

Artificial gills for robots: underwater energy autonomy with MFCs

Chris Melhuish¹ Ioannis Ieropoulos^{1,2} John Greenman^{1,2}

¹Bristol Robotics Laboratory, Bristol Business Park

University of Bristol and University of the West of England

²School of Biomedical Sciences, Faculty of Applied Sciences

University of the West of England, Coldharbour Lane, Frenchay

Bristol BS16 1QY, U.K.

{chris.melhuish, ioannis2.ieropoulos, john.greenman}@uwe.ac.uk

Abstract

This paper reports on the first stage in developing microbial fuel cells (MFCs) which can operate underwater by utilizing dissolved oxygen. In this context, the cathodic half-cell is likened to an artificial gill. Such an underwater power generator has obvious potential for autonomous underwater robots.

The electrical power from these devices increased proportionately both with water flow rate and temperature. A power increase of 175% was recorded for a corresponding temperature increase (ΔT) of 37°C. Similarly, a power increase ranging from 75-100% was observed as a result of doubling the water flow rate. Both these findings can be advantageous in the design of underwater autonomous robots.

1 Introduction

Energy autonomy in robots is an area, which is gradually receiving increasing attention. Different strategies can be employed to achieve energy autonomy, primarily depending on the application for which the agent is being designed for. One such strategy is to employ the microbial fuel cell (MFC) technology, that allows the extraction of energy from real food substrates (plants, insects or marine crustaceans), through microbial degradation [Ieropoulos *et al.* 2005a,b; Melhuish *et al.* 2006]. Robots have been constructed, which employ MFCs as their power generator. To date, these robots have been used terrestrially and have employed atmospheric oxygen [Ieropoulos *et al.* 2005a,b; Melhuish *et al.* 2006].

This paper looks at the possibility of using MFC power generation technology underwater. In this way, one could envisage organic matter used as the biomass 'fuel' for the bacteria and oxygen used in an aqueous cathode. In some ways, the latter can be likened to an artificial gill.

MFCs comprise two half-cells; an anode and a cathode, which are necessary for the electricity-generating redox (reduction-oxidation) reactions to take place. The anode half-cell contains the bacterial cultures that generate the electricity and is therefore the negative terminal of the MFC. The cathode half-cell, is the positive terminal of the MFC that closes the 'circuit' for the electricity to flow. In general, there are two types of MFC cathodes commonly used; a chemically enhanced cathode system based on ferricyanide, and a gas diffusion cathode system based on oxygen.

Our experimental work supports earlier findings that gas diffusion cathode can employ oxygenated water – such as in river or marine environments. We refer to such a cathodic half cell as an 'aqueous oxygenated cathode' as distinct from the 'atmospheric oxygenated cathode' currently employed in robots such as EcoBot-II [Ieropoulos *et al.* 2005a,b; Melhuish *et al.* 2006].

In this study, we describe the experimental work carried out with aqueous oxygen (O_2)-diffusion cathode MFCs running in continuous hydration flow. The aim of the present study was primarily to repeat and empirically confirm the results of previous workers reporting on the aqueous O_2 -diffusion cathode. It would then be possible to make the case for artificial gills onboard autonomous robots, using our own results.

The following section presents an overview of the different forms of aquatic respiration and provides a comparison between the O_2 -intake in aquatic animals, with the O_2 -diffusion in MFC cathodes, which can be used onboard robots.

2 Overview of aquatic respiration

2.1 Fish respiration (natural gills)

Aquatic respiration refers to the ability of marine animals to collect and utilise oxygen (O_2) from the surrounding water. Very small marine animals can collect small

amounts of O₂ via their skin, e.g. the flatworm. Larger animals on the other hand, must have special structures to be able to more efficiently collect higher amount of O₂. For this purpose, fish have developed gills, which have some unique characteristics such as: a) high surface area, b) short gas diffusion distances and c) high blood flow rate (Hughes, 1984; Gilmour, 1998). In most marine animals, the gills are protected by a special type of bone flap known as the operculum, which is also used to pump water into the gills. Animals like sharks, employ a different technique, known as ventilation, whereby water entering their mouth, is pushed through to the gills, to supply the gill layers with O₂ and remove CO₂.

Gills consist of a number of arches on each side of the head and each arch has two rows of filaments, which have small secondary cross-folds on them to enlarge the respiratory surface (Lagler *et al.* 1977). The transfer of O₂ into the blood stream occurs at the gill pouch section, between which there are septa (diaphragms) that contain venous blood sinuses and the carrier of O₂ in the blood is hemoglobin (Hb) (Lagler *et al.* 1977). A detailed description of the respiratory gas exchange in marine animals is given by Perry (1986) and Gilmour (1998).

2.2 Amphibian respiration

Amphibians are amongst the more versatile animals, since they can live both on land and underwater. These animals have four respiratory mechanisms, depending on the species and habitat (Beebee, 1996). Gas exchange (O₂ intake and CO₂ removal) can therefore take place through the gills, lungs, skin surface and buccal cavity (Beebee, 1996).

