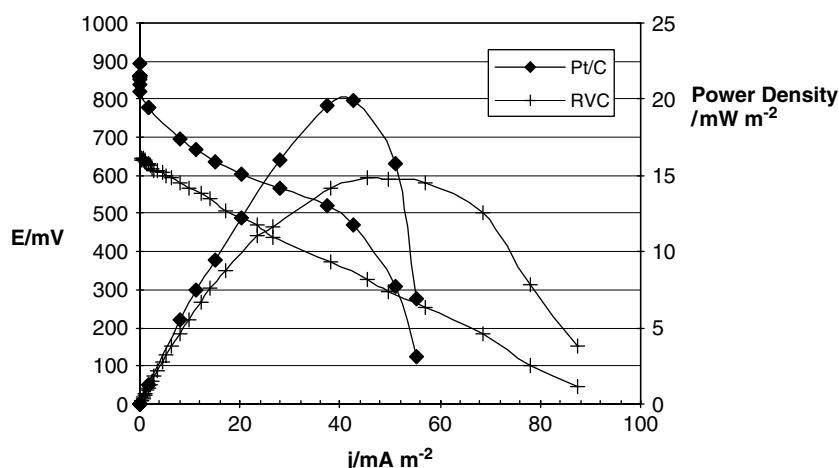


Figure 3. Cell polarisation and power densities for Pt/C and RVC cathode materials.

He *et al.*¹⁸ used Pt coated RVC cathode in a river sediment microbial fuel cell, with a carbon cloth cathode, and obtained power of 29 mW m⁻². The higher performance by He *et al.*¹⁸ can be largely attributed to the Pt coating on the RVC; achieved by simple chemical deposition. Although they achieved improved performance by rotating their cathode this is not a practical option considering the low power generated; which in practice would not be sufficient to actually rotate the electrode.

A contributing factor to the relatively poor performance of the Pt/C electrode was that it was made with a hydrophobic PTFE binder. Although such electrodes are suitable for standard fuel cell electrodes operating with gases, when operated with dissolved reactants, the electrode is likely to exhibit poorer performance due to poor wetting of the catalyst in the pores of the electrode. Thus catalyst surface area that is exposed to the dissolved oxygen would be relatively small in relation to the physical area of the catalyst. An additional factor could also be that the PTFE impedes proton mass transport to the catalyst sites. The involvement of protons in the oxygen reduction mechanism under the measured neutral (slightly alkaline) conditions in this work has yet to be confirmed. However, at the pH values measured in the sea water Cheng *et al.*¹⁵ also reported a deleterious effect of PTFE binder on MFC performance; although this was with a glucose-fed cell using an air cathode as opposed to a flooded electrode in the present case.

The cathode polarisation characteristics exhibited a linear variation in current density with potential at low overpotentials. Current density then rose approximately exponentially until the cathode appeared to exhibit mass transport limitations. Measured dissolved oxygen concentrations in the sea water were typically 7.5 mg dm⁻³, i.e. 2.5 mol m⁻³. At these concentrations mass transport limiting current densities j for oxygen reduction are given by

$$j = 4Fk_1C_{O_2} \approx 10^9 k_1 \text{ (mA m}^{-2}\text{)} \quad (1)$$

where k_1 is the mass transport coefficient (m s⁻¹) for oxygen; C_{O_2} is the dissolved oxygen concentration (mol m⁻³) and F is Faraday's constant (C mol⁻¹).

For the platinised carbon electrode the effective mass transport coefficient for oxygen through the hydrophobic layers was estimated, from the diffusion coefficient of oxygen in water and the porosity, as around 10⁻⁷ m s⁻¹. The limiting current densities would thus be of the order of 100 mA m⁻² and less for MFCs with such electrodes. Such values agree with those determined in the sand sediment fuel cell tests. Because the RVC was very porous, mass transport limitations were not reached with this electrode. Consequently future developments should consider alternative methods of catalysing cathodes with Pt or other materials; which of course assumes that platinised electrodes are a viable, economic option for the MFC.

