Marine microbial fuel cell: Use of stainless steel electrodes as anode and cathode materials

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Abstract

Numerous biocorrosion studies have stated that biofilms formed in aerobic seawater induce an efficient catalysis of the oxygen reduction on stainless steels. This property was implemented here for the first time in a marine microbial fuel cell (MFC). A prototype was designed with a stainless steel anode embedded in marine sediments coupled to a stainless steel cathode in the overlying seawater. Recording current/potential curves during the progress of the experiment confirmed that the cathode progressively acquired effective catalytic properties. The maximal power density produced of $4\,mW\,m^{-2}$ was lower than those reported previously with marine MFC using graphite electrodes. Decoupling anode and cathode showed that the cathode suffered practical problems related to implementation in the sea, which may found easy technical solutions. A laboratory fuel cell based on the same principle demonstrated that the biofilm-covered stainless steel cathode was able to supply current density up to $140\,mA\,m^{-2}$ at $+0.05\,V$ versus Ag/AgCl. The power density of $23\,mW\,m^{-2}$ was in this case limited by the anode. These first tests presented the biofilm-covered stainless steel cathodes as very promising candidates to be implemented in marine MFC. The suitability of stainless steel as anode has to be further investigated.

Keywords: Microbial fuel cell; Stainless steel; Biofilm; Seawater; Sediments

1. Introduction

Microbial fuel cells (MFC) are fuel cells that use bacteria adhering to the electrode surfaces as catalyst of the electrochemical reactions. It has been demonstrated for a few years that micro-organisms contained in different natural environments such as marine sediments [1,2], waste water [3,4], and soils [5] can form biofilms on graphite anodes, oxidize the dissolved organic matter contained in the environment and use the electrode as the final electron acceptor. MFC present promising advantages with respect to standard abiotic fuel cells [6]. They offer the possibility of harvesting electricity from organic waste and renewable biomass, as the catalysing bacteria can adapt to different organic matters contained in a large variety of 'dirty' environments such as wastewaters or sediments. The expensive

catalysts that are required in abiotic fuel cells (platinum-based materials in PEM fuel cells for instance) are replaced by naturally growing micro-organisms. The blooming literature on the topic has been exhaustively reviewed from the point of view of both microbial mechanisms [7,8] and engineering aspects [9,10].

Marine MFC have been largely investigated with the view to operate low-power consuming marine instrumentations [11], such as oceanographic sensors, monitoring devices and telemetry systems [12]. Marine MFC consists typically in a graphite anode embedded in anaerobic marine sediments and connected to a cathode set-up in the overlying aerobic seawater. Such a system with plain graphite electrodes has sustained power density around $20\,mW\,m^{-2}$ of anode surface area during 4 months, with maximal values up to $28\,mW\,m^{-2}$ [1]. A similar laboratory system has provided around $10\,mW\,m^{-2}$ for 240 days with graphite fibers anode and cathode [2]. Using carbon brush cathode has given $34\,mW\,m^{-2}$ during 125 days [13]. To our knowledge, the highest power densities that have been provided by field marine MFC have been reached with graphite anodes modified with

charge transfer mediators [11]: 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. Nevertheless, the power has decayed over time to the performance of standard graphite anodes, likely due to mass transfer limitation of the anode reactants.

Cathode materials have been poorly investigated in the framework of marine MFC. A few studies dealing with seawater battery have compared the effectiveness of graphite, copper or stainless to design dissolved-oxygen cathodes. Although graphite cathodes operate at higher open-circuit potential, graphite has sometimes been believed to be too brittle for scaling up practical devices. On the contrary, copper and stainless steel meshes, which are commercially available, should facilitate the construction of compact cathodes with large surface area and a proper open structure that favours oxygen transfer towards their surface [14]. Comparing carbon fiber and spinel coated stainless steel wool cathodes in a seawater battery prototype has revealed higher effectiveness of carbon fiber, nevertheless the authors have hesitated to dismiss stainless steel because of its better mechanical features [15,16].

