

## *In situ* continuous current production from marine floating microbial fuel cells



Giulia Massaglia<sup>a,b,1</sup>, Valentina Margaria<sup>a,1</sup>, Adriano Sacco<sup>a,\*</sup>, Tonia Tommasi<sup>a,b</sup>,  
Simona Pentassuglia<sup>a,b</sup>, Daniyal Ahmed<sup>a,b</sup>, Roberto Mo<sup>b</sup>, Candido Fabrizio Pirri<sup>a,b</sup>,  
Marzia Quaglio<sup>a</sup>

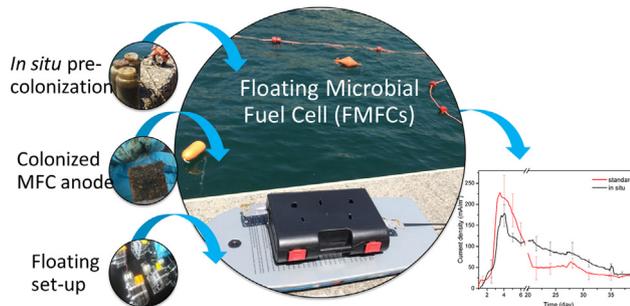
<sup>a</sup> Center for Sustainable Future Technologies @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129 Torino, Italy

<sup>b</sup> Applied Science and Technology Department, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

### HIGHLIGHTS

- Marine floating microbial fuel cells exploited as portable power supplies.
- Novel devices able to continuously produce electricity using seawater as fuel.
- Average power density of 6 mW/m<sup>2</sup> during summertime and wintertime.
- The concept of floating microbial fuel cells Livestock is proposed.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

In order to power remote sensors and/or data transmission devices in an aquatic environment, sedimentary microbial fuel cells and floating microbial fuel cells have been proposed in the literature, representing a continuous source of renewable and sustainable energy. However, both classes of devices are characterized by large dimensions and are immobilized in the environment within which they are working. Accordingly, when portability and small dimensions are strict requirements, these configurations cannot be exploited.

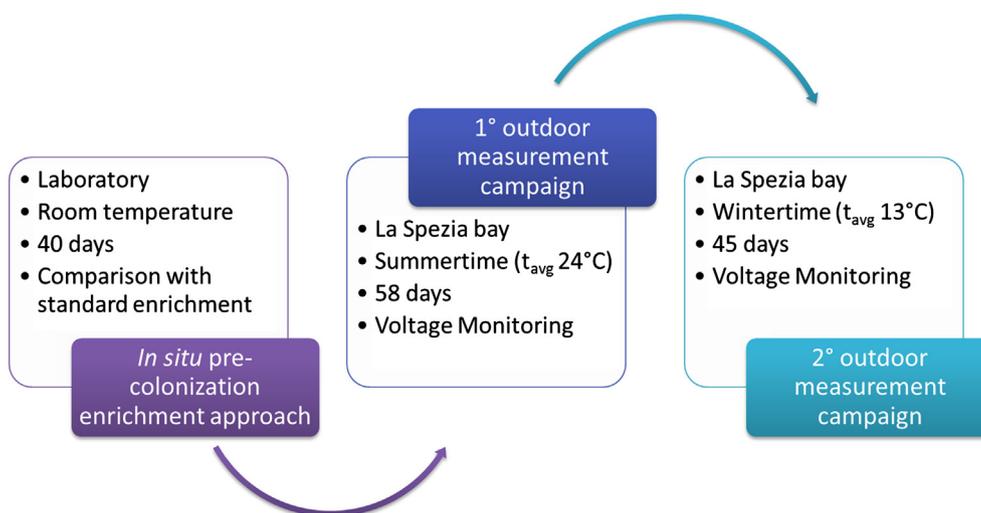
The present work proposes a novel, compact and cost-effective floating set-up based on small-scale microbial fuel cells. A method for *in situ* anodic biofilm formation was validated through experiments conducted in laboratory and in a real marine environment. Carbon felt-based anodic electrodes were used to build different replicas of floating microbial fuel cells. Their overall performance was evaluated during two field measurement campaigns carried out in the Mediterranean Sea. The study demonstrated a high stability of the floating microbial fuel cells even in a real, uncontrolled environment. The devices were able to continuously produce electricity using seawater as fuel and electrolyte.

This study suggests that these devices can be used as portable power supplies for sensors in a complex environment such as the open sea due to the easy preparation of anodic electrodes, together with the simple architecture of floating microbial fuel cells.

\* Corresponding author.

E-mail address: [adriano.sacco@iit.it](mailto:adriano.sacco@iit.it) (A. Sacco).

<sup>1</sup> These authors contributed equally to this work.



Scheme 1. Overview of the structure of the experimental work.

