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# Increased power from a two-chamber microbial fuel cell with a low-pH air-cathode compartment

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## ABSTRACT

Pt-supported air-cathodes still need improvement if their application in MFC technology is to be sustainable. In this context, the efficiency of an air-cathode was studied with respect to the pH of the solution it was exposed to. Voltammetry showed that oxygen reduction was no longer limited by H<sup>+</sup> availability for pH lower than 3.0. A new MFC was designed with a catholyte compartment setup between the anode compartment and the air-cathode. With a catholyte compartment at pH 1.0, the MFC provided up to 5 W/m<sup>2</sup>, i.e., 2.5-fold the power density obtained with the same anode and cathode in a single-chamber MFC working at pH 7.5. Current density exceeded 20 A/m<sup>2</sup>. The benefit of low-pH in the catholyte chamber largely counterbalanced the mass transfer hindrance due the membrane that separated the two compartments. The MFC kept 66% its performance during nine days of continuous operation.

### Keywords:

Microbial fuel cell  
Air-cathode  
Oxygen reduction  
pH  
High power

## 1. Introduction

Microbial fuel cells (MFCs) utilise microbial biofilms as catalysts to convert the chemical energy contained in a large variety of organic compounds directly into electricity. MFCs produce a lower power density than traditional fuel cells but the increasing interest in sustainable energy sources is promoting intense research leading to fast improvements. In this framework, developing efficient cathodes able to reduce oxygen remains an important research issue [1,2]. Different approaches for lowering the cathodic overpotential for oxygen reduction have been explored: the use of mediators [3], electrode modifications with biotic or abiotic catalysts [4,5], and optimisation of the operational conditions within the cathodic compartment [6,7].

The complete reduction of oxygen to water requires a platinum catalyst. Catalysts with poor efficiency may convert oxygen to hydrogen peroxide, which can severely inhibit the growth of anaerobic microorganisms [8,9]. The low solubility of oxygen in solution can be overcome by using air-breathing cathodes exposed directly to air, but air-cathodes lose a considerable part of their efficiency when used in contact with a solution at neutral pH, as required in MFCs [10]. Activation losses on the cathode have been identified as the dominant limitation in MFCs [11], particularly due to low proton availability [12]. Moreover, precious metal catalysts are highly sensitive to biological and chemical fouling [11].

In this work, a new MFC design is proposed that avoids most of these drawbacks. The anode compartment is limited by a proton exchange membrane and an intermediary catholyte compartment is setup between the membrane and the air-breathing cathode (Fig. 1). This intermediary catholyte compartment allows the pH to be adjusted to the optimal value for the cathode and avoids fouling of the cathode by the (bio)chemical compounds contained in the anode compartment. Conversely, the catholyte compartment hinders the diffusion towards the bioanode of hydrogen peroxide that might be produced on the cathode.

## 2. Experimental procedure

### 2.1. Electrochemical measurements and analysis

The 0.5 mg Pt/cm<sup>2</sup> carbon-felt air-breathing cathode (Paxitech, France) had a projected surface area of 7 cm<sup>2</sup>. It was tested with one side exposed to air and the other exposed to seawater at room temperature using a three-electrode system implemented with a multipotentiostat (Bio-Logic SA). The auxiliary electrode was a platinum grid (6 cm<sup>2</sup>) and all potentials were expressed with respect to a saturated calomel standard reference electrode (SCE).

The graphite-thin felt microbial anodes have a total projected surface area of 150 cm<sup>2</sup> (0.4 cm thickness). They were divided into six equal parts in order to optimise the current distribution in the cell. The graphite anodes were prepared under polarisation at -0.10 V in reactors containing 0.25 L seawater and 0.25 mL marine biofilm suspension, supplemented with 10 mM acetate. Marine biofilms and seawater were collected from the harbour of La

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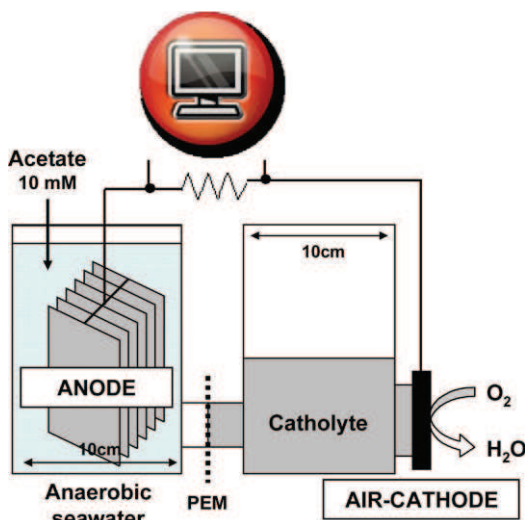


Fig. 1. Scheme of the low-pH air-cathode MFC.