Sterilised and de-oxygenated operation

In the operation of the MFC we attempted to ascertain which factors were principally responsible for power generation by operating with sterilised sand and with de-oxygenated seawater. The effects of sterilising and deoxygenating the Pt/C-based cell on OCP and cell polarisation are shown in Fig. 4. The autoclaved (sterilised) cell gave an initial rise in potential, up to 200–250 mV, after 1 day, and this potential was maintained for the following 15 days. On application of an increased current, the potential fell linearly (Fig. 4) up to a current density of 11 mA m⁻² and then quickly collapsed at a maximum current density of 15.5 mA m⁻². The peak power density was 1.5 mW m⁻². On comparing the polarisation with the corresponding data for the un-sterilised MFC (Fig. 3), microbial activity in the sediment was responsible for most of the power generation. Upon discharge, the cell displayed the usual Ohmic drop in potential, and mass transfer limitations led to a maximum current density of just 15 mA m⁻².

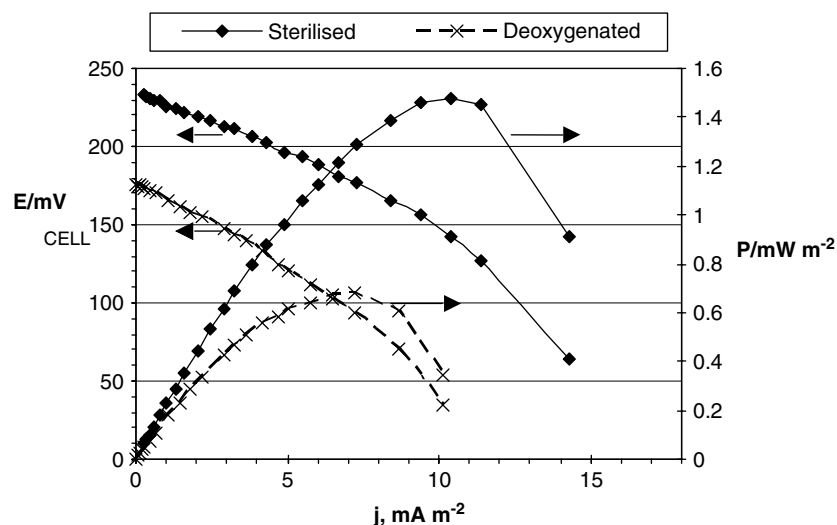


Figure 4. Cell polarisations and power densities of sterilised and deoxygenated cells.

With the deoxygenated cell the OCP rose over 7 days of operation, eventually reaching a steady-state value of around 175 mV. After 7 days, during which oxygen was sparged into the seawater, the potential rose and reached a value of approximately 425 mV, indicating increased activity due to oxygen reduction in the overlying seawater. At the lower potential, during which oxygen was not introduced into the cell, the MFC polarisation behaviour was measured and data are shown in Fig. 4. The cell potential fell in a similar way as experienced with the sterilised cell, reaching 0.0 V at a current density of 11 mA m⁻². The dissolved oxygen content in the water was 4% saturation (0.4 mg dm⁻³), some 20 times smaller than that measured in the open MFC. This DO would not be sufficient to maintain a current density of 11 mA cm⁻². The generation of the low level of power (peak power density of 0.7 mW cm⁻²) would thus appear to come from the complex microbial and chemical environment produced by the sediment and sea water. Certain metal-reducing bacteria are facultative anaerobes (e.g. *Shewanella putrefaciens*), and can exist in both aerobic and anaerobic conditions. As microbes consume oxidisable carbon, transferring electrons to the anode surface, redox coupling can take place, with a variety of combinations possible depending on the nature of the surroundings; e.g. Fe(III) and Mn(IV),^{12,13} sulphate and nitrate reductions.^{2,11}

Sea sediment performance

The MFC potential was monitored daily for approximately 130 days. The fuel cells were subjected to intermittent polarisations and to the natural variations in temperature experienced in the laboratory environment. Most cells achieved constant OCPs in the range of 720–630 mV, (Table 2) after 7 to 14 days. The cells showed slight variations in OCP with time, on a day to day basis, due mainly to the effect of polarising the cells for significant times and the displacement of the cells from equilibrium. Only in the case of the platinised titanium electrode was there any evidence of a loss of performance; indicated by OCP falling to around 100 mV after 100 days of operation. The reason for this was the loss of catalyst activity of the electrode.