## 1. Introduction

Microbial fuel cells (MFCs) are bioelectrochemical devices that convert the chemical energy stored in organic compounds into electricity [1,2]. They represent a viable and low-cost solution for wastewater treatment, while simultaneously producing electrical energy [3,4]. According to Trapero et al. [5], MFC technology is now ready to enter the market for substituting conventional activated sludge. As opposed to common fuel cells, in MFCs the oxidation of the organic matter is carried out by microorganisms, called exoelectrogens [6], mainly proliferating under anaerobic conditions and usually arranged in the form of a biofilm onto the anodic electrode [7]. At the cathodic electrode, the circuit is closed through a reduction reaction. The most common reaction involves molecular oxygen, which is reduced to water exploiting protons and electrons from the anode. In order to speed up the kinetics of this reaction, a Pt-based catalyst is often employed [8]. When dealing with applications in aquatic environments, sedimentary microbial fuel cells (SMFCs) are usually exploited [9]. In this configuration, the anode is completely buried in sediment, which is rich in organic matter, while the cathode is suspended in overlying water [10]. The anoxic conditions are preserved at the anode due to the presence of the sediment and the device can work for long time with low or null maintenance costs [11]. Usually, SMFCs are characterized by large dimensions [12,13], and thus, after deployment, they are used *in situ* [14]. SMFCs were employed by Tender et al. to supply power to a meteorological buoy in river and salt marsh environments [11]. Arias-Thode et al. fabricated a 30 m-long linear array of SMFCs to power a seafloor magnetometer for the detection of passing ship movements [15]. Zhang and Angelidaki reported the use of a SMFC based on two pieces of bioelectrodes to remove nitrates and nitrites from eutrophic lakes [16]. Nevertheless, SMFCs are characterized by some disadvantages, including low operating voltages [17], large ohmic losses due to a large distance between the electrodes [18], restricted dissolved oxygen availability which limits cathode performance [19] and difficulty in providing continuous power [20]. In order to overcome some of these limitations, floating MFCs (FMFCs) have recently been proposed for aquatic applications, either with wastewater [21] or seawater [22]. This configuration is similar to an air cathode single-chamber MFC [23], in which both electrodes share the same reactor volume, using oxygen from air for the reduction reaction at the cathode [24]. Since FMFCs can float on the water surface, the cathode is directly exposed to air. Moreover, to limit the ohmic losses, the interelectrode distance is reduced. FMFCs with dimensions up to 0.3 m<sup>2</sup> were employed in the denitrification tank of a wastewater plant [21] and in a “floating garden” over a pond [25], to power remote environmental sensors and

data transmission devices.

In all the works described above, the devices were immobilized in the environment in which they worked, either providing power to an external load or acting as water treatment elements. However, portability and small dimensions are strict requirements for several applications, for example when the device to be powered (sensor, instrumentation, etc.) is moving in the water or along its surface. To this aim, this work proposes a novel and compact floating set-up, based on small-scale single-chamber MFCs, able to continuously produce electricity when working in a real marine environment using seawater as fuel and electrolyte. To the best of our knowledge, this is first application of small-scale FMFCs in a real marine environment, in view of a future exploitation as portable power sources for low-power sensors and devices. To minimize manual operation and to exploit the potentiality of the marine biological community as a catalyst [26,27], the present work proposes an *in situ* pre-colonizing enrichment approach and compares it to standard enrichment procedure. Moreover, to boost microbial metabolism, especially during the start-up phase, the anodic electrode is used in conjunction with an agar-based synthetic solid-state electrolyte (SSE), containing carbonaceous and nitrogen sources, recently proposed by our group [28] and employed here for the first time in outdoor experiments. In this configuration, the SSE ensures nutrients for microbial growth and provides a physical filter for O<sub>2</sub>, thus maintaining the anode partially anaerobic. No catalyst layer was applied to the cathodes, allowing the spontaneous formation of an aerobic cathodic biofilm able to carry out the oxygen reduction reaction, like that exploited by Wetser and co-workers [29]. The devices were successfully tested in our laboratory and then in a marine environment in the bay of La Spezia (north of Italy), exploiting a dedicated set-up for data acquisition and transmission. Field tests were repeated twice during summer and winter, in order to investigate the effect of seasonal changes and temperature on the microbial activity and consequently on MFCs’ performance.

## 2. Materials and methods

### 2.1. Structure of the work

The work was structured as described in the following and resumed in Scheme 1. Initially, the *in situ* pre-colonization enrichment approach was validated in laboratory tests. For this purpose, MFCs were fabricated using anodic electrodes prepared through: (1) the novel *in situ* pre-colonization enrichment approach based on seawater sediment (named *in situ* MFCs); (2) a standard enrichment approach performed in laboratory (named standard MFCs). The performance of *in situ* MFCs