Tremblade (Atlantic Ocean, France). The electrodes were embedded vertically down to the bottom of the reactor with titanium wires as electrical contacts. Polarisation used a conventional three-electrode system with a 20 cm<sup>2</sup> platinum grid auxiliary electrode and a SCE reference electrode. Voltammetry was performed at 1 mV/s in situ on the active anode after suspending polarisation.

### 2.2. Low-pH air-cathode MFC

The MFC consisted of a 0.5 L anodic microbial compartment coupled to a 0.2 L, 10 cm wide catholyte chamber, separated by a Nafion<sup>®</sup> 117 PEM. The 7 cm<sup>2</sup> air-breathing cathode was pressed into contact with the catholyte chamber through a brass grid, which was used to retrieve the current. The catholyte chamber was filled with seawater and its pH adjusted in the range of 1.0–9.0 with concentrated HCl or NaOH. The 150 cm<sup>2</sup> microbial anode was prepared as described in Section 2.1. The MFC operated in batch conditions at room temperature (20 °C) with a 100 Ω external resistance for 10 days. Power–current curves were recorded by varying the external resistance from 1 Ω to 100 kΩ.

## 3. Results and discussion

### 3.1. Effect of pH on air-cathode efficiency

Current–potential curves were recorded by voltammetry at 1 mV/s with pH values of the solution varying from 1.0 to 9.0 by addition of HCl or NaOH (Fig. 2). At pH 1.0 the cathode furnished more than 14.0 A/m<sup>2</sup> (with respect to the 7 cm<sup>2</sup> surface area) at 0.45 V/SCE and did not show any mass transfer limitation. At pH values higher than three, the current started to be limited by the H<sup>+</sup> availability for current densities higher than 4 A/m<sup>2</sup>. The pH of the anodic compartment in single-chamber MFCs generally varies from 6.5 to 8.5. Here, at pH 7.5, the potential dropped to –0.15 V/SCE to provide 14.0 A/m<sup>2</sup>, which represents a voltage loss of 580 mV with regard to pH 1.0. The equilibrium redox potential of oxygen reduction varies by 390 mV from pH 7.5 to pH 1 (0.059 V per pH unit), the depletion of protons was consequently responsible for an increase of around 190 mV in the overpotentials.

### 3.2. Microbial anode formation

A 150 cm<sup>2</sup> microbial anode was prepared under constant potential polarisation at –0.10 V/SCE in seawater inoculated with a

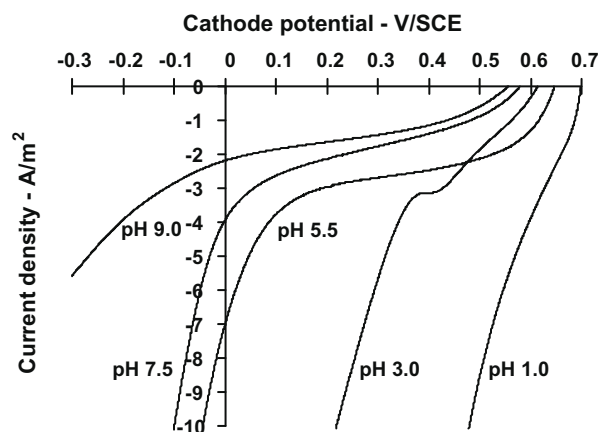


Fig. 2. Current–potential curves recorded at 1 mV/s of a Pt-carbon air-cathode (7 cm<sup>2</sup>) exposed on one side to seawater with pH adjusted to different values; room temperature; potential scan rate 1 mV/s.