Respiration via the skin surface requires that the skin is naked without fur, feathers or scales and maintained wet (Beebee, 1996). This implies that amphibians must live very close to water in order to remain moistened, and indeed for the majority of amphibians, desiccation would be lethal (Stebbins and Cohen, 1997). They are, therefore, equipped with behavioural and physiological response- as well as structural adaptation systems to deal with dry conditions (Stebbins and Cohen, 1997). Interesting examples of behavioral responses and structural adaptations are the American leaf frogs *Phyllomedusa bicolor*, which secrete a waxy substance over their body to minimize water loss, and a highly adapted breed of desert frogs, that burrow and create underground 'tideland' cocoons, during the dry season (Beebee, 1996). Furthermore, toads in particular, use their pelvic patch as a rapid H₂O uptake 'blotter' and also skin wrinkles or furrows, which by capillary action can draw water from a wet surface (Stebbins and Cohen, 1997).

As a group, amphibians live first as gill- and skin-breathing aquatic larvae and later as completely or partly terrestrial lung- and skin-breathing adults (Stebbins and Cohen, 1997). The gills used for breathing during larvae development are typically lost later in their development. However, there are some permanently larval amphibians that retain their gills (Stebbins and Cohen, 1997). Examples of these species are the mudpuppies *Necturus*,

whereas the eel-like *Siren intermedia* is a permanently gilled species, which also has elongated lungs (Stebbins and Cohen, 1997). Lungs present in many amphibians can also serve as hydrostatic organs that aid in the control of buoyancy (Stebbins and Cohen, 1997). A common feature, of most amphibian animals, is the pulsation of the throat regardless of the respiratory mechanism (Stebbins and Cohen, 1997; Beebee, 1996). This technique increases the flow of water or air, thus resulting in exchanging higher O₂ concentrations at low energy cost.

The similarity between the natural respiring mechanisms of aquatic or amphibian animals, and the O₂-cathode MFC is that both systems are vital mechanisms to 'harvest' oxygen which is then employed as the terminal electron acceptor in metabolic reactions either in tissue cells or at the end of the MFC electron transfer process. This is discussed further, after a brief introduction into the MFC technology.

3 O₂-cathode Microbial Fuel Cells (MFCs)

Microbial Fuel Cells (MFCs) are energy transducers that convert biochemical energy into electricity. This technology has been in its present existence (analytical form) for about 3 decades [Bennetto *et al.* 1984]. It was only until recently, however, that MFC technology was first introduced as a potential onboard power source for mobile robots [Wilkinson, 2000].

In terms of analytical laboratory work, several synthetic compounds have been employed, in both the anode and cathode compartments, to investigate the improvement of energy output in these systems. One such enhancement is the addition into the cathode compartment, of a highly oxidative agent, called ferricyanide. This chemical substance offers excellent short-term characteristics in consuming the electrons generated at the anode electrode and keeping the redox-cycle system balanced, however it is consumed during the processes. In terms of robotic autonomy, therefore, employing ferricyanide would be a limiting factor, as it requires frequent replacement to maintain system viability.

The O₂-diffusion cathode has been extensively employed by many workers in the field of MFC research as an alternative to the chemically-based systems [Kang *et al.* 2003; Kim *et al.* 2003; Chang *et al.* 2004; Liu *et al.* 2004; Liu and Logan, 2004; Min and Logan, 2004; Moon *et al.* 2004; Oh *et al.* 2004; Logan *et al.* 2005]. This is mainly due to the superior standard redox properties that O₂ possesses, as it is one of the most electropositive molecules in nature and for many aerobic reactions the ultimate end-terminal electron acceptor. When assembled in the MFC cathode configuration, due to the sub-optimum gas diffusion rates at the electrode stage, the performance of this system is (for the short term) inferior to the chemically enhanced cathode systems. Nevertheless, it is a system which requires no replenishment and can, in theory, remain operational for prolonged periods, therefore potentially suitable for autonomous robots.

3.1 EcoBots-I and -II

It was previously shown that a primitive form of autonomy could be exhibited by EcoBot-I and -II robots powered by MFCs [Ieropoulos *et al.* 2003; 2005a,b; Melhuish *et al.* 2006]. EcoBot-II was a robot powered by O₂-based MFCs, in which the anodic bacterial cultures were fed with dead flies [Ieropoulos *et al.* 2005a,b; Melhuish *et al.* 2006]. This robot was able to perform temperature and light sensing, information processing, communication of the processed information and actuation based on the sensed light intensity [Ieropoulos *et al.* 2005a,b; Melhuish *et al.* 2006].

3.2 Comparison between the natural and artificial systems

In the first instance of natural respiration, O₂ is supplied (via Hb) as the 'fuel' for oxidation to occur and provide the required energy for life (Lagler *et al.* 1977). The O₂ intake depends on the gas diffusion rates at the gill surface-stage, which is the extraction of gaseous O₂ from the liquid stream that greatly depends on the affinity of Hb in the blood. High Hb affinity, can work with low O₂ concentrations, whereas low Hb affinity requires high O₂ concentrations to drive the oxidative reactions in the tissues. This is an indication of the highly adaptive abilities of aquatic organisms, which also allows them to survive conditions of hypoxia. The O₂ gas transfer is greatly enhanced by the extremely efficient design-structure of the gills, which incorporate high surface areas in small volumes.

