Marine floating microbial fuel cell involving aerobic biofilm on stainless steel cathodes

B. Erable [a,*], R. Lacroix [b], L. Etcheverry [a], D. Féron [c], M.L. Delia [a], A. Bergel [a]

[a] Laboratoire de Génie Chimique, CNRS, Université de Toulouse, 4 allée Emile Monso, 31029 Toulouse, France
[b] 6T-MIC Ingénieries, 4 rue Brindejonc des Moulinais, 31500 Toulouse, France
[c] SCCME, CEA Saclay, Bat 458, 91191 Gif-sur-Yvette, France

HIGHLIGHTS

The seawater depth has a big impact on the power density (by modelling study).
Our first generation of marine floating marine MFC gave approximately 20 mW/m^2.
The floating MFC performance was very sensitive to seawater temperature variations.
The performance stability was 1–2 months depending on the current supplied.

Keywords:
Microbial fuel cell
Seawater
Microbial anode
Microbial cathode
Stainless steel

ABSTRACT

Here is presented a new design of a floating marine MFC in which the inter-electrode space is constant. This design allows the generation of stable current for applications in environments where the water column is large or subject to fluctuations such as tidal effects.

The operation of the first prototype was validated by running a continuous test campaign for 6 months. Performance in terms of electricity generation was already equivalent to what is conventionally reported in the literature with basic benthic MFCs despite the identification of a large internal resistance in the proposed design of the floating system. This high internal resistance is mainly explained by poor positioning of the membrane separating the anode compartment from the open seawater.

The future objectives are to achieve more consistent performance and a second-generation prototype is now being developed, mainly incorporating a modification of the separator position and a stainless steel biocathode with a large bioavailable surface.

1. Introduction

Benthic MFCs, described for the first time in 2001, were at the origin of the attention that is currently turned towards the topic of MFCs as a whole. This kind of fuel cell typically consists of a graphite anode embedded in anaerobic marine sediments and connected, through an electrical circuit (e.g., a marine scientific instrument or capacitor), to a cathode set up in the overlying aerobic seawater (Reimers et al., 2001; Tender et al., 2002). A main feature of marine MFCs is their sustainability, which is attributed to the constant supply of fuel and oxidant by environmental processes, typically derived from the settling of dead phytoplankton and/or plant debris, and the constant regeneration of the microbial electrode catalysts.

Since 2001, the performance of benthic MFCs has been constantly optimised. Initial benthic MFCs implemented in marine sediments with plain graphite electrodes sustained power densities of around 20 mW/m^2 of anode surface area for 4 months, with maximal values up to 28 mW/m^2 (Tender et al., 2002). A similar laboratory system, with graphite fibre anode and cathode, provided around 10 mW/m^2 for 240 days (Reimers et al., 2001). Performances continued to increase when the electrode configuration has evolved from a planar to a three-dimensional structure (Wei et al., 2011). With a carbon brush cathode, the power density reached 34 mW/m^2 for 125 days (Reimers et al., 2006). To the best of our knowledge, the highest power densities that have been provided by field benthic MFCs have been reached with graphite anodes modified with charge transfer mediators (Lowy et al., 2006): 1,6-disulphonic acid (AQDS)-modified graphite and graphite-ceramic containing Mn^{2+} and Ni^{2+} have given maxima of 98 mW/m^2 at the cell voltage of 0.24 V, and 105 mW/m^2 at 0.35 V, respectively. This performance has been matched by a Benthic MFC implemented with a stainless steel cathode supplying around 100 mW/m^2 for 45 days (Dumas et al., 2008a).

In terms of applications, benthic MFCs have been largely investigated with the goal of operating low-power-consuming

* Corresponding author. Tel.: +33 (0) 534323623.
E-mail address: benjamin.erable@ensiacet.fr (B. Erable).

marine instrumentation, such as oceanographic sensors, monitoring devices and telemetry systems as has already been done by Shantaram et al. (2005) in fresh water (Shantaram et al., 2005). In 2008, Tender et al. (2008) described the first demonstration of a marine MFC as a practical alternative to batteries for a low-power-consuming application. To generate enough power for the telemetry system, energy produced by the microbial fuel cell was stored in a capacitor and used in short bursts when needed. The specific application reported was a meteorological buoy (about 18 mW average consumption) measuring air temperature, pressure, relative humidity, and water temperature, that was configured for real-time telemetry of data. The prototype sustained 36 mW power equivalent to 26 alkaline D-cells per year at 25 °C.

Despite the rusticity of the technology, a significant limitation of the power delivered by benthic MFCs is evident when the inter-electrode spacing (i.e. anode–cathode distance) increases. For example, in the case of oceanic implantation, the large distance between the electrodes (corresponding to the depth) can drastically affect the power output of the benthic MFC as demonstrated in Section 3.1 below. A parallel can be made with the work of Ghangrekar and Shinde (2007) which showed for the first time the influence of the spacing between the electrodes on the performance of a membrane-less MFC.