marine biofilm and supplemented with 10 mM acetate. The current started to increase exponentially between the first and second day and stabilised at a maximal value of 8.0 A/m<sup>2</sup> after eight days of polarisation. This kind of current increase has been commonly linked to the development of electrochemically-active biofilms on polarised electrodes [13]. The voltammetry performed after 10 days of polarisation (Fig. 3a) showed a zero-current potential around –0.50 V/SCE, instead of –0.15 V/SCE before polarisation and biofilm formation. Such a negative zero-current potential value is a significant advantage in an MFC. The current at –0.1 V was identical to the value recorded at steady-state (8.0 A/m<sup>2</sup>),

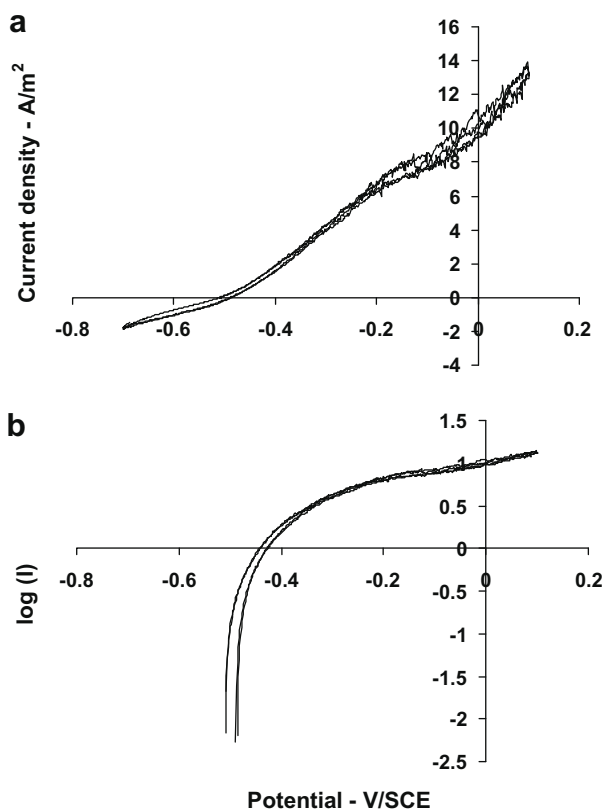
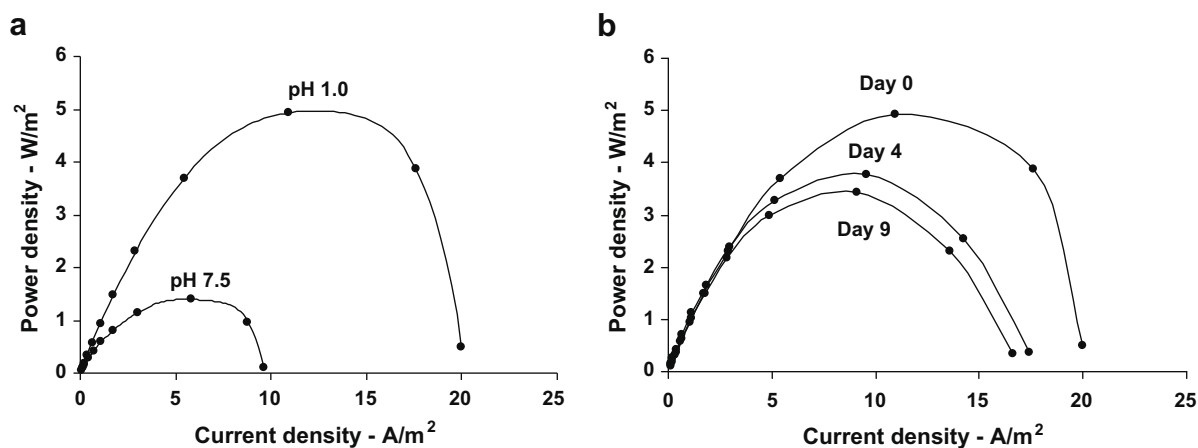


Fig. 3. Current–potential curve recorded at 1 mV/s with a graphite felt bioanode derived from the marine environment (a) and the corresponding Tafel plot (b).