It has been shown for a long time in the framework of biocorrosion that the biofilms that form naturally in aerobic seawater on the surface of stainless steels and other alloys induce an efficient catalysis of the reduction of oxygen on these materials [17–19]. A previous work, has demonstrated that it was possible to implement this biofilm-driven catalytic effect in a hydrogen fuel cell. A stainless steel cathode covered with a seawater biofilm that has been formed under proper operating conditions has revealed able to sustain $64\,mW\,m^{-2}$ and current density up to $1.89\,A\,m^{-2}$ [20,21]. This new catalytic effect might lead to reconsider the efficiency of stainless steel as cathode material for seawater dissolved-oxygen cathodes.

The purpose of this work was to check the effectiveness of such biofilm-covered stainless steel cathodes for the first time in a MFC prototype. By the way, as a first attempt to our knowledge, stainless steel was also used as anode. The sea prototype deployed in Genoa harbour (Italy) was composed of two identical stainless steel electrodes, a cathode placed in the seawater and an anode inserted into the underlying sediments. A similar device was installed in parallel in a marine laboratory close to the sea.

2. Material and methods

2.1. Marine microbial fuel cell

The marine microbial fuel cell device described in Fig. 1 was set-up in the Mediterranean sea (Italy). The anode, composed of two plates made from super austenitic steel with 6% of molybdenum (UNS S31254[1]; $20\,cm \times 30\,cm$, total surface area $0.12\,m^2$) was inserted into marine sediments (anaerobic),
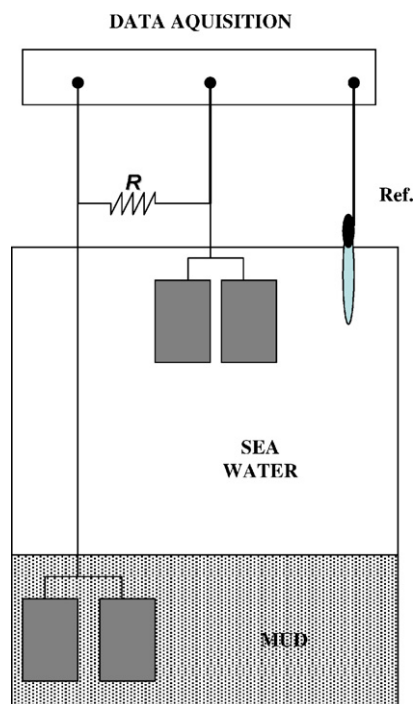

Fig. 1. Marine microbial fuel cell set-up: stainless steel anode ($0.12\,m^2$) placed in anaerobic sediments, stainless steel cathode ($0.12\,m^2$) placed in aerated seawater.

at about 15 m under seawater surface. The cathode, composed of two identical stainless steel plates, was immersed in the surface seawater (aerobic). The connection between the electrodes was ensured by sheathed cables. The stainless steel electrodes were connected to the electric cable with a titanium wire. All stainless steel-titanium and cable-titanium welds were insulated with epoxy resin (STUERS Epofix resin and hardener) in order to prevent any corrosion. A silver wire (diameter 1.5 mm, length 200 mm) covered with silver chloride was used as a reference electrode in the surface seawater. A zinc wire (diameter 7 mm, length 100 mm) could be used as a pseudo-reference. Anode and cathode were connected through electrical resistances varying from $1\,\Omega$ to $33\,k\Omega$. Polarisation curves could be plotted using the current and potential measured for each resistance value. At the beginning of the experiment, the temperature of the seawater was $13\,°C$.