To minimise the ohmic loss due to the anode–cathode spacing, a new type of marine MFC has been developed based on the floating MFC concept already described by An et al. (2010) and Huang et al. (2012). This new design of a marine floating MFC, working with a constant inter-electrode spacing of 15 cm, is very interesting for areas subject to variations in the height of the water column (tidal phenomena). In addition, a cell working with a floating system can benefit from the "natural" agitation created by the movement of the waves, which can promote mass transfer within the anodic compartment.

A prototype of floating MFC was tested in Atlantic Ocean coastal waters during a six-month campaign. The microbial anodes were prepared in the laboratory from wild marine biofilm while the aerobic cathodes were built directly on site in open seawater. A test size was used in order to (i) assess the relevance of the design and (ii) evaluate the robustness of this first generation of "floating" MFCs in real conditions.

2. Methods/experimental work

2.1. Electrodes

The electrodes were 15 × 20 × 0.1 cm plates of 254SMO stainless steel (Fe 56.1%, Cr 19.9%, Ni 17.8%, Mo 6%, N 0.2%) or 10 × 20 × 0.5 cm plates of dimensionally stable anode (DSA®, Electro Chemical Service). DSA® are common industrial anodes made of titanium covered with iridium and tantalum oxides. Before the experiments, the stainless steel plates were cleaned with 50–50% ethanol/acetone to dissolve organic adsorbed species, and then with a 2–20% fluoridric/nitric acid solution to remove the oxide layer. DSA® material was electrolysed at 200 A/m^2 for 5 h in 0.1 M H_2SO_4 with a platinum grid (90% Pt-10% Ir, Platecxis) as auxiliary electrode. The Ag/AgCl reference electrode was made with a 1.5-mm-diameter silver wire dipped into an HNO_3 solution and then immediately transferred into saturated KCl.

2.2. Electro-active biofilm formation under constant electrode potential

Before being implemented in the floating MFC, the bioanode and biocathode were prepared in independent experiments under constant potential polarisation (chronoamperometry) as already described in recent studies (Erable and Bergel, 2009; Erable et al., 2009a,b).

2.3. Microbial anodes

Microbial anodes were developed in 500-mL reactors containing 250 mL seawater supplemented with acetate, 10 mM final concentration, and inoculated with 250 mL of marine biofilm samples using a conventional three-electrode system implemented with a multi-potentiostat (VMP2 Bio-Logic SA, software EC-Lab v.8.3, Bio-Logic SA). The reactors were closed hermetically, without any gas flow. The DSA working electrodes were embedded vertically down to the bottom of the reactor and the electric contact was made with a titanium wire. The auxiliary electrode was a 20 cm^2 surface area platinum grid. The potential of the anodes was fixed at −60 mV/Ag–AgCl. From time to time, the chronoamperometry was stopped and voltammetry was performed in situ on the active anodes. The potential was scanned from the open circuit potential to 0 mV/Ag–AgCl at a scan rate of 10 mV s^{-1}.

2.4. Aerobic marine biocathodes

Aerobic microbial cathodes were formed in natural seawater in the port of La Tremblade, France. Stainless steel electrodes were immersed in open seawater for one month (December 2007) under constant polarisation (low current potentiostat, Sycopel, UK). The seawater characteristics were: 9 °C < temperature < 11 °C; 6 mg/L < dissolved oxygen < 8 mg/L; 36‰ < salinity < 39‰. An Ag–AgCl electrode and a 400 cm^2 graphite electrode were used as reference electrode and auxiliary electrode respectively. The potential of the stainless steel working electrodes was fixed at −200 mV/Ag–AgCl as described by Erable et al. (2009b). Electrical connections between electrodes were made with titanium wires (diameter 2 mm) directly screwed onto the electrodes.

2.5. Floating MFC prototype

The floating MFC was 30 cm in diameter and 40 cm high. In its initial configuration, the anodic compartment of 600 mL was attached to a ring-shaped buoy. This anodic compartment was sealed and contained 2 DSA® electrodes (2 × 200 cm^2) immobilized vertically through guides made in PVC. The bottom of the anodic compartment was removable and it hosted a proton exchange membrane (Nafion 117, 12.5 cm^2). Septa with four nozzles were located on the top of the anodic chamber (1.5 cm diameter) for adding fuel or taking samples. On the outside, two stainless steel electrodes (2 × 300 cm^2) were attached to the anodic core. These stainless steel electrodes were fixed by Teflon® nuts screwed directly on the core of the anodic compartment. Current was collected from the stainless steel electrodes by waterproof cables insulated with a high strength epoxy resin.

A secondary polystyrene box (10 × 12 × 9 cm) contained a reference electrode (Ag–AgCl) to follow the cathode potential and a set of different resistances to characterise and connect the MFC. This floating box was attached directly to the float of the MFC.