The role of the O₂-diffusion system in an MFC is somewhat similar in the sense that, it provides the means for O₂ supply to drive the oxidative reactions at the cathode half-cell. Although it does not provide the necessary energy for (bacterial) life, it is vital in order to keep the MFC system working. Furthermore, the material size and conformation of the cathode electrode, are important parameters governing the affinity of the system to O₂ concentrations and also the O₂ diffusion rates into the system. In contrast to Hb in the blood stream of aquatic respiring organisms, there is no 'carrier' for the O₂ molecules in this MFC system, since the oxidation reactions are taking place at the cathode surface. In effect, the carrier of O₂ is the incoming water. Finally, the electrode configuration was of a high surface area-to-volume ratio to maximize oxygen availability. In the following section, the materials and methods employed in the O₂-cathode MFC work, are described.

4 Experimental setup

4.1 Part I: Fresh sludge MFCs

Four MFCs were employed in total for the purposes of the first part of this investigation. Two of them were of the fully open-to-air cathode as shown in Figure 1a and the remaining two were of exactly the same type and size, however with a closed chamber for the cathode as shown

in Figure 1b. These 4 units were seen as appropriate for investigating the various possible under or near water operation scenarios. Using the closed-chamber MFCs (with water inflow and outflow ports) it would be possible to examine the properties of cathode electrodes fully submerged in both running and standing water. On the other hand, the open-to-air cathode would 'indicate' the effects of evaporation when the electrode is to be periodically moistened. In the case of continuous flow, this could be more efficient than the closed chamber with the excess weight of the entrapped water and vessel wall. This is a question to be addressed in the future.



Figure 1: a) Left: MFC with the cathode half-cell open-to-air, b) Right: MFC with the closed chamber cathode half cell

The volume of the anode chamber, which was the same for the cathode chamber in the case of the closed cathode MFCs, was 25mL. In all four MFCs the bacterial cultures employed as the bio-catalyst were of the types found in anaerobic sewage sludge and were fed with 5mM acetate as the CE (carbon energy) source.

For both the anode and cathode half-cells, the electrodes employed were carbon-fibre veils, with a macro surface area of 270cm² (PRF Composites, Dorset, UK). In the case of the cathodes (see Fig. 1) filter paper of the same surface area, as the electrode, was folded inside the carbon-fibre veil, to enhance the moisture retention (Wattman, UK). A 2.7k Ω resistive load was connected across the terminals of all four MFCs. The proton-exchange-membranes (PEM) used in this experiment were of the cation-exchange type (VWR, Leicestershire, UK).

The four MFCs were placed in a sink downstream from running tap water which continuously flowed over the open-to-air and into the enclosed-chamber cathodes. The first of the two open-to-air cathode MFCs was periodically moistened (denoted as per-moist), using a 3mL pipette, at the same time that the water flow was on. This was to compare the effects of continuously running water over an open cathode as opposed to a small stationary amount of water, sufficient to keep the electrode moistened.

The temperature of the running water was manually controlled (by mixing flows of hot and cold water) and measured with a TENMA® 72-6870 data logger, using the manufacturer's waterproof temperature probe (TENMA, Centerville, Ohio, OH 45459). The same temperature water was used to manually moisten the open

cathode of the (per-moist) MFC. Figure 2 below shows pictures from the MFC experimental setup.

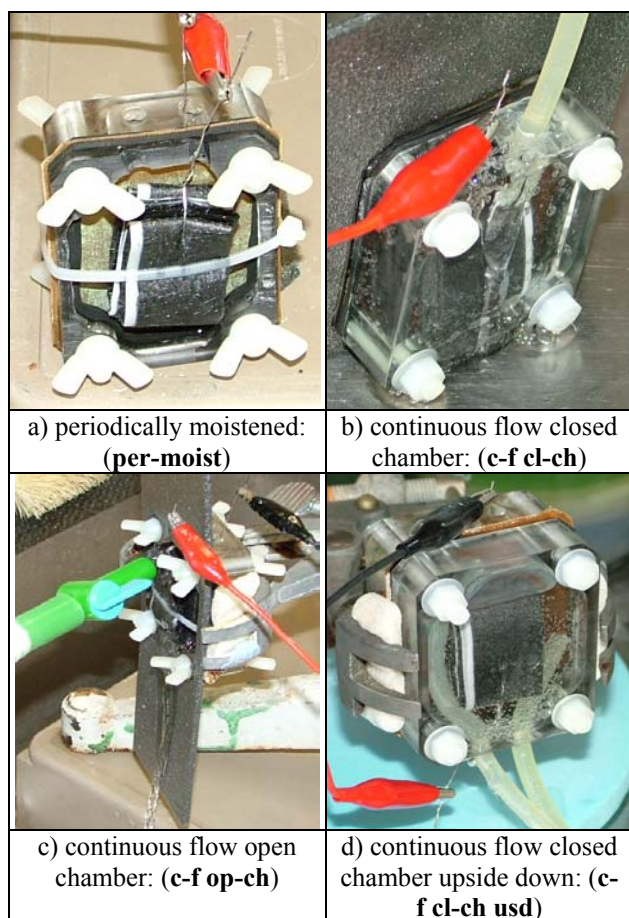


Figure 2: Experimental setup

4.2 Part II: Adapted (mature) sludge MFCs

Sludge cultures, which have adjusted to the MFC environment for a period of 3-4 weeks, are referred to as mature cultures and tend to produce higher levels of energy as a result of both adaptation and ecological enrichment. In this second part of the experiment, the aim was to investigate the MFC output profile, in a similar scenario (i.e. downstream of running tap water, see Fig 2c), when cultures of this more powerful anode biocatalyst type were employed. This would allow the investigation to be repeated with cultures producing a higher output level.