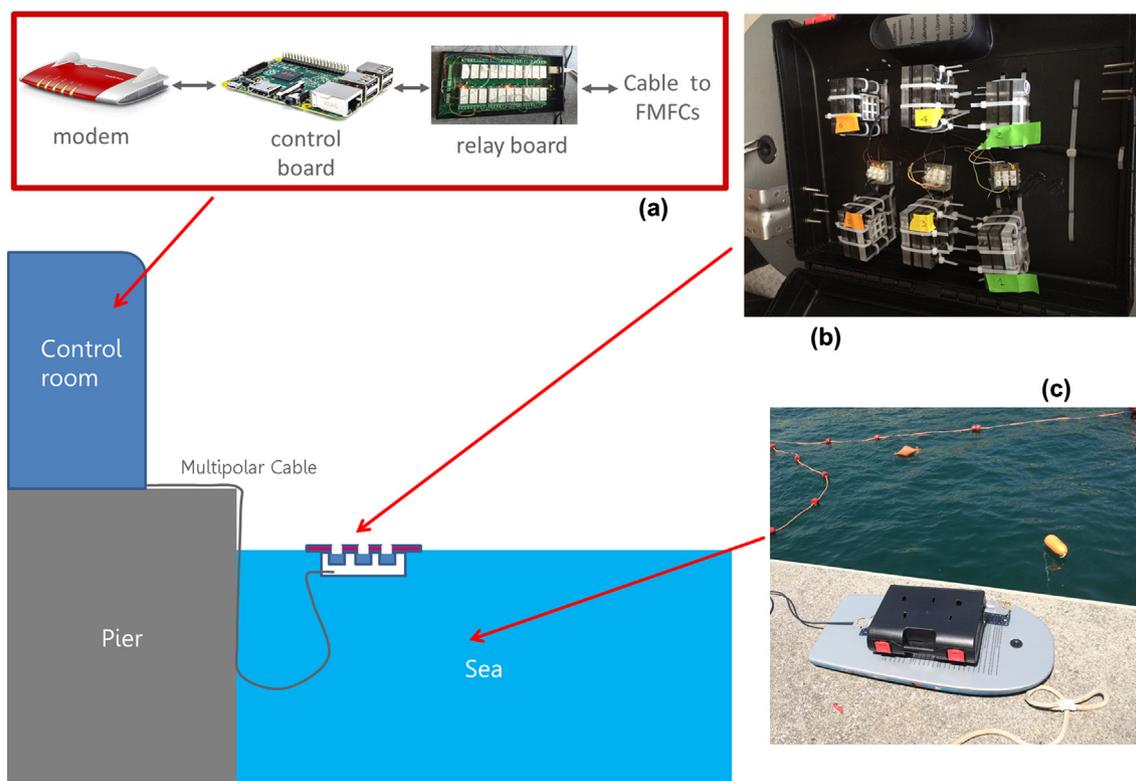


Fig. 1. Sketch of the set-up employed for field tests in the bay of La Spezia: (a) data acquisition system; (b) internal view of the floating set-up; (c) floating housing system (bottom view).

was compared with the one of standard MFCs during a lab experiment, by voltage monitoring (VM) over time with a fixed external load and electrochemical impedance spectroscopy (EIS). Results showed no appreciable difference in the performance of the two types of MFCs. Therefore, *in situ* colonized electrodes have been used during the subsequent tests, in light of the fact that this method enables us to obtain well-working anodic electrodes without the need for time-, energy- and reagent-consuming enrichment processes. Before starting with the field measurement campaigns, six novel devices were prepared using *in situ* pre-colonized electrodes and mounted on a floating housing system. The first campaign was conducted during summertime. The performance of the MFCs was evaluated by VM over time with a fixed external load, for a period of two months. After this, MFCs were moved from the bay of La Spezia to our laboratory for some analyses, and then four out of six devices were re-used for the second measurement campaign. The latter was carried out during late autumn/winter for a period of 45 days.

## 2.2. *In situ* and standard enrichment approaches

All reagents were purchased from Sigma-Aldrich (unless otherwise specified) and used without purification.

*In situ* pre-colonization enrichment approach is based on the formation of the biofilm directly on the material that will be used as the anode in the MFCs, i.e. a commercial carbon felt (Soft felt SIGRATHERM GFA5, SGL Carbon). The setup comprises of a plastic bottle containing seawater sediment collected from the bay of La Spezia (Italy). The carbon felt was buried into seawater sediment and left at 3 m underwater for 1 month. In order to maximize biofilm formation, the felt was previously soaked in PBS containing 2.5 g/L of sodium acetate.

For what concerns the standard colonization enrichment approach, the seawater sediment sample (bay of La Spezia, Italy) was enriched in 250 mL serum bottles containing commercial carbon felts. The liquid medium was based on seawater with dissolved compounds, namely

30 mM (2.5 g/L) of sodium acetate used as carbon source and 5.8 mM (0.75 g/L) of ammonium chloride selected as nitrogen source, able to support the bacterial growth on anodic surface. The microbial cultures were subjected to three sequential enrichments for 1 month of total growth, at room temperature conditions ( $21 \pm 2^\circ\text{C}$ ) and under gentle orbital shaking (150 rpm). At each step, 10% (v/v) of the microbial cultures were inoculated in fresh media.