2.6. Performance measurements

When the microbial anode was placed in the anodic compartment of the floating MFC and connected through an external electrical resistance, the voltage of the fuel cell (ΔV) and the potential of the cathode (E_C) versus the Ag–AgCl reference electrode were monitored using a data acquisition system (mobile data logger, Data HOG, Skye, Wales). Electrochemical polarization curves were plotted by varying the external resistance over a range from 1 to

10 kΩ. The potential of the microbial anode was calculated as $E_A = E_C - \Delta V$.

3. Results and discussion

3.1. Modelling of a conventional benthic MFC performance

In order to evaluate the water depth limit beyond which it is not possible to use a conventional benthic MFC, a modelling study of a benthic MFC was conducted using Comsol Multiphysics (R) v3.2. A two-dimensional system with two electrodes of the same size (width 10 cm) arranged parallel to one another was considered. The bioanode was buried under 10 cm of sediment. The biocathode was located in the overlying seawater, with a water depth ranging from 10 to 100 m as shown in Fig. 1A. The total width used to define the geometry of the system in the software was 50 cm (Fig. 1A).

The AC module incorporated in the software was used to calculate potential and current density distribution in the electrolyte (seawater and sediments) as well as cathodic and anodic currents. Conditions in the electrolyte and at the boundaries of the system had to be defined in order to perform a simulation. In the electrolyte, the relationship between the current and the potential was Ohm's law:

$$\vec{J} = -\sigma\overrightarrow{grad}(E) \quad (1)$$

With J: Current density vector (A m^{-2}), E: potential (Volts) and σ: conductivity (S m^{-1}).

Two values of conductivity were considered: a sediment layer conductivity of 5.0 S m^{-1} and a seawater conductivity of 5.3 S m^{-1}.

The kinetics of cathodic and anodic reactions were used as boundary conditions at the surface of the electrodes. These kinetic data were based on experimental results (potential-intensity curves) available in the literature (sediment bioanode (Dumas et al., 2007, 2008b); seawater biocathode (Erable et al., 2009b). Polynomial equations were used to fit the boundary conditions expression in the model with experimental data (data not presented). The polynomial curve (model) and the experimental curve were superimposed. The zero current condition was used for the other boundaries.

After defining the conductivities of the kinetic parameters, the final data used as an input variable in the software was the voltage (difference between anodic and cathodic potentials) expressed in volts. The range of potential values varied from 0 to 0.32 V. Fig. 1B shows an example of the modelled potential distribution with a seawater depth of 10 cm and a voltage of 0.2 V. The anodic and cathodic current densities, calculated by the software, were both equal at 159 mA m^{-2}. The power of the microbial fuel cell was then 31.8 mW m^{-2} in these conditions.

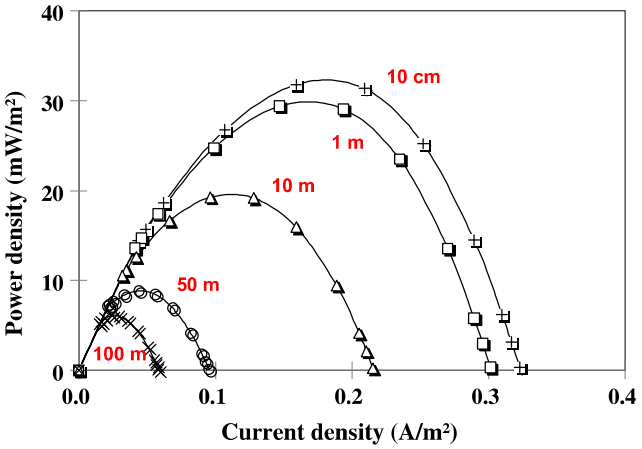

Fig. 2. Modelling of the influence of seawater depth (anode–cathode distance) on the power and current density output of a conventional benthic MFC.

Several simulations were carried out with voltages ranging from 0 to 0.32 V and seawater depths ranging from 10 to 100 m. For each simulation, the power of the MFC was calculated. The influence of seawater depth on the power density of the MFC is presented in Fig. 2.

The power output was evaluated to be maximum, around 32 mW/m^2, when the water column was 10 cm deep and was five times less when the water depth increased to 100 m. This demonstration of the performance limitation of a benthic MFC when the spacing between the electrodes becomes too high was encouraging to think about a new design in which the spacing between the electrodes would be minimal and mostly constant. This reflection has led to propose the concept of a floating marine MFC as precisely described in Section 2.5. Here, the anode compartment contains anaerobic microbial anodes prepared in the laboratory from wild biofilm. The anode compartment is maintained at the surface of the sea water with a buoy. The aerobic microbial cathodes based on stainless steel material are exposed to the open seawater surface to take maximum advantage of the saturating concentration of O_2 present in the upper layers of sea water.

Electro-active biofilms were first established independently on the anode and the cathode surfaces one month before running the floating marine MFC. Then, a field study of electrical performance of this MFC was conducted for 6 months (January–July).