Two MFCs containing adapted sludge cultures, with an age of ~4 weeks, under continuous MFC operation, were therefore employed. This means that these sludge-based MFCs had been continuously connected to a resistive 2.7kΩ load, for a period of 4 weeks, during which time they were periodically fed (once a week) and spent medium replaced.

The electrode material and surface area were the same as with Part-I of the experiment and the substrate fed was again 5mM acetate.

4.3 Data collection and analysis

The analogue data produced by the MFCs was recorded on a Windows® running pc, via the Pico ADC-16 hardware interface and using the PicoLog software (PicoLog 5.13.9, PicoTech, Cambridgeshire, UK).

Current, power and internal resistance values were calculated as previously described (Ieropoulos *et al.* 2005c). The area under curve (AUC) and non-linear regression curve fits were performed using the GraphPad Prism® 4.0 statistical analysis software (GraphPad, San Diego, CA 92130, USA). The coefficient of variation was calculated by dividing the standard deviation by the mean average of the mean I_{out} values.

The main aim in both Parts-I and -II of the experiment was to observe the effect of the supply and disruption of water, at the cathode electrode, on the MFC output performance.

5 Results

The first parameter investigated was the open-circuit (no load) voltage ($V_{o/c}$) output from each of the MFCs. This would establish the maximum voltaic output that could be achieved by such units operating in a river. It was also used to calculate the internal impedance of the MFCs under hydration ON-OFF conditions. The open-circuit voltage produced by the MFCs, for a period of ~2½ hours of continuous water flow, is shown below in Figure 3.

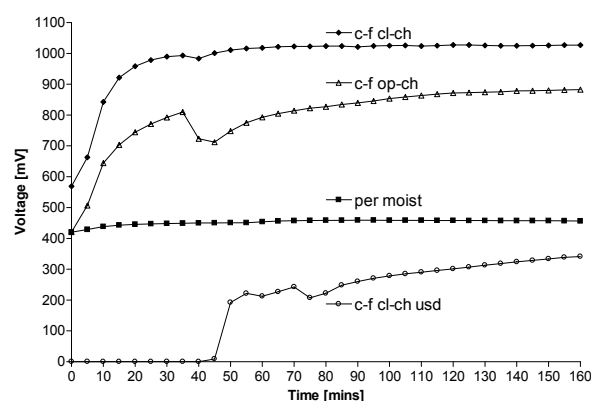


Figure 3: Open-circuit voltage from the O₂-cathode MFCs for the initial 2½ hours

As can be seen from the data in Figure 3, the highest $V_{o/c}$ was recorded from the closed-chamber MFC (see Fig. 2b), which was approximately 1V. This appears to be the highest $V_{o/c}$ level reported for this type and size of MFC. The output from the open-chamber MFC (see Fig. 2c) was ~0.9V, (87% of the highest). The per-moist MFC (see Fig. 2a) output was ~50% of the highest, at a value of 0.45V and finally the $V_{o/c}$ from the c-f cl-ch usd (see Fig. 2d) was 0.33V (~30% of the highest).

5.1 Hydration ON-OFF effect on the cathode

Subsequent to connecting the resistive load (2.7kΩ), the power output was monitored both under hydration ON

and OFF conditions. Figure 4 below shows the current output (I_{out}) profile from the four MFCs.

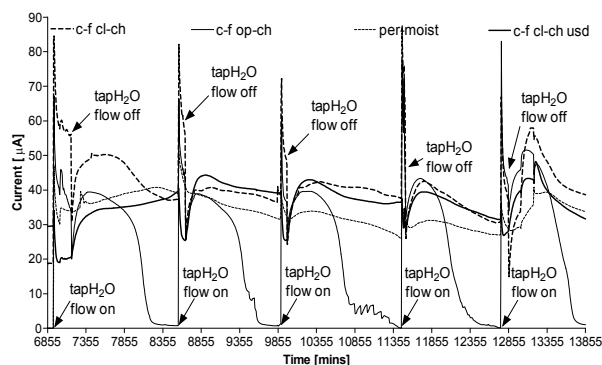


Figure 4: Current (I) output from the four MFCs under hydration ON-OFF conditions.

The mean I_{out} , during this repeated hydration ON-OFF cycles, from the two closed cathode chamber MFCs was $40\mu A$. The mean I_{out} from the periodically open-to-air cathode MFC was 63% of this value, i.e. $25\mu A$. For the open-to-air cathode with continuous hydration, the I_{out} was only 38% (i.e. $15\mu A$) of the maximum produced by the closed chamber MFCs.

The mean current (I_{mean}) and power (P_{mean}) output values for the total duration of the experiment, together with the internal resistance values (R_{INT}) of each MFC, are shown below in Table 1.