## 2.3. Microbial fuel cell fabrication

Single-chamber microbial fuel cells with an open-air cathode configuration were fabricated by 3D printing technology (OBJET 30, Stratasys), using a polymeric UV-curable material (polymethyl-methacrylate, PMMA) [30]. The presence of some holes along the PMMA contour allowed the inlet of liquids inside the device. Similar to anodes, cathode electrodes were also made of commercial carbon felt, both having a nominal geometric area of 5.76 cm<sup>2</sup>. Cathodes were modified by applying four polytetrafluoroethylene diffusion layers on the external side of the electrode, as in [30]. Internal volume was 12.5 mL. Ti wires, threaded along each electrode, were employed as current collectors.

The solid-state electrolyte composition was fixed as reported in Supporting Information (SI) (see SI for more details and characterization of SSE). For each MFC, 6 mL of SSE at a temperature equal to 50 °C (liquid state) were poured into a Petri dish until solidification. The SSE was then broken into small pieces and placed onto the anode's surface. A sketch of MFC assembly and some pictures are reported in Fig. S2 of the SI.

## 2.4. Laboratory tests

Three nominally identical MFCs for each biofilm enrichment approach (i.e. *in situ* and standard) were fabricated for the laboratory tests. All the devices were put in a bucket filled with seawater. The level

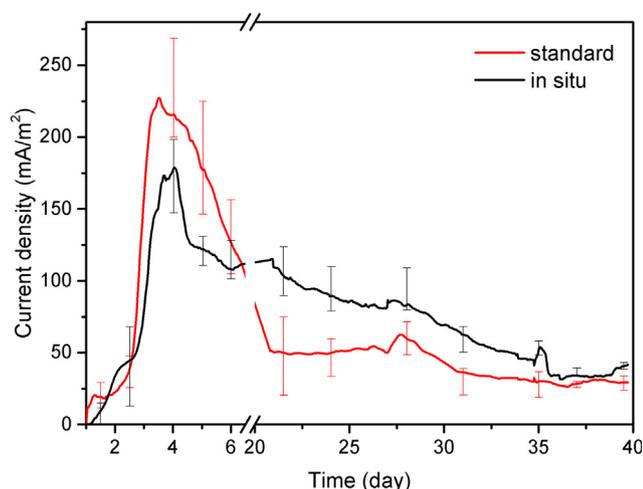


Fig. 2. Current density as a function of time during the indoor tests for MFCs fabricated with anodes colonized with the two enrichment approaches. Each point is the average of data obtained from three nominally identical MFCs, and maximum and minimum values are reported as error bars. The break between days 7 and 20 was due to an electrical black-out.

of liquid allowed cathodes to be directly exposed to air, while the anodes remained completely immersed. The level was maintained constant by refilling with seawater (every 7 days). No additional nutrients were introduced. Laboratory tests were conducted at room temperature ( $21 \pm 2^\circ\text{C}$ ). The performance of MFCs was monitored for a period of 40 days while acquiring the cell voltage across a  $560 \Omega$  resistor using an Agilent 34972A data acquisition unit. After this period, EIS measurements were carried out using a BioLogic VSP potentiostat in 2-electrodes configuration, employing the external resistor method [31], with a load of  $560 \Omega$ ; the AC signal amplitude was 10 mV and the measurement was performed over a frequency range of 10 mHz–20 kHz.

### 2.5. Field tests

Field tests were carried out in the Mediterranean Sea, in a bay near La Spezia (Italy), using a dedicated set-up, sketched in Fig. 1. MFCs were placed in a floating housing system (panel (c) in Fig. 1, described below), which was anchored at a distance of 2 m from the pier. A multipolar cable with protective outer shell (Igus CF9.02.12) was used to electrically connect the cell outputs (cathodes and anodes) to the control room, where the data acquisition system was set-up. The latter consisted of a programmable relay board (Devantech ETH8020), a control board (Raspberry Pi 2 model B) and a modem (panel (a) in Fig. 1). The relay board was equipped with eight data acquisition channels and different resistors, thus allowing the measurement of each MFC voltage over a fixed load. Voltage signals acquired by the different channels were transduced by analog/digital converters and sent to the modem through the control board. A custom software was developed to facilitate the remote acquisition of MFCs' voltage data and the programming of the relay board, using a PC or a smartphone connected to the internet. Inside the floating set-up (panel (b) in Fig. 1), Ti wires corresponding to anode and cathode of each MFC were connected with the wires of the multipolar cable. A thermosetting resin was used to insulate the electrical connections. As a result of this setup, the anodes are always submerged in seawater while the cathodes are constantly exposed to air due to the floating housing system. Therefore, it is evident that these devices belong to the FMFCs category.