Cell power density and polarisations

The cell with carbon cloth electrodes was used as a benchmark for comparisons of other materials. When a stable OCP was reached, polarisation tests were performed to determine the current density and the power density of the cells. Depending on the OCP recovery, certain cells were polarised two or three times. Figure 5(a) shows the current density and power density data of the MFC with carbon cloth anode and cathode. This data were collected over two days and for two successive polarisations. The potential started from around 680 mV and fell reasonably steadily with increasing current density. The peak power density was 25 mW m⁻² at a current density of 80 mA m⁻² and voltage of 300 mV. The second set of data essentially followed the same trend as the first, although it started from a slightly lower OCP; due mainly to the cell not quite returning to its maximum OCP after the first cell polarisation.

Figure 5b shows the anode and cathode potentials obtained during the cell polarisations with carbon cloth electrodes. As can be seen the anode and the cathode exhibited similar extents of polarisation; around 250 mV at current densities of 120 mA m⁻². The performance of the cathode was similar to that obtained in a MFC using manure sludge although the latter's power performance was lower, mainly due to the different fuel substrate used in the anode.²³

The cell potential and electrode potential data of all cells showed the significance of the cathode in determining the cell performance. One objective of this work was to identify carbon materials that could be used without catalysts or modification in the MFC. By using un-modified cathodes it was hoped to enable more sustained performance, avoiding problems of cathode de-activation or catalyst loss. Carbon foam was found to give the highest power density of all carbon materials tested. Figure 6 shows typical anode and cathode potential vs. current density data obtained with MFCs. The behaviour of the anode was similar in all tests and it was the cathode polarisation that effectively dictated the performance.

Table 2 summarises the performance (peak power densities) of the cells. The best performance was obtained with a cathode of FeCoTMMP (Fig 7). For

Table 2. Microbial fuel cell performance and relative activities of cathodes measured by slopes of the linear overpotential current density variation

Cell OCP (mV)	Anode	Cathode	Peak power density (mW m ⁻²)	$b/(a_j C_O)$ mV{mA m ⁻² } ⁻¹ {mol m ⁻³ } ⁻¹
680–720.	Carbon cloth	Fe – CoTMPP	62	0.3
580–610	Carbon sponge	Carbon cloth	55	1.2
700	Carbon cloth	Carbon sponge	38	0.6
700	Carbon cloth	CoTMPP	32	1.2
650–680.	Carbon cloth	Carbon cloth	25	
550–600	Carbon cloth	RVC	12	1.8
720	Carbon cloth	Pt/C	8	3.6
320	Carbon cloth	Graphite	7	1.5
680	Carbon cloth	Pt/Ti mesh		0.36
450–580	Carbon cloth	Carbon paper	0.2	

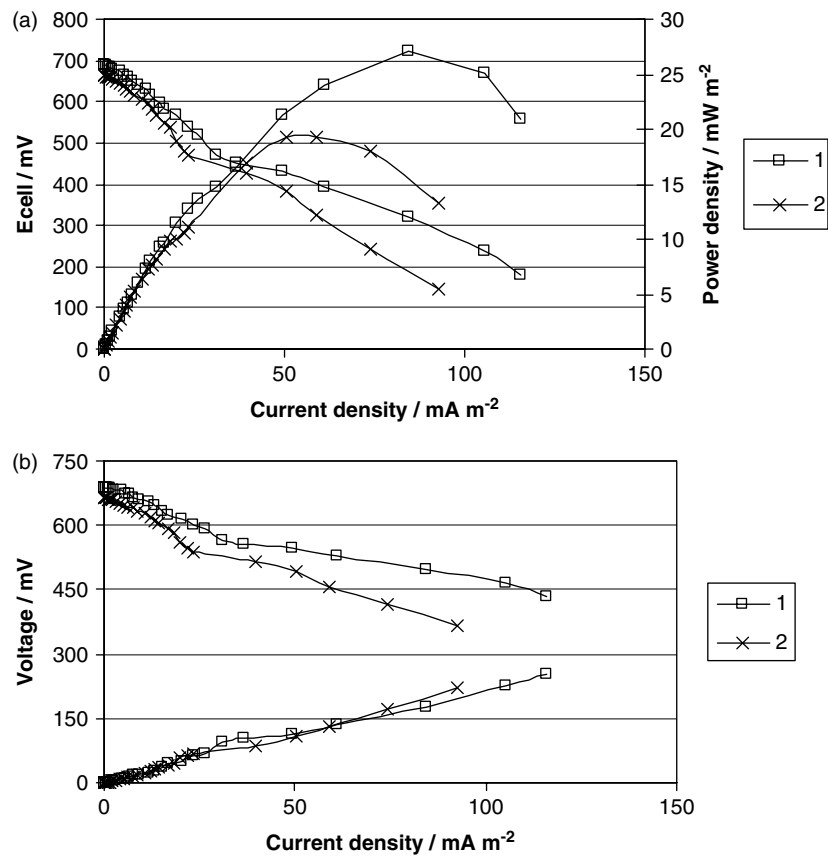


Figure 5. Microbial fuel cell performance of sediment fuel cell with carbon cloth electrodes. (a) Polarisation and power density curves. Numbers refer to first (1) and second (2) polarisations. (b) Anode and cathode polarisations.