2.2. Laboratory microbial fuel cell

A similar set-up was reproduced in a marine laboratory close to the sea. It was composed of two stainless steel electrodes (UNS S31254, $20\,cm \times 30\,cm$, total surface area $= 0.06\,m^2$). The cathode was plunged in a 100 L basin of seawater that was continuously renewed (6 L/h) and thermostatically maintained at $25\,°C$. The anode was dipped in a closed tank (35 L) that contained around 0.2 L marine sediments collected at 15 m under the seawater surface in Genoa harbour. The anode compartment was immersed in the cathode part. A tube full of cotton wool ensured the ionic connection between the two environments and maintained anaerobic conditions in the anode tank. At the beginning of the experiments, oxygen was driven out
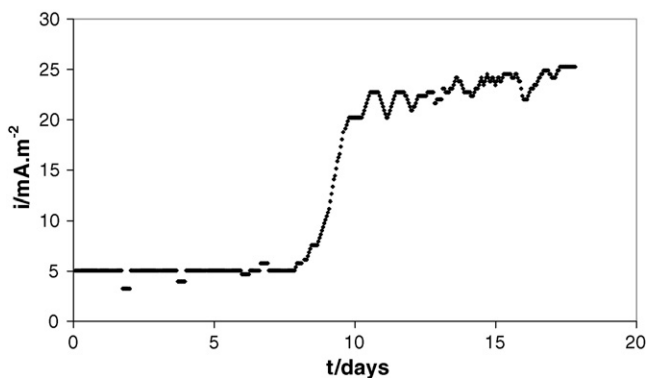
Fig. 2. Current density in mA m^{-2} vs. time during the first 18 days of experiment. Surface area 0.12 m^2, coupling resistance 33 Ω.
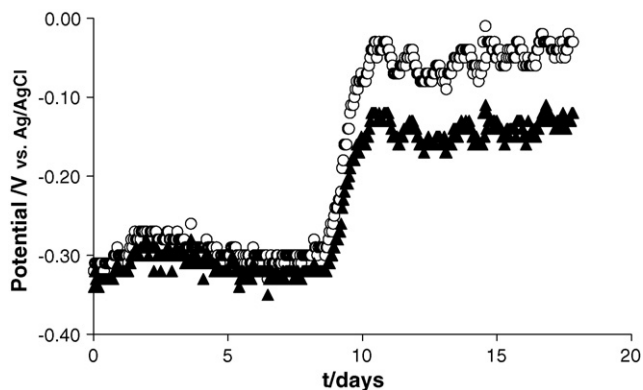

Fig. 3. Anode and cathode potential vs. Ag/AgCl reference when coupled with a 33 Ω resistance. ($\bigcirc$) Cathode potential in aerated seawater. ($\blacktriangle$) Anode potential in marine sediments.

of the anode tank by the addition of an excess of sulphite (Na$_2$SO$_3$). A zinc electrode placed in the cathode compartment was used for galvanic coupling; it was also used in some cases as a pseudo-reference electrode. Cathode and anode were connected through an electrical resistance or through an electric motor.

2.3. Data acquisition

When the anode and cathode were coupled through an electrical resistance, the voltage drop at the resistance, ΔV, and the potential of the cathode, E_C, with respect to the reference electrode were measured every hour and the potential of the anode was calculated as $E_A = E_C - \Delta V$. At open circuit, both anode and cathode potentials were measured with respect to the reference electrode. The data acquisition system was composed of a Pentium III computer with a PCI-6034E (National Instrument) acquisition card, monitored via a Labview6 graphic interface. When indicated, an electric motor (http://www.boutiquesolaire.com, reference KG054) was used, which turned a propeller. The internal resistance of the motor was 25 Ω and the propeller turned when the system provided at least 0.15 V. So, to operate the propeller, the system had to sustain at least 6 mA, i.e.100 mA m^{-2}.

3. Results and discussion

3.1. Marine fuel cell

The set-up was installed in Genoa harbour in Italy on March 17, 2005. The anode was placed in marine sediments and coupled through a 33 Ω resistance to the cathode placed in aerated seawater. The current density (Fig. 2) and the anode and cathode potential values were recorded (Fig. 3). The current density remained stable for ∼8 days at around 5 mA m^{-2} (calculated with respect to the total surface area 0.12 m^2) and then started to rise up to 25 mA m^{-2}. During the first 9 days, cathodic and anodic potential values were stable around −0.30 V versus Ag/AgCl. After the 9th day, the potentials rose and reached −0.04 V versus Ag/AgCl and −0.14 V versus Ag/AgCl, respectively.