The first field measurement campaign was carried out between July 22nd, 2016 and September 18th, 2016 (58 days). For this campaign, six nominally identical MFCs were fabricated employing *in situ* pre-colonized electrodes mounted in a black opaque enclosure. Currents produced by the six devices during the whole period were obtained by

measuring the voltages across fixed  $560 \Omega$  resistors. After the end of the first campaign, MFCs were stored in our laboratories, immersed in seawater, and VM measurements were carried out using an Agilent 34972A data acquisition unit.

The second field measurement campaign was carried out between December 1st, 2016 and January 15th, 2017 (45 days). For this campaign, four out of six MFCs used during the first campaign were re-employed. Currents produced by the four devices during the whole period were obtained by measuring the voltages across fixed  $560 \Omega$  resistors.

Throughout the period of investigation, physico-chemical parameters related to seawater in the bay of La Spezia (temperature, pH, conductivity, salinity and dissolved oxygen) were acquired using a Geoves SMx-485 multiparametric meter. All these parameters are summarized in Table S1 in the SI.

Additional pictures of the experimental set-up and of the measurement campaigns are reported in the Figs. S3 and S4 of the SI.

## 3. Results

### 3.1. Laboratory tests

To investigate the feasibility of the *in situ* pre-colonization enrichment approach for anode preparation, the performance of three *in situ* MFCs was compared with that of three standard MFCs. Results of the VM measurements over time are shown in Fig. 2. During the first four days, after device start up, a substantial increment in electrical power production was observed for both types of cells, with maximum values of about  $18 \pm 2 \text{ mW/m}^2$  and  $10 \pm 3 \text{ mW/m}^2$  for standard and *in situ* MFCs, respectively (corresponding to  $227 \text{ mA/m}^2$  and  $178 \text{ mA/m}^2$ ). This initial rise of current density may be attributed to the presence of carbon and nitrogen sources in the SSE, which helps the biofilm metabolic activity [32]. Vice versa, the drop of current production observed around day 4 can likely be related to the depletion of nutrients within the SSE, consumed during the biofilm formation. Eventually, seawater was the only fuel source remaining, containing a lower concentration of organic compounds with respect to SSE. It is worth noting that starting from the sixth day, performance of *in situ* MFCs appeared to be higher with respect to standard MFCs. This behavior can be explained by considering that *in situ*-developed biofilms are accustomed to grow and proliferate in marine environment, using seawater as nutrient source; on the contrary, standard-enriched microorganisms need to be acclimated into the new environment, and their adaptability resulted to be lower. After 35 days, both kind of devices exhibited quite constant power density values, equal to about  $1.0 \pm 0.3 \text{ mW/m}^2$  and  $0.8 \pm 0.1 \text{ mW/m}^2$  for *in situ* and standard MFCs, respectively; the corresponding current density values are  $40 \text{ mA/m}^2$  and  $33 \text{ mA/m}^2$ .

The results of VM measurements were successfully confirmed by EIS analysis [33,34]. Typical Nyquist plots related to the MFCs fabricated with anodes colonized with the two different methods are reported in Fig. 3. Both impedance spectra exhibit two features, a high-frequency one (on the leftmost part of the graph) related to the cathode polarization, and a low frequency one, related to the anode [32]; no feature related to ionic diffusion was evidenced in these Nyquist plots, probably because it was masked by the large capacitive behavior characterizing the felt electrodes [31]. As evident, both kind of devices exhibit similar cathode resistance: this result was expected, since this electrode is identical in all the fabricated devices. On the contrary, *in situ* MFCs were characterized by slightly lower anodic resistances, in accordance with the above reported VM results. In order to quantitatively evaluate the internal resistances, impedance spectra were fitted through the equivalent electrical circuit shown in the inset. This comprises of: (1) a series resistance  $R_s$  related to the ohmic losses in the devices, (2) a parallel combination of the charge transfer resistance  $R_1$  and the Helmholtz layer capacitance  $Q_1$  (fitted with a constant phase element [35]) accounting for the cathodic process and (3) a parallel

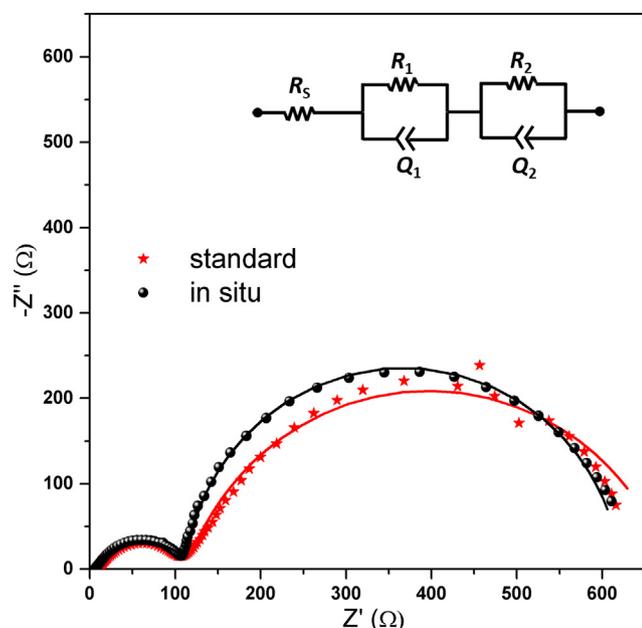


Fig. 3. Typical impedance response (Nyquist plot) of MFCs fabricated with anodes colonized with the two enrichment approaches. The points are experimental data, while the lines are related to the fitting procedure performed using the circuit shown in the inset.