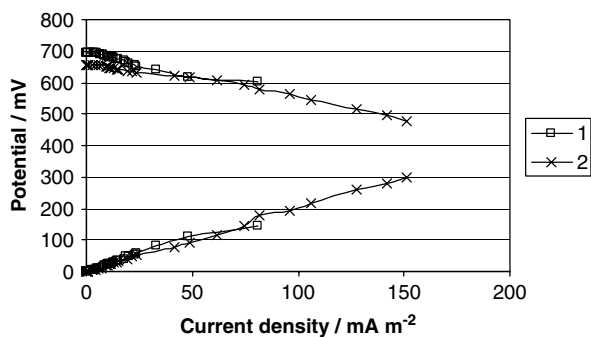


Figure 6. Microbial fuel cell performance of sediment fuel cell with carbon sponge cathode. Anode and cathode polarisation curves of the sediment fuel cell.

this cathode, three polarisations were taken at intervals of approximately 2 weeks. Potentials started at around 700 mV and fell steadily with current density up to a value of around 160 mA m⁻², after which the fall in potential was not as great. This behaviour resulted in an extended plateau region of the peak power densities. Peak power density was initially around 50 mW m⁻² and; for the third polarisation; reached 63 mW m⁻² at a cell voltage of 350 mV and a peak current density of 200 mA m⁻². The cathode exhibited a relatively small amount of polarisation; 80 mV over 100 mA m⁻²; in comparison to that with the carbon cloth cathode (Fig. 5). Thus the anode limited the cell performance with the FeCoTMMP cathode.

The graphite cathode gave relatively poor power density performance (7 mW m⁻²), which was in general agreement with the study of Tender *et al.*¹¹ The Teflon bonded Pt/C electrode performance was similar to that experienced with the sand sediment study and did not give high power densities. Thus, even though Pt would be expected to be a good oxygen reduction catalyst, preparation of the electrode using a PTFE binder is not suitable for this type of MFC using a flooded cathode relying on dissolved oxygen for activity. An alternative method of preparing a platinised electrode is therefore needed. A carbon paper cathode also gave low power densities. The polarisation behaviour of the cell with the Pt/Ti electrode is not given in this table, as although good OCPs were measured, after 90 days of operation the potential fell to approximately 100 mV and did not recover due to a loss of catalyst from the surface. The carbon sponge and CoTMMP electrodes gave similar peak power densities; above 30 mW m⁻². Thus the CoTMMP catalyst proved to be inferior to the FeCoTMMP catalyst and no better than the best un-modified carbon material.

Included in Table 2 are data for a system reported in a companion study using carbon foam as the anode material.²⁴ This data would suggest that a combination of carbon sponge anode with either a carbon sponge or a FeCoTMMP cathode would achieve even higher power densities approaching values of 80–90 mW