The experiments were run continuously for 2 weeks and on some occasions (overnight and weekends) the cathodes became sufficiently dehydrated that output was temporarily halted as shown in Figure 5. This was taken into account when calculating the mean current and power values for these two MFCs by setting a baseline current value of $10\mu A$.

MFC type	I_{init} [μA]	I_{mean} [μA]	P_{mean} [μW]	R_{INT} [$k\Omega$]
per-moist	20.51	30.07	2.54	8.26
c-f cl-ch	71.15	39.02	4.65	4.90
c-f op-ch	48.94	38.67	4.44	5.74
c-f cl-ch usd	9.00	34.89	3.53	6.74

Table 1: Mean current and power output values from the MFCs together with the calculated internal resistance

The maximum difference between the current outputs from the 4 MFCs was less than 20%, with the minimum being at 5%. In terms of the mean power output, the difference between the maximum ($4.65\mu W$) and minimum ($2.54\mu W$) was 45%. The lowest R_{INT} ($4.90k\Omega$) was recorded from the c-f cl-ch (see Fig. 2b), which had a 15% difference from the closer value recorded from the c-f op-ch ($5.74 k\Omega$) and a 40% difference from that recorded for the per-moist ($8.26 k\Omega$).

The data in Figure 5 illustrate the effect of total cathode dehydration. In both open-to-air cathode MFCs, the current decreased to zero (as is also shown in Figure 4

for c-f op-ch MFC). The coefficient of variation for the area under the curve (AUC) was 7.42%.

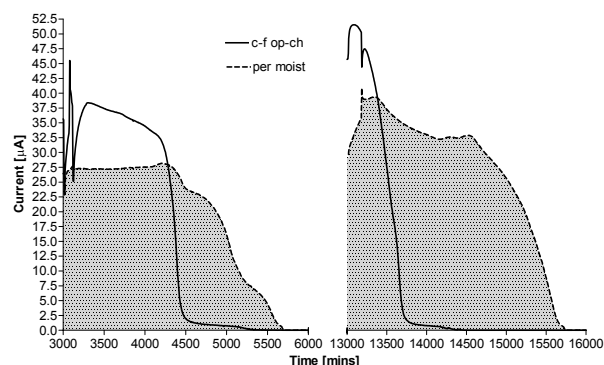


Figure 5: Current output decreasing to zero as a result of cathode desiccation. AUC coefficient of variation was 7.42%.

5.2 Temperature effect on cathode

The temperature of the running water was manually controlled to establish a response profile from the various MFC cathode setups. The water temperature for these experiments ranged between $13^{\circ}C$ - $51^{\circ}C$.

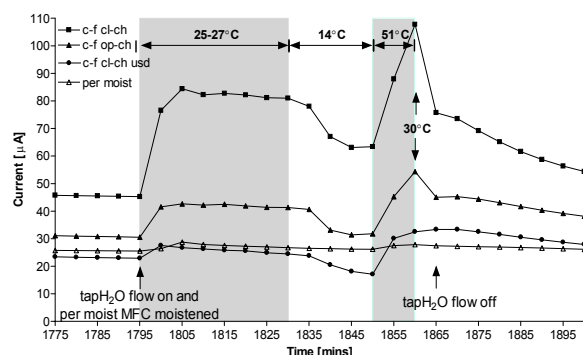


Figure 6: Temperature effect on the different MFC cathodes.

The data in Figure 6 show a 97% increase in the current output of the c-f cl-ch usd MFC and a corresponding 80% increase from the c-f cl-ch and c-f op-ch MFCs, as a result of a $37^{\circ}C$ increase in temperature.

Figure 7 shows the c-f op-ch MFC overall I_{out} profile with respect to temperature, recorded for the total duration of the experiment. As can be seen from the data, the MFC output increased, in response to water temperature increases, thus producing a direct relationship.

5.3 Flow rate effect on cathode

The effect of water flow rate on the cathode was investigated, simply to establish a relationship between this parameter and the MFC output. This was carried out in a qualitative manner but was necessarily performed on approximations of increase or decrease in the flow rate, since an accurate and quantifiable flow of water could not

be established without the employment of a fluidic pump. The flow of water was manually controlled from the water tap, with an approximate gauge (20mL syringe placed in line), to roughly indicate non-quantified increases or decreases in flow, in terms of water level in the syringe. This also served to oxygenate the water.

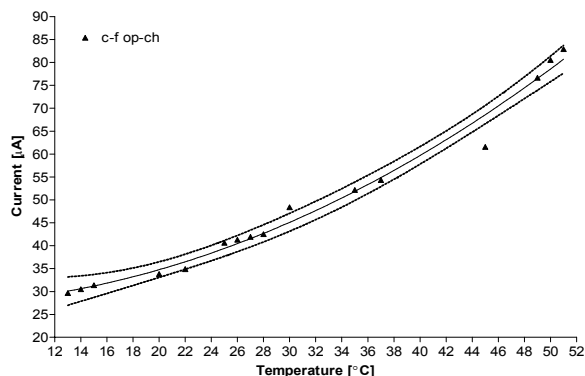


Figure 7: Relationship between MFC current output and water temperature, with non-linear regression fit (solid line) and 95% confidence interval (CI) (dotted lines).