3.2. Acetate-oxidising biofilm formation in bioelectrochemical reactor

The electro-active anodic biofilm development was driven by constant electrode polarization in laboratory conditions using a

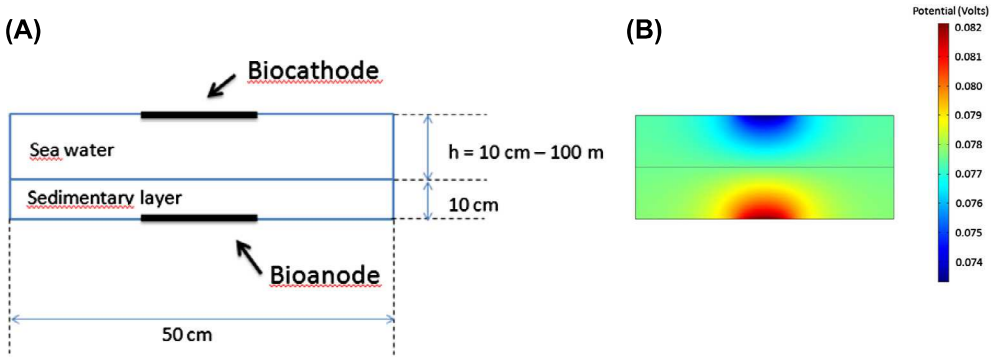

Fig. 1. (A) Definition of the geometry of the system for benthic MFC modelling. (B) Electrode potential distribution in sediments and seawater layers (V = 0.20 V and h = 10 cm).

wild marine biofilm collected from an inert surface as inoculum. Using a natural, already established biofilm as inoculum rather than the marine sediments commonly used in studies performed in marine environments (Tender et al., 2002; Dumas et al., 2007) has been shown to lead to more efficient microbial anodes (Erable et al., 2009a). Dimensionally stable anode (DSA®) was chosen for the anode material because of its robustness and its low ohmic resistance. This titanium-based material is corrosion resistant and is basically used in industry to replace graphite in aggressive environments (Trasatti, 2000). Moreover, DSA® has already been demonstrated to be a suitable material support for forming a microbial anode with *Geobacter sulfurreducens* (Dumas et al., 2008a).

Concretely, two DSA® electrodes, each 200 cm^2 in area, were polarised at −0.06 V/Ag–AgCl in seawater) in a 500 mL bioelectrochemical reactor containing 10 mM acetate natural seawater inoculated with the marine biofilm sample. The electrical current generated by the development of an electro-active biofilm on one of the DSA® electrode surfaces was then followed by chronoamperometry ($I = f(t)$). After two days of latency, the current began to grow exponentially and reached a maximum current density of 2.5 A/m^2 at day 5. Every day, chronoamperometry was stopped and the free potential (or open circuit potential (OCP)) of the microbial electrode was followed. During the anodic biofilm growth, the open circuit potential (OCP) of the microbial anode decreased from +90 mV/Ag–AgCl (observed on day 1) to −410 mV/Ag–AgCl (observed on day 6). Note, here, that these two microbial anodes were kept at fixed potential for a further 3 weeks and fed with successive additions of 10 mM acetate up to their implantation in the anodic compartment of the floating MFC. Voltammetry ($I = f(E)$) was also performed with the microbial anode before implantation in order to evaluate its bioelecrochemical performance. At open circuit, the potential of the microbial anode was −440 mV/Ag–AgCl. A current density greater than 4.0 A/m^2 was obtained for an electrode potential close to 0 mV/Ag–AgCl.

No particular care was taken in the transport and handling of these microbial anodes on site as Erable and Bergel (2009) have demonstrated that this kind of electro-active biofilm is not significantly inhibited by the presence of oxygen.

3.3. Oxygen reducing biofilm formation in open seawater

Unlike microbial anodes, the stainless steel cathodes had their marine aerobic biofilms developed directly on site, i.e. in open seawater. For that, two stainless steel electrodes (2 × 300 cm^2) were exposed and polarised at −0.2 V/Ag–AgCl in the surrounding seawater, i.e. in the most oxygenated layer of the seawater column. The electrode potential was fixed at −0.2 V/Ag–AgCl because this value had already been determined as the most efficient for the development of marine aerobic biofilms capable of catalysing oxygen reduction (Bergel et al., 2005; Faimali et al., 2008). This kind of electro-active aerobic biofilm has already been microbiologically characterised by Vandecandelaere et al. (2010). Bacterial communities isolated from the stainless steel microbial cathode were phylogenetically highly diverse. DGGE analysis also revealed the presence of phyla such as *Alpha-* and *Gamma-proteobacteria*, *Firmicutes*, *Flavobacteriaceae* or *Actinobacteria*. All these phyla have been commonly described in microbial population analyses of the surrounding seawater and are not really specifically found in electro-active biofilms.