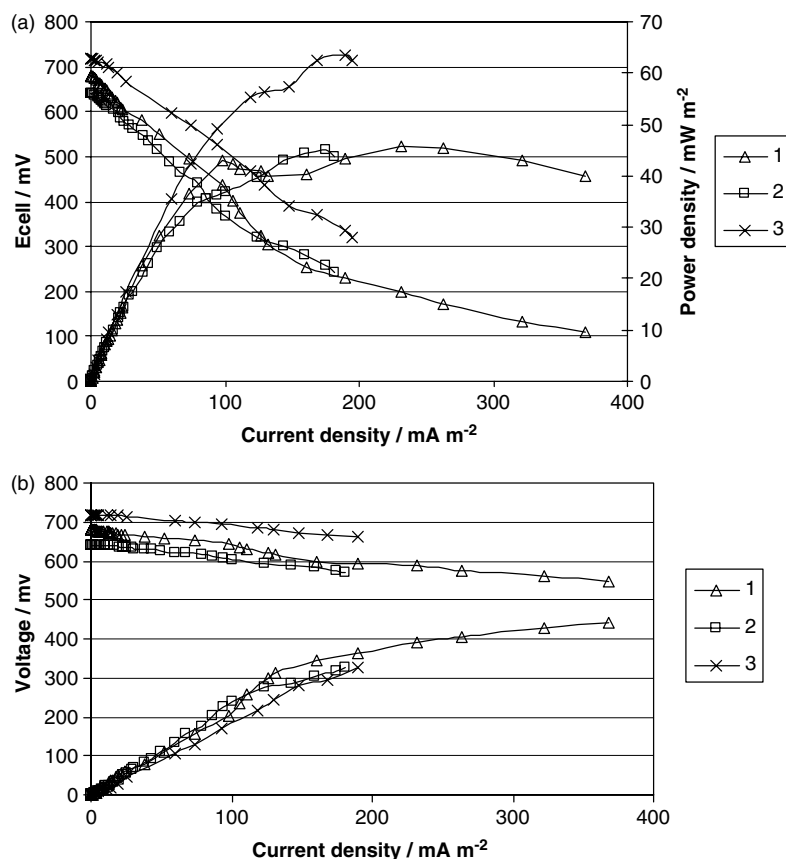


Figure 7. Microbial fuel cell performance of sediment fuel cell with FeCoTMPP cathode. Catalyst loading 0.4 mg cm^{-1} applied on Toray Carbon Paper TGP 90 OWP. (a) Cell polarisation and power density curves. (b) Anode and cathode polarisations of the sediment fuel cell with FeCoTMPP cathode.

m^{-2} . Such values of power density are close to those reported by Lowy *et al.*,²⁰ in which they used redox catalysed anodes in conjunction with a graphite disc cathode, albeit with a different source of sea sediment. It would thus appear possible to achieve even higher power densities using a combination of catalysed anode and cathode, from marine sediment.

Cathode comparison

As shown previously the cathode behaviour can have a dominant effect on MFC performance. To compare the cathode materials in the MFC environment we consider the relative activity of different materials as described by the Butler–Volmer equation for electrochemical kinetics. In this respect we use the two limiting forms of the equation for low and high overpotentials.

At high overpotentials the Butler–Volmer equation reduces to the exponential form; the Tafel equation

$$j = a_j C_{O_2} [\exp(\alpha n F \eta / RT)] = a_j C_{O_2} \exp(\eta / b) \quad (2)$$

where j_0 , the exchange current density, is a measure of the relative activity of the cathode material and the transfer coefficient is a measure of the polarisation of the electrode. a is the active area of the electrode per unit cross sectional area of the electrode, and $b = RT / \alpha n F$ is the Tafel slope.

At low overpotentials the Butler–Volmer equation approximates to a linear form as

$$j = a_j C_{O_2} 2 \alpha n F \eta / RT = 2 a_j C_{O_2} \eta / b \quad (3)$$

Thus a plot of overpotential against current density (or specifically $j/2 C_{O_2}$) gives a slope $= b/a_j$.

In practice overpotentials are measured against the mixed potential for a particular material measured at zero current density. Table 2 compares the slopes of the plots of overpotential against current density for the cathodes materials tested in this work. The value of oxygen concentration is taken as that measured in

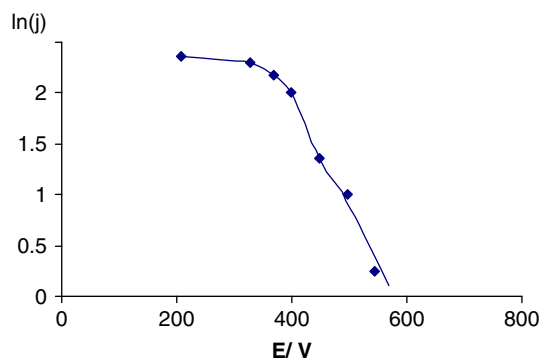


Figure 8. Tafel plot of cathode polarisation with carbon cloth cathode.