Figure 8, illustrates the response from the four MFCs when the flow rate was ‘doubled’.

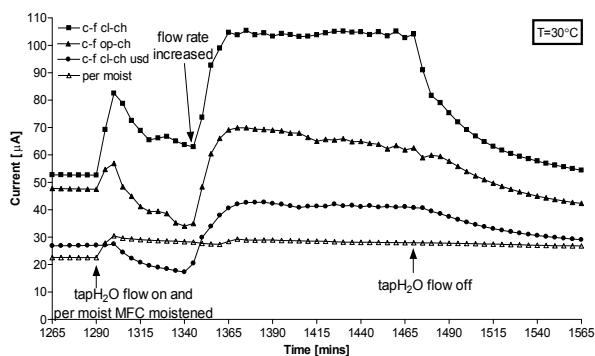


Figure 8: MFC I_{out} response as a result of an increase in the water flow rate. The temperature was kept constant at 30°C.

The highest I_{out} increase was recorded from the c-f cl-ch used MFC, which was 165%, followed by a 100% increase given from the c-f op-ch MFC and a corresponding 84% increase from the c-f cl-ch MFC. These were responses to a water flow rate ‘doubling’ (i.e. 100% increase according to the syringe gauge).

The overall relationship, between the MFC I_{out} and the water flow rate, was produced for the open-to-air cathode MFC and is shown in Figure 9. These data illustrate a direct relationship between the water flow rate and the MFC I_{out} , with a total increase of 100% recorded between the lowest and highest flow rates.

5.4 Part-II: Adapted (mature) sludge

In the final stages of the investigation, the open-to-air cathode experiments were repeated with an adapted sludge consortium, in order to test the response to hydration

ON-OFF cycles, at a higher output level. Figure 10, shows the current output from the two open-cathode MFCs, similar to the ones employed in the first part of the investigation (see Fig. 2c).

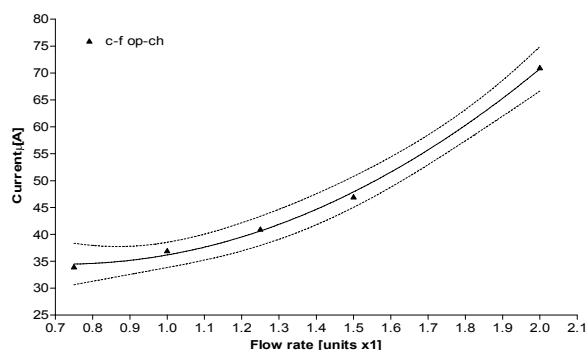


Figure 9: I_{out} and H_2O flow rate relationship for the op-ch MFC, with non-linear regression (solid line) and 95% CI (dotted lines).

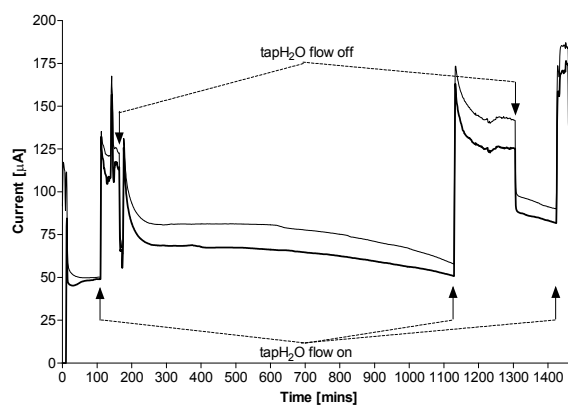


Figure 10: MFC I_{out} response to hydration ON-OFF cycles, at a higher output level.

As can be seen from Fig. 10, a similar response was recorded from both the open cathode MFCs, containing the mature-adapted sludge. The coefficient of variation between the mean I_{out} from the two MFCs was 6.55%, with the highest mean being at 93 μ A (for the total duration) and 147 μ A (only for the hydration duration). The total duration mean output was 2.4-fold higher than that recorded from Part-I of the investigation (39.02 μ A).

6 Discussion

The open circuit voltage ($V_{o/c}$) data recorded from the 4 different MFCs, show a good redox reaction system, with a maximum output value of 1V and a minimum of 0.3V. This is an indication of the force with which electrons will flow, and obviously the higher it is, the better is the MFC output performance. The large variation (coefficient of variation was 100%) existing between the two closed chamber systems, could be attributed to the fact that at the initial stages of the investigation, the water circulation and mixing, into the upside-down chamber was inadequate. This would have probably resulted in a ‘dead-space’ volume of H_2O in which the mixing was slow thus

resulting in low O_2 diffusion rates. This explanation is further strengthened by the fact that the continuous hydration of the open and closed cathode MFCs, resulted in further increases in the $V_{o/c}$.