Practically, the stainless steel cathodes were polarised using a portable potentiostat available on site throughout the month of December. During the polarization period, the cathodes were already fixed to the buoy. Although winter is not the most favourable season for the development of microbial biofilm, daily measurements showed a constant increase of the stainless steel cathode OCP starting from the 2nd week of constant polarization (data not shown). Slow development of aerobic biofilm continued for two more weeks until a maximal constant value of OCP of about +300 mV/Ag–AgCl was reached in the first days of January, i.e. after one month of exposure to seawater. After the establishment of the oxygen reducing biofilm on stainless steel electrode surface, the microbial cathode was able to sustain a stable current density of 100 mA/m^2.

3.4. On site measurement campaign of "floating MFC" performance

The first measurement campaign started in January (midwinter in France). The floating MFC prototype was located in the estuary port of La Tremblade, Charente-Maritime, France.

In January, the two microbial DSA® anodes were transferred, with the anodic medium, from the laboratory-scale bio-electrochemical reactor to the anodic compartment of the floating MFC. The anodic compartment received 10 mM of acetate and was sealed to maintain anaerobic conditions. Immediately, an open circuit voltage (OCV) of 180 mV was recorded (Fig. 3). This value was far below the theoretically expected value of about 750 mV (Theoretical voltage: $OCP_{cathode} - OCP_{Anode}$ = +300 mV − (−450 mV) = 750 mV). The microbial anode's transfer was suspected of being partly responsible for the decline in its electro-activity. Possible ohmic loss due to the design of the prototype was also considered despite the high conductivity of the seawater (47.934 mS/cm, 20 °C). A polarization curve ($I = f(voltage)$) was recorded the first day by varying the external resistance and a maximum power of less than 0.05 mW was obtained, corresponding to 1.25 mW/m^2 with respect to the anode surface area. At the same time, the short circuit current was measured at 1.4 mA, corresponding to 35.0 mA/m^2 (Fig. 4 12 January). The MFC was left on site with anodes and cathodes connected through an external resistor of 1000 Ω. The voltage under external load and the OCV of the MFC were followed periodically. Both of them improved gradually over the weeks, reaching maximum values of 170 and 690 mV respectively at the end of the winter (middle of March). A polarization curve recorded at this period showed a maximal power of 0.25 mW (6.25 mW/m^2) and a maximal current of 2.0 mA (50.0 mA/m^2) (Fig. 4 02-March).

After the first two months of floating MFC operation, technical problems related to the aggressive environment, such as corrosion

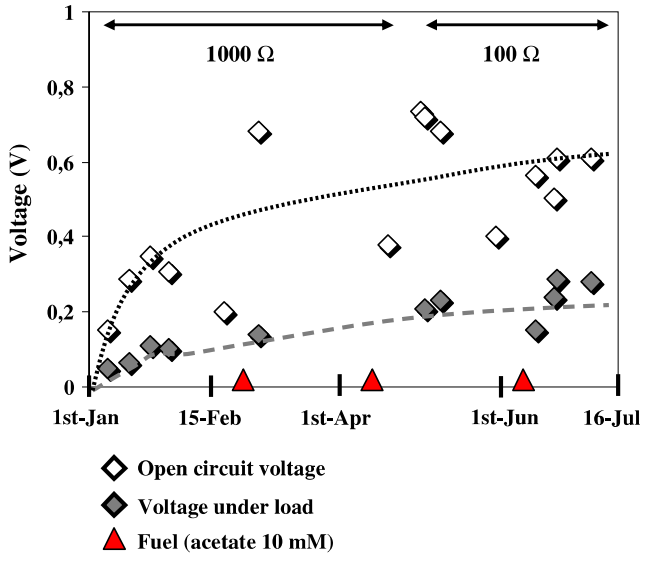

Fig. 3. Voltage output of the "floating" MFC under 1000 or 100 Ω external load and open circuit voltage (OCP) vs. time during the 6-month experimental campaign (January–July).

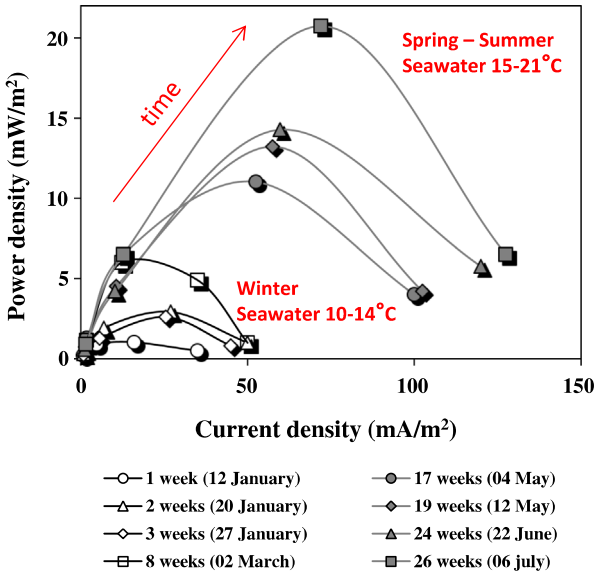

Fig. 4. Polarization curves (power vs. current) obtained with different external resistances (10–10,000 Ω) applied between the electrodes of the "floating" MFC.

