Bioresource Technology 221 (2016) 691–696

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Removable air-cathode to overcome cathode biofouling in microbial fuel cells

Manon Oliot *, Luc Etcheverry, Alain Bergel

Laboratoire de Génie Chimique CNRS – Université de Toulouse (INPT), 4 allée Emile Monso, 31432 Toulouse, France

HIGHLIGHTS

- An innovative MFC design allowed the air-cathode to be removed and replaced.
- Replacing the air-cathode immediately boosted power density from 0.7 to 1.96 W/m^2.
- Initial biofouling of air-cathodes may be a widespread cause of underperformance.
- Air-cathode replacement was modelled numerically.

ARTICLE INFO

Article history:
Received 22 July 2016
Received in revised form 16 September 2016
Accepted 22 September 2016
Available online 24 September 2016

Keywords:
Bioelectrochemical system
Bioanode
Reactor design
Numerical modelling

ABSTRACT

An innovative microbial fuel cell (MFC) design is described, which allows the air-cathode to be replaced easily without draining the electrolyte. MFCs equipped with 9-cm^2 or 50-cm^2 bioanodes provided 0.6 and 0.7 W/m^2 (referred to the cathode surface area) and were boosted to 1.25 and 1.96 W/m^2, respectively, when the initial air-cathode was replaced by a new one. These results validate the practical interest of removable air-cathodes and evidence the importance of the cathode biofouling that takes place during the MFC starting phase. As this biofouling is compensated by the concomitant improvement of the bioanodes it cannot be detected on the power curves and may be a widespread cause of performance underestimation.

1. Introduction

Microbial fuel cells (MFCs) can convert the chemical energy contained in a large variety of organic compounds into electrical energy. Such systems are composed of a microbial anode, which catalyses the oxidation of organic matter and is associated with a cathode, which is most often an abiotic air-cathode that ensures oxygen reduction (Ahn et al., 2014; Ye et al., 2016). Considerable advances have been made in bioanodes (Rimboud et al., 2014) but, in contrast, the oxygen-reducing cathodes remain a major rate-limiting step. There are several reasons for this, including the modest solubility of oxygen in water, the poor efficiency of O_2-reduction catalysts at the neutral pH values that are required to grow microbial anodes and, particularly in the case of abiotic air-cathodes, sensitivity to fouling.

When implemented in an MFC, the side of the air-cathode in contact with the electrolyte is exposed to a solution rich in microorganisms, organic compounds and salts. Bacteria colonize the cathode surface, forming a biofilm (Ma et al., 2014; Rismani-Yazdi et al., 2008), which may hinder the transport of the hydroxide ions away from the electrode and consequently enhance alkalinization in the vicinity of the cathode surface (Ma et al., 2014; Yuan et al., 2013):

$$O_2 + 2\ H_2O + 4e^- \rightarrow 4\ OH^- \quad (1)$$

Local alkalinization is detrimental to the oxygen reduction reaction from the point of view of thermodynamics and it also contributes to the deactivation of the cathode via the precipitation of cations in the form of hydroxides and scale (Tlili et al., 2003), particularly Ca^{2+} or Mg^{2+}, which are commonly present in the MFC electrolytes (Santoro et al., 2013; Ma et al., 2014; Santini et al., 2015). Various solutions have been proposed to mitigate air-cathode biofouling (Chatterjee and Ghangrekar, 2014; Li et al., 2014; Liu et al., 2015) including a separator to protect the cathode

* Corresponding author.
E-mail address: manon.oliot@ensiacet.fr (M. Oliot).

http://dx.doi.org/10.1016/j.biortech.2016.09.095
0960-8524/

surface from organic compounds (Song et al., 2015), antimicrobial coating to mitigate biofilm formation (Pu et al., 2014), or modification of the cathode composition (Wang et al., 2014; Zhou et al., 2016).

The solutions envisioned so far are one-shot options, i.e. they are designed at the beginning of the MFC's life and do not allow intervention during MFC operation. Once the air-cathode has been placed in the system, it cannot be removed without draining the anolyte because the air-cathode is generally part of the cell wall. With common MFC architecture, removing the air-cathode results in the loss of a large part of the electrolyte, which could severely disturb the bioanode, through exposure to ambient air, for instance.

The present study describes an innovative MFC design, which allows the air-cathode to be replaced easily. The fouled air-cathode can thus be cleaned or replaced without changing the electrolyte and without altering the bioanode. Surprisingly, using this new device to change the air-cathode in the course of MFC operation revealed the unsuspected magnitude of initial biofouling, which may have been a widespread cause of underestimation of MFC performance up to now.