combination of the charge transfer resistance  $R_2$  and the Helmholtz layer capacitance  $Q_2$  accounting for the anodic process. The curves obtained through the fitting procedure are reported in Fig. 3, superimposed over the experimental data, while the obtained resistance values are summarized in Table S2 in the SI. In agreement with the qualitative analysis above reported, series and cathodic resistances are quite similar for both kind of devices, while anodic resistances were found to be about 448  $\Omega$  and 500  $\Omega$  for *in situ* and standard MFCs, respectively.

All of these results confirmed that our novel pre-colonization enrichment approach allowed obtaining anodic biofilms able to successfully be employed in MFCs without the need of any laboratory procedure. The latter, indeed, requires multiple steps to be carried out by the operator and involves the use of several reagents. Moreover, it requires the removal of the microbiota from its natural environment with possible effects on its composition. On the other hand, the novel enrichment approach presents various advantages: (1) it minimizes operator tasks, since it involves only the burial of the carbon electrodes in the sediment and their subsequent immersion in seawater; (2) drastically reduces the use of reagents; (3) leaves the microbiota in its natural environment. For all these reasons, we adopted this approach for the anodic biofilm preparation during the remaining part of the experimental activity.

### 3.2. Field tests

As introduced above, for the first field measurement campaign, six nominally identical FMFCs based on *in situ* pre-colonized anodes were fabricated, and their power production in real marine environment was evaluated during summertime over a period of two months. With the exception of two devices (MFC4 and MFC5, discussed below), the average current density produced by the remaining four cells is shown in Fig. 4. During the first 15 days, these devices exhibit large current production, in agreement with the initial stage of the indoor tests. After this period, they were able to produce a stable output power of about 6 mW/m<sup>2</sup> (135 mA/m<sup>2</sup>) until the end of the test. By comparing this value with the one obtained during laboratory experiments, it can be concluded that the continuous supply of “fresh” seawater, together with

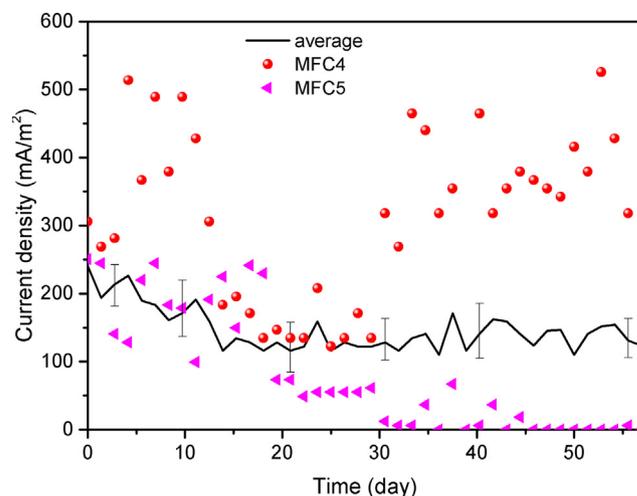


Fig. 4. Current density as a function of time during the first campaign of field tests for MFCs fabricated with *in situ* pre-colonized anodes: the continuous line represents the average value of 4 devices (MFC1, MFC2, MFC3 and MFC6) with maxima and minima reported as error bars, while the points are related to MFC4 and MFC5.

the movement of the floating system (which allows an effective fluid flow inside the devices), is responsible for the larger current production in marine environment. Interestingly, we were also able to observe the effect of seawater temperature variation between daytime and nighttime. As reported in Fig. S5 in the SI, a variation of about  $\pm 50\%$  was measured between 5:00 AM (minimum point) and 1:00 PM (maximum point). This effect was already observed in previous laboratory and *in situ* studies: Velasquez-Orta and coworkers found that among different environmental and design factors (salinity, temperature and external resistance), temperature presented a statistically significant effect on the current response [36]; Ren et al. employed a miniaturized MFC to study the power production in various temperature ranges, finding an optimal condition with larger amount of *cytochrome c* contributing to extracellular electron transfer [37]. Based on these outcomes, the variation of the current in Fig. S5 can be attributed to the influence of the external temperature on bacterial metabolism. However, it is worth noticing that the observed current density (and power) cycles are repeatable, leading to mean values which remain constant over time, as reported in Fig. 4. Concerning the remaining two devices, their performance is also shown in Fig. 4. After the initial stage, MFC5 started experiencing some issues, which led to a sudden decrease of the current density at day 19. Moreover, starting from day 30, its performance abruptly fell down, and it was characterized by low power density values for all the remaining period of investigation (about 30  $\mu\text{W}/\text{m}^2$ , corresponding to 9 mA/m<sup>2</sup>). On the contrary, MFC4 suffered from electrical connection problems: due to these issues, the device was cyclically, connected and disconnected to/from the external resistor load, thus the measured current values do not represent the actual power produced by this cell during the whole duration of the campaign.