of electrical connections, disturbed the sequence of measurements. All connections that were poorly insulated or not totally covered with resin had to be wired again with new connectors, which involved an interruption of the measurement campaign for about one month. When the prototype was returned to its original place, the performance of the stainless steel microbial cathodes was found to have collapsed dramatically (OCP = −20 mV/Ag–AgCl) suggesting that the aerobic biofilm was no longer active even though the cathodes had been carefully kept in contact with seawater during the whole stand-by period. The stainless steel electrodes were then cleaned coarsely and polarised again at −200 mV/Ag–AgCl in open seawater. Their OCP reached +300 mV/Ag–AgCl after only 10 days, certainly because the temperature of seawater was more favourable for microbial growth kinetics (April water temperature = 15.0 °C). Also, pioneer bacteria initiating the start of the biofilm development had not been completely removed from the surface of the electrode (Erable et al., 2009b). This 2nd generation of aerobic biofilm allowed the microbial cathodes to sustain a stable current density close to 120 mA/m^2.at −200 mV/Ag–AgCl.

The measurement campaign restarted at the beginning of April. The OCV of the floating MFC observed the 1st day of electrode connection was 390 mV. The polarization curve for the 1st day of connection highlighted a very low power output from the floating MFC. The performance was limited by the slow kinetics of the microbial anode, explained by substrate depletion (data not presented). Accordingly, the anodic compartment was fed with 10 mM acetate and the MFC was then connected with a 1000 Ω external resistance. After two days, the OCV was still close to 400 mV but the maximal power and the maximal current given by the MFC were 0.44 and 4.0 mA respectively, i.e. 11.0 and 100 mA/m^2 (Fig. 4 04 May). A week later (12 May), the OCV reached 670 mV and the MFC voltage exceeded 200 mV under 1000 Ω external load (Fig. 4 12 May). The corresponding polarization curve led to a maximal power output of 0.51 mW (12.75 mW/m^2). These quantities were monitored and remained quite stable for 3 days, then the external resistance was decreased to 100 Ω.

Changing the external load to 100 Ω resulted in a loss of 400 mV on floating MFC voltage and the corresponding voltage at 100 Ω was 120 mV. The current at 100 Ω was consequently 1.2 mA (30 mA/m^2). The voltage at 100 Ω increased weakly by 40 mV in 5 days reaching 160 mV. Finally, the voltage quickly collapsed due to the lack of fuel in the anodic compartment (420 mV on 30 May). The addition of substrate (10 mM acetate) immediately led to a sharp increase in both the OCV and the voltage under 100 Ω (Fig. 3). Both values improved significantly over the period from June to mid-July, benefiting from the warming of the seawater, to reach an OCV and a voltage under 100 Ω of 590 and 270 mV respectively on 06 July. The polarization curve confirmed the enhanced performance since a maximal power of 0.85 mW (21.25 mW/m^2) was recorded (Fig. 4 06 July), representing eight times the maximum power delivered by the fuel cell in the middle of the winter.

The coulombic efficiencies for each 10 mM acetate additions are low on the winter period (max 1.2% for the second addition of acetate), especially because the external resistance is quite high (1000 Ω) and the reactions are slow on the electrodes. However, the coulombic efficiency improved with warmer period, it reached almost 15%, but with a smaller external resistance (100 Ω) which accelerates the electron transfer at the electrode – biofilm interface.

The electrochemical behaviour of the microbial anodes and the microbial cathodes was compared by *I*/*E* curve analysis over the different seasons (Fig. 5). The comparison of the *I*/*E* curve slopes showed an improvement in performance over time for both microbial electrodes. An improvement in the bioelectrochemical catalysis of acetate oxidation on the microbial anode can be clearly observed, since the slope of the *I*/*E* curve was multiplied by three during the 26 weeks of study. In the same way, the performance of the microbial cathode also tripled between January and July. The main hypothesis to justify these gains in catalytic activities was the warming of the sea water, with an estimated 10 °C temperature rise between March and July, which resulted in an activation of the microbial kinetics. The rate of biofilm formation was found to depend on the ambient seawater temperature, which varied with the season. Coastal seawater temperatures vary between 10 and 21 °C, depending on the time of year. This variation can affect the marine biofilm performance in two ways: by increasing the microbial density on electrode surface (cells/m^2) and/or by affecting the biological activity of the cells themselves. According to Melo and Bott (1997), the growth and development of micro-organisms forming biofilms are dependent on nutrient availability, water flow rate and temperature. In warmer seas,