Polarisation curves were plotted on days 1, 9, 11 and 17 by changing the value of the electrical resistance (Fig. 4). The anode polarisation curves only varied at low current values. The zero-current potential did not vary significantly in the range −0.41 to −0.31 V versus Ag/AgCl and the current/potential slope was not markedly modified. In contrast, the cathode polarisation curves moved towards higher zero-current potentials, from −0.15 to 0.08 V versus Ag/AgCl, and higher current/potential slopes. The cathode clearly revealed a continuous increase in its catalytic properties for oxygen reduction. The general behaviour of the cathode matched the biofilm-driven catalysis of oxygen reduction that has been demonstrated on stainless steel through chronoamperometry experiments [22]. Biofilm growth enhanced the electrocatalytic properties of the stainless steel cathode. Extracting power density values from the current/potential curves recorded at day 17 indicated that the cell was able to supply 4 mW m^{-2} with 18 mA m^{-2}.

After 18 days of connection, the system was put in open circuit in order to follow the behaviour of both electrodes independently. The potential of each electrode was measured with respect to the Ag/AgCl reference electrode immersed in the surface seawater (Fig. 5). The potential of the anode
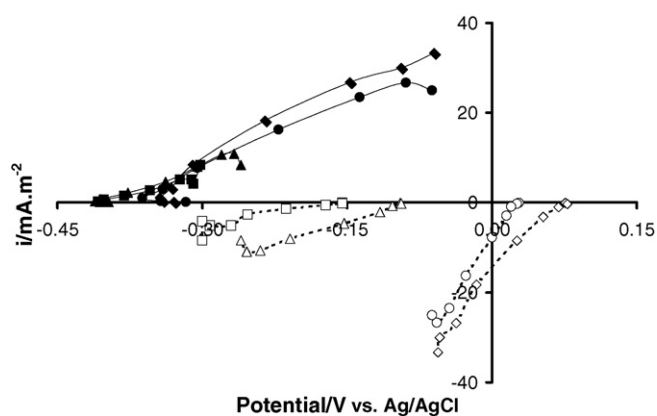

Fig. 4. Polarisation curves. Current density in mA m^{-2} vs. potential in V recorded on days 1($\square$), 9($\triangle$), 11($\bigcirc$) and 17($\diamond$) on the marine microbial fuel cell. Closed and open symbols represent, respectively anode and cathode values.
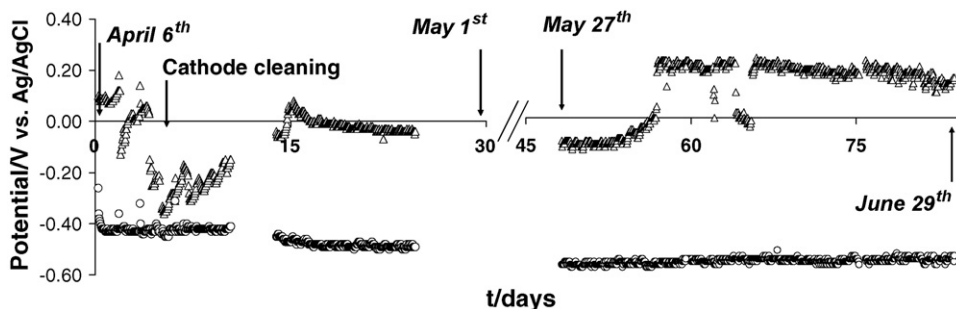
Fig. 5. Open circuit potential in V vs. Ag/AgCl vs. time in days. (△) Cathode potential of aerated seawater, and (○) anode potential in marine sediments.

remained stable in the range −0.40 to −0.50 V versus Ag/AgCl. In contrast, the potential of the cathode revealed two unexpected sharp decreases, one after 2 days and the other after 4 days. Careful examination of the cathode showed that the biofilm was partially removed by fishes grazing on it. After 5 days, the cathode was cleaned off and plunged in seawater again. The potential increased from −0.35 V versus Ag/AgCl to stabilized around −0.05 V versus Ag/AgCl. After around 50 days at open circuit, the potential values of the anode and cathode were stable at around −0.49 and −0.09 V versus Ag/AgCl, respectively (Fig. 5). From this date, the cathode potential started to increase and levelled off at 0.17 V versus Ag/AgCl in a week. The cathode potential then showed a few fluctuations but remained stable around an average value of about 0.15 V versus Ag/AgCl for more than 2 weeks, which means an open circuit potential around 0.65 V for the fuel cell.