After the end of the first campaign, in order to investigate the observed decay in MFC5 performance and to solve the connection problems of MFC4, all the six devices were transferred to our laboratory. They were kept under VM and immersed in seawater at room temperature. Results of VM measurements showed that all the devices (including MFC5) gave a stable output of about 2 mW/m<sup>2</sup> (data not shown), in agreement with the indoor tests results reported in Section 3.1; no connection issues were evidenced for MFC4. Based on these results, two out of six devices (namely MFC1 and MFC2) were kept in our laboratories for further experiments that are out of the scope of this paper, while the remaining four cells were selected to be mounted on the floating system for the second field measurement test.

Results of the VM measurements associated to the second campaign

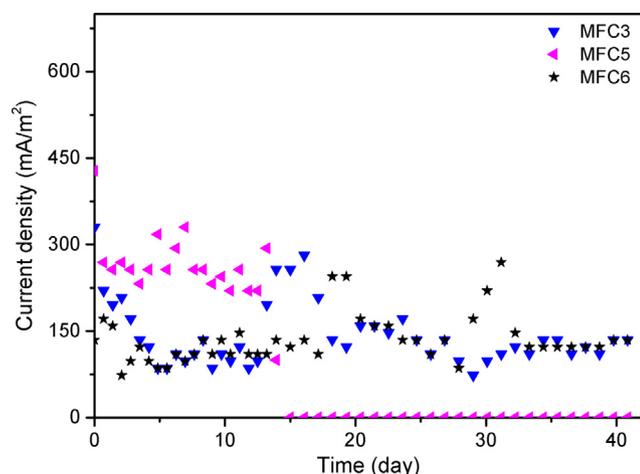


Fig. 5. Current density as a function of time during the second campaign of field tests for MFCs fabricated with *in situ* pre-colonized anodes.

are shown in Fig. 5, with the exception of data related to MFC4, which once again suffered from connection problems: therefore, current density values of this cell were not reliable and are not reported in Fig. 5. From the analysis of this graph, a large power production for MFC5 can be seen during the first 15 days, followed by a rapid decrease to minimum values, similarly to what was observed during the first field campaign. On the contrary, the remaining two cells were able to produce a quasi-constant output for all the period of investigation. By comparing these results with those obtained during the first campaign (Fig. 4), it can be concluded that no appreciable difference between the two seasons was evidenced concerning FMFCs' performance, despite about 10 °C temperature variation. The gradual temperature decrease between summer and winter allowed microorganisms to progressively adapt their metabolism to environmental temperature. On the contrary, the results observed during day/night cycle can be associated with a quick temperature change which did not allow a metabolic adjustment [38], similarly to what observed by Hall and coworkers [39].

#### 4. Discussion

The results of the two measurement campaigns shown in Figs. 4 and 5 demonstrated that small-scale FMFCs can efficiently produce electrical energy using seawater as fuel source. This feature, combined with the low cost of the used materials (basically, carbon electrodes and polymeric housing set-up) and the ease of the anode colonization enrichment approach, makes the technological approach proposed in this work an effective way to design cheap and portable systems, which are able to harvest green and renewable energy from marine environment. As shown in Table 1, very few works reported current production using FMFCs in field marine environments so far [22,40]. Both of these works presented PEM-based large-volume devices: in Huang et al. [40], the membrane, which separates granular graphite anode and Pt-covered carbon fibers cathode, is arranged as a 4.5 L tube, and the cell is able to produce 4 mW/m<sup>2</sup>; Erable et al. [22] employed titanium covered with iridium and tantalum oxides as anode, and stainless steel as cathode, obtaining 20 mW/m<sup>2</sup> using acetate and seawater as fuel. These power density values are in line or larger with respect to the one obtained in this work; however, it must be highlighted that expensive materials have been employed in the above reported papers (PEMs, cathode catalyst, Ir) and, in both cases, anodic biofilms were formed in laboratory and then transferred to the final device, thus implying additional costs. On the contrary, quite low power density values were obtained in laboratory experiments (see Table 1), with the exception of Song et al. [41], which attained 311.2 mW/m<sup>2</sup> employing composite anode, Pt-covered carbon cathode, and glucose, macro and

Table 1  
Characteristics of different FMFCs proposed in the literature.