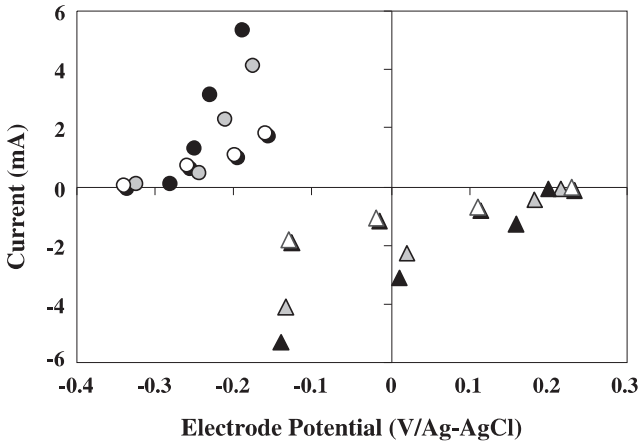

Fig. 5. Behaviour of electrode potentials during polarization performed with different external resistances (10–10,000 Ω) applied between the electrodes of the "floating" MFC after 8 weeks (white), after 19 weeks (grey), and after 26 weeks (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

biofilm formation/biofouling takes place at all times of the year whereas, in the temperate waters, biofouling is pronounced only during the warmer months. For example, on 254 SMO stainless steel, Shams El Din et al. (1996, 2003) showed that biofilm formation in seawater accelerated with rising temperature within the range 23–40 °C, which was attributed to the increase in the activity of the micro-organisms. Biofilm development during the cold months (winter) required longer times. As the seawater warmed up, the formation of biofilms on passive metal occurred readily during the summer season (June–September). Consequently, the final steady-state potential acquired by the stainless steel surface also depended on the season, being higher (more positive) when the seawater was warmer.

3.5. Performance

For this first generation of floating marine MFC, the maximal performance (approximately 20 mW/m^2) was comparable to the average performance reported with the first generation of benthic MFCs. The electrochemical kinetics of both microbial cathodes and anodes were, however, different from those usually observed in studies on benthic MFCs, such as that reported by Dumas et al. (2007), in whose work the power density of 23 mW/m^2 was limited by the low effectiveness of the microbial anode. In contrast, the power output of the floating MFC was really limited by the performance of the microbial cathode. The floating MFC performance has been described as extremely influenced by the seawater temperature, the floating MFC being very sensitive to seawater temperature variations during the different seasons (Winter vs. Summer). A warming of the seawater by 11 °C from February to July resulted in an 8-fold increase of the power generated by the floating MFC.

The performance stability was interesting since the addition of acetate provided an operating period of 1 to 2 months depending on the current supplied by the MFC. One critical point of the floating system is the necessity for external inputs of substrates in contrast to the independent functioning of conventional benthic MFCs. But the target applications will probably be different.

3.6. Future generation of marine floating MFC

The study performed with the first generation of floating marine MFCs has validated the concept but also highlighted several negative points that will have to correct if performance is to increase rapidly:

Internal resistance – First, it is clear that the membrane was not ideally positioned. Despite the high conductivity of sea water, the ion exchanges between the anode and cathode compartments were not optimal. In the present configuration, the sedimentation of solid particles (bacteria, inorganic wastes, etc.) associated with the development of a microbial biofilm on the membrane surface can be expected to contribute significantly to the increase of the internal resistance of the MFC (lower conductivity in sediments vs. in seawater). In the future, it may be worthwhile to work with a cleaner anolyte in the anodic compartment (fewer solid particles). Also, the membrane should be moved from the bottom to the side of the anodic compartment and its surface area should be increased. The Nafion® PEM used in the 1st floating MFC prototype should be replaced by a less expensive separator. Ideally, it should be completely removed.

Cathodic limitation – Second, it has been demonstrated that the performance of the microbial cathode was responsible for limiting the power generated by the floating MFC. Based on the specific kinetics of each microbial electrode, the ratio between the electrode surface areas implemented should be optimised. When the size of the microbial cathode is increased, considerable thought will have to be given to the geometry of these electrodes and their positions relative to the anodic compartment and the membrane. In parallel, there are plans to increase the kinetics of the stainless steel cathode through a return to the lab-scale experiment to work on a different grade of steel or increase the specific surface area with foam or other 3D structures.

4. Conclusion

Modelling study has clearly shown that the classic scheme of the benthic MFC has no interest when the anode–cathode distance becomes too high (over 1 m).

The idea of working with a constant anode–cathode distance through the use of a floating marine MFC has been validated. Although the design is not yet optimised, the first prototype is already producing power densities comparable to the best benthic MFC (approximately 20 W/m^2). Several points limiting performance, due to the configuration of the MFC and especially the separator implemented, have been identified. Future work will focus on changing the design of the cell.

Acknowledgements

This work was a part of the French ANR "bactériopiles" project (ANR - NT05-3_43343). The authors gratefully thank Mr J.C. Erable for access to the marine site.