2. Materials and methods

2.1. Reactor design

The reactor was designed so that three distinct operations could be carried out:

- Firstly, formation of the bioanode under controlled potential (chronoamperometry). The reactor was set in a standing position, the anode and the reference electrode were fixed on the reactor side and the auxiliary electrode was maintained on the top (Fig. 1A).
- Secondly, use of the reactor as an MFC. Once the bioanode formed in chronoamperometry was mature, the auxiliary electrode was removed and replaced by an abiotic air-cathode on the top. The reactor was then tilted to the side in order to bring the air-cathode fully into contact with the solution. The reactor was held in this lying position during MFC operation (Fig. 1B).
- Thirdly, when the efficiency of the air-cathode fell, return of the MFC to the standing position so as to change the air-cathode without draining the electrolyte and without exposing the bioanode to air or to any other disturbance. After the cathode had been changed, the reactor was tilted into the lying position again to continue MFC operation.

The reactor had a volume of 1.8 L. All experiments were carried out in a heat chamber at 40 °C. The bioanodes were designed from compost leachate with acetate as the substrate:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad (2)$$

2.2. Bioanode formation under chronoamperometry (CA)

Bioanodes were formed using a 3-electrode set-up with the reactor in the standing position (Fig. 1A). Carbon cloth (PaxiTech, Grenoble, France) was used as the anode support (working electrode). Electrodes with two different geometrical surface areas were compared: 9 cm^2 (3 cm × 3 cm) and 50 cm^2 (5 cm × 10 cm). Both electrodes had a thickness of 1 mm, so the total active surface areas used for current density calculations were 19.2 and 103 cm^2, respectively, including the edge area. A platinum grid was used as the auxiliary electrode and a saturated calomel electrode as the reference (SCE, potential +0.242 V/SHE). The working electrode was polarized at −0.2 V/SCE using a VSP potentiostat (Bio-Logic SA, France).

The bioanodes were formed under CA for 20 days in compost leachate, prepared as described elsewhere (Parot et al., 2008; Cercado et al., 2013) and supplemented with acetate. Acetate concentration was maintained at 20 mM by periodic measurements (Megazyme K-Acetak kit, Ireland) and additions. Once mature bioanodes were producing around 10 $A.m^{-2}$, the solution was replaced by a fresh synthetic medium (bicarbonate buffer 50 mM at pH 9, macronutrients 10 $mL.L^{-1}$, micronutrients 1 $mL.L^{-1}$, vitamins 1 $mL.L^{-1}$, KCl 4.5 $g.L^{-1}$ and $NaH_2PO_4{\cdot}H_2O$ 2.4 $g.L^{-1}$; pH adjusted to 7.0) and the bioanodes were polarized for 10 additional days. When they were delivering around 10 $A.m^{-2}$, the reactor was equipped with an air-cathode.

2.3. MFC operation

The air-cathode (PaxiTech, Grenoble, France) was assembled with a current collector (stainless steel) on a PVC screw cap designed with a central hole 4.5 cm in diameter, which resulted in an area of 15.9 cm^2 of the air-cathode being exposed to the electrolyte. The cap was screwed onto the top of the reactor and the reactor was tilted into the lying position (Fig. 1B). In this position, the anode and reference were on the top and the air-cathode was in a vertical position on the reactor side. During MFC operation, acetate concentration was maintained at 20 mM by periodic measurements and additions. Power curves were recorded periodically, using a variable external resistance ranging from 0 to 33,000 Ω. A high-impedance voltmeter (Keithley, 2000 multimeter, USA), in

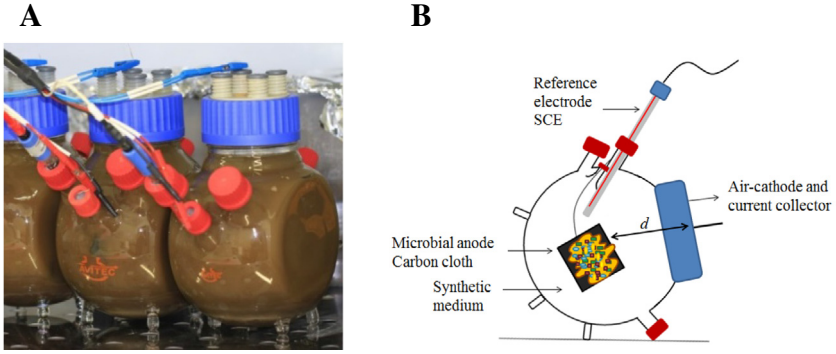

Fig. 1. Reactor design. (A) Photograph of reactors in standing position during formation of bioanodes under chronoamperometry (CA) with compost leachate as electrolyte. (B) Scheme of the reactor in lying position during MFC operation. The counter electrode was replaced by an air-cathode fixed on the blue screw cap with the current collector. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)