The calculation of the internal resistance (R_{INT}) was based on the mean value of the $V_{o/c}$ and that of the initial current (I_{init}) under load. The mean values for both the aforementioned parameters were calculated for the same period of time, which was sufficient for a steady-state to be reached. The R_{INT} value is an indication of the internal ability of the system to resist the flow of electrons, and consequently limit the magnitude of the current or power output. In this work, the highest R_{INT} value was recorded from the per-moist cathode MFC, which was probably utilising the O_2 molecules available in free air, in contrast to the continuously hydrated MFCs, of which the cathodes were utilising the increased amounts of O_2 molecules found in the oxygenated tap water. This may have resulted in less amounts of O_2 diffusing through the cathode electrode of the per-moist MFC, which therefore increased the R_{INT} of the system.

In both the per-moist and c-f open-to-air cathode MFCs, the effect of total dehydration (desiccation) was detrimental, resulting in zero current output. In the crudest possible comparison, this is akin to the effect that desiccation has on amphibians, if they happen to be in an arid environment. Although it may seem, that the per-moist MFC was more resistant to dehydration (see Figs. 4 and 5), the total area under the curve (AUC) calculations suggest otherwise. The coefficient of variation between the AUC for these two MFCs, was 7.42%, which indicates that a similar mean level of output was produced, even though the c-f op-ch MFC was dropping much more frequently to zero. This was mainly due to the high magnitude of the current output bursts, produced from this MFC upon re-hydration that compensated for the decreases of current to zero.

The main thrust of this study is in the long-term implementation of energy extraction from the environment and O_2 -utilization, into a practical application, with a level of autonomy similar to that of animals. MFCs are not at present the perfect solution to the problem of energy onboard autonomous robots, especially since the capacity of these devices can be as low as 12mA/h. However, as shown with EcoBots I and II, it is possible to successfully trade-off continuous operation with a pulsed-motion behavior. Moreover, even with low energy output, tasks such as sensing, processing, communication and actuation can be performed (see EcoBot-II).

For autonomous robots employing MFCs with O_2 cathodes, water retention seems to be very important, which is again similar to the real situations faced by amphibians. As described in Section 2, there are a number of behavioral, physiological and structural mechanisms that these animals employ to tolerate loss of water. One design feature that could be employed in the development of autonomous robots, (akin to what toads and salamanders possess), would be the incorporation of a micro-channel structure, at the lower part of the robot and

extending to trail, which by capillary action could be drawing water from the wet floor, to be driven into or onto the O_2 cathodes.

According to Henry's law, the concentration of gas in a liquid is inversely proportional to the temperature of the liquid. This is mainly to do with the partial pressure of the gas in the gas phase and the coefficient of solubility (or Henry's constant). It effectively means that less O_2 is present in water at higher temperatures. However, the investigation into the effect of water temperature on MFC I_{out} , showed that the output increased in response to increases in the water temperature (see Fig. 6). This was most probably due to three different reasons: a) the increase in the rate of diffusion reaction at the electrode surface, b) the temperature gradient created between the anode and the cathode that served as a thermo-junction for energy transfer and c) the increase in the metabolic reaction rate of the anodic bacteria as a result of the increase in temperature by conductance. All three counter-acted the decrease in the O_2 concentration that was expected to decrease the MFC output performance. Underwater robots powered by MFCs could exploit these effects by seeking warmer water which either increases metabolic rates in the anodic biocatalyst, increases the temperature differential between the two electrodes and, if the robot used plankton as its bio-mass source, benefit from better feeding opportunities.

During the hydration flow rate experiments (constant temperature) a direct relationship between flow rate parameter and the MFC I_{out} was recorded. Since a temperature gradient was no longer contributing to the MFC output, the increase in power was probably due to higher mass transfer of O_2 molecules diffusing through the electrode. Although the approach was rather crude, the hydrostatic volume in the syringe varied in response to the flow rate, thus giving a semi-quantitative measure of the flow rate as well as providing aeration upon the turbulent mix. Furthermore, the results collected were sufficient to produce the useful relationship function.

In a biological agent such as an aquatic animal, the increase in the demand for energy production, required by a high energy-consuming function (e.g. predator avoidance) is met by an increase in the rate of respiration. In this case O_2 mass transfer and CO_2 removal rates are increased at the tissue level of the animal. It is assumed that the relationship between the hydration flow rate and MFC I_{out} is of a similar nature. This can be useful in the design of MFC-powered underwater robots, in which the water supply mechanism to the cathode of the onboard MFCs can be linked – via feedback loops – to the central processing unit, governing the behavior of such agents.

The final part of these experiments, was carried out with the open-to-air cathode MFCs, containing mature-adapted sludge. In these experiments, it was shown that the MFC I_{out} was 2.4-fold higher than that produced from the same MFCs during the initial stages of this work, with a mean value of $138\mu A$ ($5.1mA/m^2$) during hydration. These results show that relatively high and improved levels of current output can be produced, even from a non-modified O_2 -cathode system (non-chemically

modified or metalized electrodes) which is generally inferior when compared with the ferricyanide cathode system. Since the O₂-cathodes do not require any replacement of liquid electrolytes, this makes them favorable for autonomous robots.