The potential of the cathode in the present experiment achieved maximal value only after ∼57 days of immersion in seawater, whereas the potential of stainless steel electrodes in seawater, generally increases to around 0.30 V versus Ag/AgCl in a few days of exposure [22,23]. Moreover, the repeated fluctuations when the potential finally reached the high value plateau seem anomalous with respect to the experience of the authors. It is to be feared that, under the action of waves, some problems occurred in the connection between the stainless steel cathode and the copper cable, possibly resulting in some form of corrosion being activated. A similar problem of galvanic coupling has been encountered with a prototype of seawater battery, because of an accidental contact between the stainless steel cathode and an electronics container [15]. The technical problems that were put in light on this prototype can be solved in a quite easy way. Biofilm grazing by fishes can be avoided with a fine plastic mesh for instance, and the connection with the copper wire must be more carefully insulated. A similar biofilm-covered stainless steel cathode has already proved to supply around 250 mA m^{-2} under constant polarisation at −0.10 V versus SCE in quiescent seawater, and up to 400 mA m^{-2} at 0.00 V versus SCE in a hydrogen fuel cell [20]. Nevertheless, in this latter case the continuous flow of aerated seawater avoided any mass transfer limitation of dissolved oxygen. In the same potential range the cathode supplied 35 mA m^{-2} in the present prototype, it should be concluded that the efficiency of the cathode may certainly be improved in a great extend after solving the techni-

cal problems identified here. The low temperature of the sea at this period of the year (13 °C) was also detrimental to the performance of the biofilm-covered cathode, while the previous results have been obtained with temperature generally around 25 °C or higher.

3.2. Laboratory fuel cell

The laboratory fuel cell consisted of a 0.06 m^2 stainless steel anode placed in a closed tank that contained marine sediments and a similar stainless steel cathode set in a container where seawater was renewed regularly and temperature was maintained at 25 °C. Ionic connection between the closed tank and the seawater basin was ensured through a tube filled with cotton wool. At the beginning of the experiment on March 10th, the anode was left on open circuit and the cathode was coupled to a zinc electrode through a 50 Ω resistance in order to maintain active oxygen reduction. Coupling with a zinc electrode that spontaneously dissolved in seawater:

$$Zn \rightarrow Zn^{2+} + 2e^-, \qquad E_{Zn}{}^0 = -0.98 \text{ V versus Ag/AgCl}$$
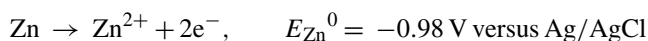
ensured a negative potential at the cathode, which may promote biofilm formation [20].

At day 13, the anode and cathode were coupled through the electrical motor. The propeller turned one complete day of operation before stopping. After 5 days back in open circuit, polarization curves were plotted on day 20. The motor was then connected to the cell and it turned for more than 1 h. It remained connected all day and new polarization curves were plotted on day 21. After leaving the electrodes in open circuit for 4 days, the last polarization curves were plotted on day 25 (Fig. 6). All cathodic curves were nearly identical, meaning that the cathode behaviour was not influenced by the motor operation. The open circuit potential values were in the range 0.30–0.35 V versus Ag/AgCl, revealing an effective catalysis of oxygen reduction by the biofilm. The current density obtained of 140 mA m^{-2} at +0.05 V versus Ag/AgCl were of the same order of magnitude as that obtained elsewhere in similar quiescent conditions (250 mA m^{-2} at −0.10 V versus SCE, i.e. −0.101 V versus Ag/AgCl [20]). As a conclusion, the current/potential curves demonstrated that well controlled conditions, i.e. protection of the cathode against biofilm grazing by fishes, avoidance of possible damage of the electrical connection by waves, and a beneficial cathode poten-
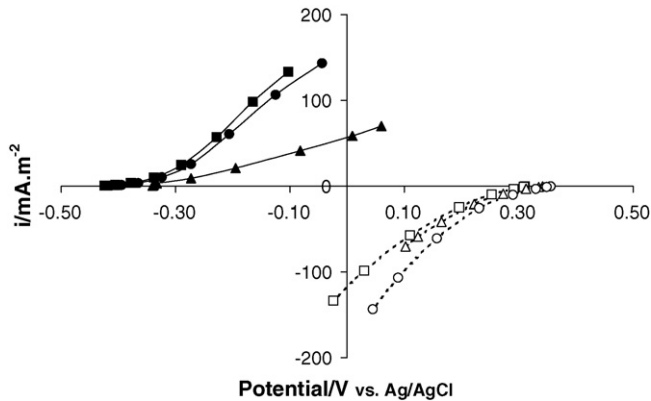
Fig. 6. Polarization curves. Current density in mA m^{-2} vs. potential in V vs. Ag/AgCl recorded at days 20($\square$), 21($\triangle$) and 25($\bigcirc$) on the laboratory microbial fuel cell. Closed and open symbols represent, respectively anode and cathode values.

