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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.

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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).

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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