7 Conclusions and further work

This work investigated the possibility of exploiting MFCs with aqueous O₂-cathodes as artificial gills for autonomous robots. The findings from this work show that these systems behaved in a manner akin to aquatic respiration via gills and therefore suggest that this type of MFC could be advantageously employed in the development of autonomous robots. It was found that there was an average of 65-fold and 5-fold (see Fig. 4) I_{out} increase from the open-to-air and closed-chamber MFCs, respectively when hydrated after dehydration. This illustrates the positive hydration effect on the energy production aspect of MFCs, which can be related to the O₂-diffusion rate. It was also found that temperature and flow rate have a significant effect on the MFC output. Such effects may be usefully exploited by robots seeking warmer water and possibly anchoring themselves to maximise current flow over the 'cathode gill'.

The fact that agents designed primarily for terrestrial operations, utilizing biomass found on land, could also beneficially utilize oxygenated water found in rivers or in the sea, may lead to the design of a new class of artificially amphibious robots.

As part of our team's future work, the artificial gill characteristics of the aqueous O₂-cathode MFCs will be further explored. It is envisaged that these units will be implemented as part of the design of an underwater autonomous robot.

References

- Beebee, T., J., C. (1996). *Ecology and Conservation of Amphibians*. Chapman and Hall. ISBN: 0412624109.
- Chang, I. S., Jang, J. K., Gil, G. C., Kim, M., Kim, H. J., Chob, B. W., Kim, B. H. (2004). Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. *Biosensors and Bioelectronics*, 19:607–613.
- Gilmour, K., M. (1998). Gas Exchange, in *The Physiology of Fishes*, 2nd Edition. Evans D., H., Ed. CRC Press. ISBN: 084384273.
- Hughes, G., M. (1984). General Anatomy of the Gills, in *Fish Physiology*, Vol. XA. Hoar, W., S. and Randall, D., J., Eds. Academic Press.
- Ieropoulos, I., Melhuish, C. and Greenman, J. (2003). Artificial Metabolism: Towards True Energetic Autonomy in Artificial Life. In *Proceedings of the 7th European Conference in Artificial Life (ECAL 2003)*, pages 792-799.
- Ieropoulos, I., Melhuish, C., Greenman, J. and Horsfield, I. (2005a). Artificial symbiosis: Towards a robot-microbe partnership. In *Proceedings of Towards Autonomous Robotic Systems (TAROS '05) Conference*, pages 89-93.
- Ieropoulos, I., Melhuish, C., Greenman, J. and Horsfield, I. (2005b). Artificial symbiosis: Towards a robot-microbe partnership. In *Proceedings of Towards Autonomous Robotic Systems (TAROS '05) Conference*, pages 89-93.
- Ieropoulos, I., Greenman, J., Melhuish, C. and Hart, J. (2005c). Comparison of three different types of microbial fuel cell. *Enzyme and Microbial Technology*, 37(2):238-245.
- Kang K. H., Jang J. K., Pham T. H., Moon H., Chang I. S. and Kim B. H. (2003). A microbial fuel cell with improved cathode reaction as a low biochemical oxygen demand sensor. *Biotechnology Letters*, 25:1357-1361.
- Kim, M., Youn, S. M., Shin, S. H., Jang, J. G., Han, S. H., Hyun, M. S., Gadd, G. M. and Kim, H. J. (2003). Practical field application of a novel BOD monitoring system. *Journal of Environmental Monitoring*, 5:640-643.
- Lagler, K., F., Bardach, J., E., Miller, R., R. and May Passino, D., R. (1977). *Ichthyology 2nd Edition*. John Wiley and Sons. ISBN: 0471024899.
- Liu, H., Ramnarayanan, R. and Logan, B., E. (2004). Production of electricity during wastewater treatment using a single chamber microbial fuel cell. *Environmental Science and Technology*, 38(7):2281-2285.
- Liu, H. and Logan, B., E. (2004). Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environmental Science and Technology*, 38(14):4040-4046.
- Logan, B., E., Cassandro, M., Scott, K., Gray, N., D. and Head, I., M. (2005). Electricity generation from cysteine in a microbial fuel cell. *Water Research*, 39:942-952.
- Melhuish, C., Ieropoulos, I., Greenman, J. and Horsfield, I. (2006). Energetically Autonomous Robots: Food for Thought. *Autonomous Robots*, DOI: 10.1007/s10514-006-6574-5.
- Min, B. and Logan, B., E. (2004). Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. (2004). *Environmental Science and Technology*, 38(21)5809-5814.
- Moon, H. Chang, I. S., Kang, K. H., Jang, J. K. and Kim, B. H. (2004). Improving the dynamic response of a mediator-less microbial fuel cell as a biochemical oxygen demand (BOD) sensor. *Biotechnology Letters*, 26:1717–1721.
- Moon, H., Chang, I. S. and Kim, B. H. (2006). Continuous electricity production from artificial wastewater using a mediator-less microbial fuel cell. *Bioresource Technology*, 97:621–627.
- Oh, S., Min, B. and Logan, B., E. (2004). Cathode Performance as a Factor in Electricity Generation in Microbial Fuel Cells. *Environmental Science and Technology*, 38:4900-4904
- Stebbins, R., C. and Cohen, N., W. (1997). *A Natural History of Amphibians*. Princeton University Press. ISBN: 0691102511.
- Wilkinson, S. (2000). "Gastronome" – A Pioneering Food Powered Mobile Robot. In *Proceedings of the 2000 IASTED Int. Conference on Robotics and Applications*, Paper # 318-037.