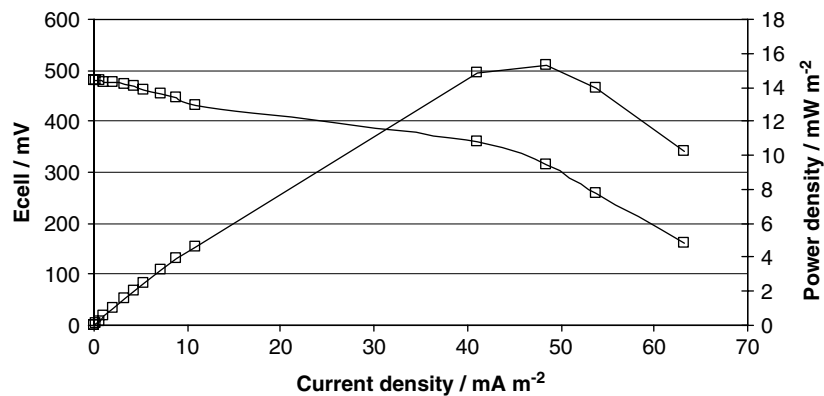


Figure 9. Cell polarisation and power density performance at 5 °C. Carbon cloth anode and cathode.

the experimental work, i.e. 2.5 mol m^{-3} . In general the values of the slopes of the polarisation plots correspond to the measured performance of the electrodes in the sediment fuel cell, i.e. lower values of slope give higher performance. Low values of slope correspond to higher electrode areas, higher exchange current densities and smaller Tafel slopes.

At high overpotentials (current densities) the cathode performance can exhibit mass transport limitations. Under such conditions the overpotential current density relationship is given by

$$\begin{aligned} \eta &= b[\ln(j/aj_o) - \ln(1 - (j/nFk_lC_{O_2}))] \\ &= b[\ln(j/(j_{lim} - j)) + \ln(j_{lim}/aj_o)] \end{aligned} \quad (4)$$

where j_{lim} is the mass transport limiting current density.

Thus a linear plot of η versus $j/(j - j_{lim})$ should give a slope equal to the Tafel slope b and an intercept that is a function of exchange current density.

Figure 8 shows typical potential versus log(current density) Tafel plot for the carbon cloth cathode. From this plot the value of b is 39.1 mV^{-1} . The exchange current density (aj_o) is 0.4 mA m^{-2} .

By allowing for the influence of mass transport, as determined from the measured limiting current density, the current density (Equation (4)) for the carbon cloth cathode can be expressed as:

$$\begin{aligned} j &= aj_oC_{O_2} [\exp(\eta/b)] / \left[1 + \frac{aj_o[\exp(\eta/b)]}{nFk_l} \right] \\ j &= [\exp(\eta/39.1)] / \left[1 + \frac{[\exp(\eta/39.1)]}{nFk_lC_{O_2}} \right] \end{aligned}$$

The values of Tafel slope b and exchange current will be different for other materials. Similarly the mass transport coefficients will vary with material structure.

Effect of temperature

The nature of our laboratory experiments using many relatively large-scale MFCs made it impossible to operate them at a low temperature as experienced in the North Sea marine environment. Thus the effect of temperature was investigated by operating one MFC

at a low temperature of 5 °C appropriate for the marine environment in the North Sea. Figure 9 shows data for a carbon cloth cathode, which achieved a peak power density of 15 mW m^{-2} ; significantly lower than that achieved at the higher ambient laboratory temperature. Notably the MFC still generated power at the lower temperature and a contributing factor to the lower power density was the slower oxygen reduction kinetics and greater cathode polarisation, although this will have been partly counteracted by the higher oxygen solubility at the lower temperature.

It is clear from the results that low-level power can be produced from the sediment MFC under laboratory conditions. Comparing results with those of Holmes *et al.*,¹² it should be noted that experiments were conducted without any form of agitation or aeration, and transport processes occurred by diffusion alone. The study by Tender was undertaken in field conditions, with wave- and tide-assisted transport supplying fresh aerated seawater to the electrodes. Making an assumption that 45 mA m^{-2} can be achieved in the field at 550 mV , any equipment requiring 50 mW of power, such as a sensor, would require an electrode area, assuming no losses, of 2 m^2 . However, it is expected that performance could be greatly enhanced in a field environment, and with improved material selection. It has been estimated that sediments containing around 2% organic matter have energy density capabilities of approximately 17 Wh dm^{-3} .¹ A sensor that uses typically 50 mW of power requires $\approx 440 \text{ Wh}$ per year. Assuming a voltage of 0.55 V at 45 mA m^{-2} requires only 50 mm depth of sediment to produce power.

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