tial during biofilm formation, resulted in efficient biofilm-coated cathodes.

The anode features proved to be affected by the motor operation. After one full day of motor operation, the power available had been consumed and the slope of the polarisation curve decreased significantly (day 21). The anode sustained only 70 mA m^{-2}, which was not sufficient for the propeller to turn. A current of 6 mA was required to turn the propeller, i.e. a current density of 100 mA m^{-2}. The polarisation curve plotted at day 25 showed that the anode recovered its full capacity to provide current after 4 days in open circuit (motor disconnected). Loss of its power capacity was fully reversible; it was not caused by a mass transfer limitation due to depletion of the substrate around the electrode, as moving the electrode briskly did not increase the current.

Turning the current/potential curves into power density curves (Fig. 7) shows that the laboratory MFC was able to produce 23 mW m^{-2} under 80 mA m^{-2}, or 140 mA m^{-2} at half power. When powering the motor, it sustained at least 15 mW m^{-2} (6 mA required, internal resistance 25 Ω) during one day, but was limited by the behaviour of the anode.
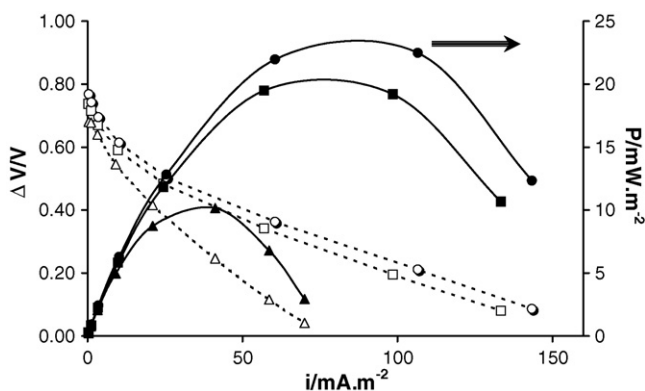

Fig. 7. Power density in mW m^{-2} and potential drop ΔV in V vs. current density in mA m^{-2}, recorded at days 20($\square$), 21($\triangle$) and 25($\bigcirc$) on the laboratory microbial fuel cell. Closed symbols represent power, open symbols represent voltage.

4. Conclusions

The marine MFC prototype presented here was the first attempt to use stainless steel electrodes for both the anode and the cathode. Without any particular care, it revealed able to supply power density of 4 mW m^{-2}. This first experiment performed in the sea put in light a few technical problems related to the direct use in the sea, which could be overcome quite easily in order to test the prototype for long-term performance. The laboratory MFC indicated that the biofilm-covered cathode can supply current density of 140 mA m^{-2} at +0.05 V versus Ag/AgCl. In this case, the power density of 23 mW m^{-2} was limited by the lower effectiveness of the anode. The discrepancy observed here on the cathode effectiveness between the sea prototype and the laboratory cell may explain why stainless steel has been generally dismiss in previous works devoted to seawater batteries implemented in the sea.

This first assessment of a stainless steel air-dissolved cathode in a MFC prototype revealed its promising quality for sediment MFC. Taking into account the mechanical properties of steels and their large commercial availability gave to stainless steel biocathodes a great interest. In comparison, the suitability of stainless steel for the anode still needs to be investigated, and the causes of the limitation that was observed here have to be clearly identified before to conclude on this issue.

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