References

An, J., Lee, S.J., Yong, Ng.H., Chang, I.S., 2010. Determination of effects of turbulence flow in a cathode environment on electricity generation using a tidal mud-based cylindrical-type sediment microbial fuel cell. J. Environ. Manage. 91, 2478–2482.

Bergel, A., Féron, D., Mollica, A., 2005. Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm. Electrochem. Commun. 7, 900–904.

Dumas, C., Mollica, A., Féron, D., Basseguy, R., Bergel, A., 2007. Marine microbial fuel cell: uses of stainless steel electrodes as anode and cathode materials. Electrochem. Acta 53, 468–473.

Dumas, C., Basseguy, R., Bergel, A., 2008a. DSA to grow electrochemically active biofilms of *Geobacter sulfurreducens*. Electrochim. Acta 53, 3200–3209.

Dumas, C., Mollica, A., Féron, D., Basseguy, R., Etcheverry, L., Bergel, A., 2008b. Checking graphite and stainless anodes with an experimental model of marine microbial fuel cell. Bioresour. Technol. 99, 8887–8894.

Erable, B., Bergel, A., 2009. First air-tolerant effective stainless steel microbial anode obtained from a natural marine biofilm. Bioresour. Technol. 100, 3302–3307.

Erable, B., Roncato, M.A., Achouak, W., Bergel, A., 2009a. Sampling natural biofilms: a new route to build efficient microbial anodes. Environ. Sci. Technol. 43, 3194–3199.

Erable, B., Etcheverry, L., Delia, M.L., Vandecandelaere, I., Faimali, M., Bergel, A., 2009b. Marine aerobic biofilm as cathodic catalyst. Bioelectrochemistry 78, 51–56.

Faimali, M., Chelossi, F., Garaventa, F., Corrà, C., Greco, G., Mollica, A., 2008. Evolution of oxygen reduction current and biofilm on stainless steels cathodically polarised in natural aerated seawater. Electrochim. Acta 54, 148–153.

Ghangrekar, M.M., Shinde, V.B., 2007. Performance of membrane-less microbial fuel cell treating wastewater and effect of electrode distance and area on electricity production. Bioresour. Technol. 15, 2879–2885.

Huang, Y., He, Z., Kan, J., Manohar, A.K., Nealson, K.H., Mansfeld, F., 2012. Electricity generation from a floating microbial fuel cell. Bioresour. Technol. 114, 308–313.

Lowy, D.A., Tender, M.L., Zeikus, J.G., Park, D.H., Lovley, D.R., 2006. Harvesting energy from the marine sediment–water interface II: Kinetic activity of anode materials. Biosens. Bioelectron. 21, 2058–2063.

Melo, L.F., Bott, T.R., 1997. Biofouling in water systems. Exp. Therm. Fluid Sci. 14, 375-38.

Reimers, C.E., Tender, L.M., Fertig, S., Wang, W., 2001. Harvesting energy from the marine sediment–water interface. Environ. Sci. Technol. 35, 192–195.

Reimers, C.E., Girguis, P., Stecher III, H.A., Tender, L.M., Rychelynck, N., Whaling, P., 2006. Microbial fuel cell energy from an ocean cold seep. Geobiology 4, 123–136.

Shams El Din, A.M., Saber, T.M.H., Hammoud, A.A., 1996. Biofilm formation on stainless steels in Arabian Gulf water. Desalination 107, 251–264.

Shams El Din, A.M., El-Dahshan, M.E., Tag El Din, A.M., 2003. Bio-film formation on stainless steels Part 2. The role of seasonal changes, seawater composition and surface roughness. Desalination 154, 267–276.
Shantaram, A., Beyenal, H., Veluchamy, R.R.A., Lewandowski, Z., 2005. Wireless sensors powered by microbial fuel cells. Environ. Sci. Technol. 39, 5037–5042.
Tender, L.M., Reimers, C.E., Stecher III, H.A., Holmes, D.E., Bond, D.R., Lowy, D.A., Pinobello, K., Fertig, S.J., Lovley, D.R., 2002. Harnessing microbially generated power on the seafloor. Nat. Biotechnol. 20, 821–825.
Tender, L.M., Gray, S.A., Groveman, E., Lowy, D.A., Kauffman, P., Malhado, J., Tyce, R.C., Flynn, D., Petrecca, R., Dobarro, J., 2008. The first demonstration of a microbial fuel cell as a viable power supply: powering a meteorological Buoy. J. Power Sources 179, 571–575.
Trasatti, S., 2000. Electrocatalysis: understanding the success of DSA®. Electrochim. Acta 45, 2377–2385.
Vandecandelaere, I., Nercessian, O., Faimali, M., Segaert, E., Mollica, A., Achouak, W., De Vos, P., Vandamme, P., 2010. Bacterial diversity of the cultivable fraction of a marine electroactive biofilm. Bioelectrochemistry 78, 62–66.
Wei, J., Liang, P., Huang, X., 2011. Recent progress in electrodes for microbial fuel cells. Bioresour. Technol. 102, 9335–9344.