Architecture	Total volume (L)	Anode	Cathode	Carbon energy source	Electrolyte	Inoculum source	L/F	Maximum power density (mW/m <sup>2</sup> )	Reference
Circular tube made of PEM	4.5	GG	Ni-coated GF + Pt/C layers	None	Seawater	50/50 mixture of anaerobic and aerobic sludge collected from a WW treatment plant	F	4 <sup>a</sup>	[40]
Sediment-like MFC installed in a container	121	FB	FB	None	Lake water	Lake sediment layer	L	2.2	[42]
2 anodes, 1 PEM, 2 cathodes	0.6	Ti covered with iridium and tantalum oxides	Biofilm-covered SS	10 mM sodium acetate	Seawater	Marine biofilm samples	F	20	[22]
Rectangular box-type acrylic reactor	1.9	GG + GF	GC + Pt	Glucose, macro- and micro-nutrients, and sodium bicarbonate	Synthetic WW	Unknown	L	311.2	[41]
Cylindrical polyacryl-pipe, 1 PEM	0.1	CF	CF	0–50 mM sodium acetate	Synthetic WW	ADF and WI, collected from a domestic brewery WW treatment plant	L	6	[43]
Hybrid sediment/plant MFC	3.1	GC	GC	Initially, 3 g/kg sodium acetate	Lake water	Unknown	F	12.2	[25]

L/F: laboratory/field; PEM: proton exchange membrane; GG: granular graphite; GF: graphite fibers; Pt/C: platinum-covered porous carbon; WW: wastewater; FB: fiber brushes; SS: stainless steel; GC: graphite cloth; CF: carbon felt; ADF: anaerobic digestion fluid, WI: wastewater influent.

<sup>a</sup> Calculated value.

micronutrients as fuel.

Despite the relatively low values, power densities obtained in this work are nevertheless sufficient to provide power to small sensors and devices. As an example, Zhang et al. [42], whose SMFCs were able to produce  $2.2 \text{ mW/m}^2$ , demonstrated the possibility to power a wireless temperature sensor employing a power management system (PMS) based on a supercapacitor to store the energy produced by MFCs. In the work of Gong et al. [44], a seawater oxygen sensor and an acoustic modem capable of routing data from the sensor itself (with power needed for the modem quiescent state equal to  $3 \text{ mW}$ ) were powered through MFCs. In this case, the PMS was based on a  $200 \text{ F}$  supercapacitor and a backup battery. These examples suggest that, if coupled with an appropriate PMS, our FMFC system could be employed as a low-power source, especially when portability is essential.

However, considering the malfunctioning of MFC4 and MFC5, the proposed technology and experimental set-up need to be optimized. As discussed in Section 3.2, during the field tests, MFC4 experienced electrical issues, which caused repeated connection/disconnection cycles to/from the external resistor load. The connection issue may be attributed to the field experimental setup, in particular to some failures of the relay board, which rendered the link between device and resistive load unstable (a different setup was exploited during laboratory experiments, as reported in Section 2.5). On the other hand, a different mechanism lies behind the observed behavior of MFC5: in this case, during both field campaigns, after an initial stage characterized by a current production of about  $200 \text{ mA/m}^2$ , its performance substantially reduced (Figs. 4 and 5). This feature could be explained by considering a mechanical failure between one of the electrodes and its current collector, induced by the seawater flow. The optimization of the electrical connections is out of the aim of the present work, but the use of 3D printing technology is of key importance to drive future optimization. Certainly, this technological approach offers a great opportunity to re-design the electrical interfaces of a floating system similar to the one we have proposed here.

To effectively employ these MFCs as floating power producers, we will explore the concept of *in situ* FMFCs Livestock. This concept envisages to place a very large number of *in situ* pre-colonized FMFCs in the seawater and to constantly monitor their performance. Based on this monitoring, only the best performing FMFCs can be employed, while the malfunctioning devices can be discarded and replaced by new ones. This approach would make it possible to always have well-functioning FMFCs, ready to power sensors or other devices.

## 5. Conclusion

This work presents a cost-effective floating set-up for MFCs operating in a real marine environment. This set-up can be especially useful when portability and small dimensions are needed.

An *in situ* pre-colonization enrichment approach of the anodic electrode coupled with the exploitation of a solid-state electrolyte allowed us to obtain a continuous current production from floating microbial fuel cells during two distinct field measurement campaigns, using seawater as the sole fuel. An average power density of  $6 \text{ mW/m}^2$  was obtained during summertime and wintertime, with a negligible dependence on season, despite a water temperature difference of about  $10^\circ\text{C}$ .

Even though connection issues were encountered in one of the cells, generally, the floating MFC setup gave promising results. Additionally, the concept of microbial fuel cells Livestock will be implemented, considering its potential in providing back-up MFCs in case one or more of the operational MFCs experience problems.

Future steps will involve the testing of the novel devices in various marine environments, in order to analyze the reproducibility of the obtained results or the possible variations of cell response to different external parameters.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apenergy.2018.08.061>.

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