**Fig. 4.** Power density versus current density for the two-chamber MFC obtained by varying the cell resistance: day 0 with pH 1.0 or 7.5 in the catholyte chamber (a); pH in catholyte compartment fixed at 1.0 (b).

indicating that the potential scan rate was low enough to give the steady-state characteristics of the electrode. The anode provided up to 13 A/m<sup>2</sup> (with respect to the 150 cm<sup>2</sup> projected surface area) at +0.1 V/SCE. Up to now, the highest values reported in the literature have been around 9 A/m<sup>2</sup> with pure cultures [14,15]. The current-potential curve showed a limitation above -0.2 V, which did not correspond to a traditional mass transfer limiting effect (mass transfer limitation would lead to horizontal current-potential curves). The Tafel representation (Fig. 3b) resulted in an exchange current density  $j_0$  around 1.5 A/m<sup>2</sup>. This fairly high value indicated a good capacity for electron exchange between the biofilm and the electrode.

### 3.3. Low-pH air-cathode MFC

A control experiment was carried out with a traditional single-chamber MFC connected to a 100 Ω resistance. The 7 cm<sup>2</sup> air-breathing cathode was sealed directly on the 0.5 L anode compartment filled with seawater and marine biofilm (pH 7.5). The 150 cm<sup>2</sup> bioanode was prepared as described in Section 2.1. The large ratio between the anode and cathode surface areas was chosen to make the cathode process rate-limiting. In this way the behaviour of the MFC was mainly controlled by the behaviour of the cathode. Comparing the current-potential curve of the cathode (Fig. 2) multiplied by a factor of seven to the current-potential curve of the anode (Fig. 3) multiplied by a factor of 150 confirmed that the anode had in the MFC system an almost vertical characteristics with respect to the cathode. The MFC provided a maximum power density near 2.0 W/m<sup>2</sup> and a maximum current density of 13 A/m<sup>2</sup> (with respect to the cathode surface area). Power densities were of the same order of magnitude as the best values reported in the literature with air-cathode MFCs, around 2.7–2.8 W/m<sup>2</sup> [16,17]. Ringeisen et al. achieved 2 W/m<sup>2</sup> using air-cathode, but in smaller systems (only 1.2 mL) [18,19]. Maximum current densities reported in the literature with air-cathode MFCs are around 6 A/m<sup>2</sup> [20]. A remarkably high value was obtained here thanks to quality of the anode and the surface areas ratio, which allowed the air-cathode to work at low potential values. The high ionic conductivity of natural seawater (5 S/m at 20 °C) was also a very positive factor.

The catholyte compartment of the new MFC design (Fig. 1) was filled with a seawater solution adjusted to pH 7.5 to be close to the conditions used with the single-chamber MFC. The maximum power density and current density (Fig. 4a) reached 1.4 W/m<sup>2</sup> and 9.9 A/m<sup>2</sup>, respectively. The proton exchange membrane and

the catholyte compartment caused considerable ohmic losses that reduced the performance by around 30% with respect to the single-chamber MFC.

When the pH of the catholyte was decreased to 1.0, the maximum power density reached 5.0 W/m<sup>2</sup>, i.e., 3.5-fold the maximum power obtained at pH 7.5, and 2.5-times that with the single-chamber MFC. These high performance values were due to two additional effects: thermodynamically, the MFC took advantage of the pH difference between anode and cathode and, kinetically, the acidic catholyte decreased the cathode overpotential. These effects largely counterbalanced the ohmic losses introduced by the proton exchange membrane. The maximum current density was 20.1 A/m<sup>2</sup> as against 13 A/m<sup>2</sup> with the single-chamber MFC. The MFC operated with a 100 Ω external resistance for 10 days. Power-current curves were recorded at days 4 and 9 (Fig. 4b). The maximum power density dropped to 3.3 W/m<sup>2</sup> at day 9. The open circuit voltage decreased from 0.68 V initially to 0.55 V at day 9. The pH decreased from 7.5 to 6.4 (day 9) in the anode compartment and increased from 1.0 to 1.5 in the catholyte chamber.

The pH evolution in the anode and catholyte compartments was due to H<sup>+</sup> diffusion through the membrane because of the pH gradient, coupled with the electrochemical production/consumption of protons on the anode/cathode. After 10 days of operation, the maximum power density remained 66% of the initial value (5 W/m<sup>2</sup>), which still represented more than 1.6-fold the power density obtained in a single-chamber MFC with the same anode and cathode (2 W/m<sup>2</sup>). The proton exchange membrane may also be a cause of efficiency decrease. Sodium ions are known to block the exchange sites of Nafion<sup>®</sup> membranes irreversibly, and even to promote membrane drying [21]. Here sodium ions were the dominant cationic species, and their transfer through the membrane had a major role in charge-balancing the ion flux. Changing the medium to avoid the presence of sodium ions should be a promising way to stabilise the behaviour of the cell, but this supposes acclimatising the microbial population to a new medium. Work is in progress in this direction.

## 4. Conclusion

The new low-pH air-cathode MFC designed here ensured power densities of up to 5 W/m<sup>2</sup> and current densities exceeding 20 A/m<sup>2</sup>, which was 2.5-fold the power provided in the same conditions with a traditional single-chamber MFC. The power supplied decreased by only 33% after nine days of continuous operation. This new MFC design is a promising improvement in MFC technology.

Implementing it in continuous mode should allow its efficiency to be further improved by avoiding the pH drift.

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### References

- [1] F. Zhao, F. Harnish, U. Schröder, F. Scholz, P. Bogdanoff, I. Hermann, *Environ. Sci. Technol.* 40 (2006) 5193.
- [2] J.M. Morris, S. Jin, J. Wang, C. Zhu, M.A. Urynowicz, *Electrochem. Commun.* 9 (2007) 1730.
- [3] D.H. Park, J.G. Zeikus, *Biotechnol. Bioeng.* 81 (2003) 348.
- [4] B.E. Logan, C. Murano, K. Scott, N.D. Gray, I.M. Head, *Water Res.* 39 (2005) 942.
- [5] P. Clauwaert, D. Van der Ha, N. Boon, K. Verbeken, M. Verhaege, K. Rabaey, W. Verstraete, *Environ. Sci. Technol.* 41 (2007) 7564.
- [6] H. Liu, S.A. Cheng, B.E. Logan, *Environ. Sci. Technol.* 39 (2005) 5488.
- [7] A. Ter Heijne, H.V.M. Hamelers, C.J.N. Buisman, *Environ. Sci. Technol.* 41 (2007) 4130.
- [8] N. Leke, D. Grenier, M. Goldner, D. Mayrand, *FEMS Microbiol. Lett.* 174 (1999) 347.
- [9] A. Thibessard, A. Fernandez, B. Gintz, N. Leblond-Bourget, B. Decaris, *Res. Microbiol.* 152 (2001) 593.
- [10] J.K. Jang, T.H. Pham, I.S. Chang, K.H. Kang, H. Moon, K.S. Cho, B.H. Kim, *Process. Biochem.* 39 (2004) 1007.
- [11] H. Rismani-Yazdi, S.M. Carver, A.D. Christy, O.H. Tuovinen, *J. Power Sources* 180 (2008) 683.
- [12] Z. Du, H. Li, T. Gu, *Biotechnol. Adv.* 25 (2007) 464.
- [13] S. Parot, M.L. Delia, A. Bergel, *Bioresour. Technol.* 99 (2008) 4809.
- [14] C. Dumas, R. Basseguy, A. Bergel, *Electrochim. Acta* 53 (2008) 2494.
- [15] C.I. Torres, A. KatoMarcus, B.E. Rittmann, *Appl. Microbiol. Biotechnol.* 77 (2007) 689.
- [16] Y. Fan, H. Hu, H. Liu, *J. Power Sources* 171 (2007) 348.
- [17] B.E. Logan, S. Cheng, V. Watson, G. Estadt, *Environ. Sci. Technol.* 41 (2007) 3341.
- [18] B.R. Ringeisen, E. Henderson, P.K. Wu, J. Pietron, R. Ray, B. Little, J.C. Biffinger, J.M. Jones-Meehan, *Environ. Sci. Technol.* 40 (2006) 2629.
- [19] B.R. Ringeisen, R. Ray, B. Little, *J. Power Sources* 165 (2007) 5981.
- [20] Y.Z. Fan, H.Q. Hu, H. Liu, *Environ. Sci. Technol.* 41 (2007) 8154.
- [21] T. Okada, S. Moller-Holst, O. Gorseth, S. Kjelstrup, *J. Electroanal. Chem.* 442 (1998) 137.