



Protons accumulation during anodic phase turned to advantage for oxygen reduction during cathodic phase in reversible bioelectrodes



Elise Blanchet^{a,*}, Sophie Pécastaings^b, Benjamin Erable^a, Christine Roques^b, Alain Bergel^a

^a Laboratoire de Génie Chimique (LGC), CNRS, Université de Toulouse (INPT), 4 allée Emile Monso, BP 84234, 31432 Toulouse, France

^b Laboratoire de Génie Chimique, BioSym Department, Université de Toulouse, 35 chemin des Maraîchers, 31062 Toulouse, France

HIGHLIGHTS

- Reversible bioelectrodes were designed under polarization at -0.20 V vs. SCE.
- The bioelectrodes catalyzed both acetate oxidation and oxygen reduction.
- Proton accumulation during anodic phase enhanced oxygen reduction by the biocathode.
- Microbial community was dominated by *Chloroflexi* (49%).

ARTICLE INFO

Article history:

Received 28 July 2014

Received in revised form 15 September 2014

Accepted 16 September 2014

Keywords:

Microbial fuel cell
Biocathode
Reversible electrode
Oxygen reduction
Chloroflexi

ABSTRACT

Reversible bioelectrodes were designed by alternating acetate and oxygen supply. It was demonstrated that the protons produced and accumulated inside the biofilm during the anodic phase greatly favored the oxygen reduction reaction when the electrode was switched to become the biocathode. Protons accumulation, which hindered the bioanode operation, thus became an advantage for the biocathode. The bioanodes, formed from garden compost leachate under constant polarization at -0.2 V vs. SCE, were able to support long exposure to forced aeration, with only a slight alteration of their anodic efficiency. They produced a current density of 16 ± 1.7 A/m² for acetate oxidation and up to -0.4 A/m² for oxygen reduction. Analysis of the microbial communities by 16S rRNA pyrosequencing revealed strong selection of *Chloroflexi* ($49 \pm 1\%$), which was not observed for conventional bioanodes not exposed to oxygen. *Chloroflexi* were found as the dominant phylum of electroactive biofilms for the first time.

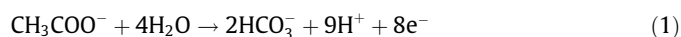
© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Microbial fuel cells (MFCs) are seen as a promising technology for producing electricity directly from the oxidation of various organic compounds that can be obtained at low cost and in sustainable way. The most widely studied MFC architectures are composed of a microbial anode associated with an abiotic oxygen-reduction cathode. Unfortunately, abiotic air-cathodes still give a rather low rate of oxygen reduction at the neutral pH values that are required for the microbial anodes. This problem remains an essential stumbling block in the development of large MFCs. Up to now, the power density provided by MFCs equipped with abiotic oxygen-reducing air cathodes has levelled off around

7 W/m² (Fan et al., 2008; Borole et al., 2011; Pocaznoi et al., 2012b) for small-sized cells and decreases drastically as soon as the system size increases (Santoro et al., 2013).

An appealing alternative solution would be to implement oxygen-reduction microbial cathodes (Erable et al., 2012), which have already proved their remarkable efficiency (Carbajosa et al., 2010). However, a major drawback of associating a microbial anode with a microbial cathode is that a pH gradient is established between the anode and cathode compartments. The pH gradient is the result of the production of protons at the anode as, for instance, in the widely used oxidation of acetate:



Coupled with the production of hydroxide ions by oxygen reduction at the cathode:



* Corresponding author. Tel.: +33 5 34323626.

E-mail address: blanchet.elise@gmail.com (E. Blanchet).

Ideally, electro-neutrality should be maintained by proton migration to the cathode compartment and hydroxide ion migration to the anode compartment, but the diffusion of these ions is too slow with respect to the other ions contained in the electrolytes (sodium, potassium, chloride, acetate, phosphate and carbonate ionic species, etc.) and proton migration plays only a minor role in charge-balancing. The pH gradient has been identified as a major source of losses in the performance of microbial electrochemical systems (Harnisch and Schröder, 2009). Membrane-less cells may provide part of the solution by decreasing the hindrance to ionic transport but, in return, they reduce electron recovery because of the direct aerobic conversion of the organic fuel due to oxygen diffusion from the cathode side (Rozenal et al., 2008). The use of a chemical buffer can compensate for the deficiency of proton transport (Torres et al., 2008), but it would be costly on a large scale. Freguia et al. (2008) addressed the problem by proposing a loop configuration: the effluent from the anode compartment was directed to the cathode compartment. This operating mode largely solved the problem of the pH gradient and it also improved the cathode performance compared with an abiotic oxygen cathode. However, such a system requires careful operation to avoid excessive chemical oxygen demand (COD) entering the cathode, which would cause the growth of aerobic heterotrophs and eventually restrict oxygen supply to the cathode biofilm.

Cheng et al. (2010) proposed the use of a reversible bioelectrode to avoid the problem of pH gradient and to improve the oxygen reduction catalysis. They showed that it was possible for a biofilm formed from activated sludge to catalyze both the anodic substrate oxidation and the cathodic oxygen reduction. The proposed MFC was operated in sequential phases by supplying acetate and oxygen to the electrode alternately. This system offers the advantage of avoiding growth of aerobic heterotrophic bacteria by separating acetate and oxygen supplies. Moreover, the protons accumulated during the anodic reaction do not need to be transported out of the biofilm: they stimulate the subsequent cathodic reaction. The concept of a reversible electrode has also been proposed by Strik et al. (2010), who used a reversible electrode inoculated with sludge to design a solar energy powered MFC. More recently, Li et al. (2014) have described a dual bioelectrode MFC with periodic reversal of polarity which results in a 36% increase in power density compared to that produced by the MFC without polarity reversal.

Reversible microbial anodes may be a very good solution to overcome the problem of pH gradient. The proton accumulation that occurs during the anodic phase (Reaction 1) prepares favorable conditions for oxygen reduction during the cathodic phase (Reaction 2). Despite their obvious advantages, studies of such reversible microbial electrodes remain rare and, in particular, little is known about the microbial composition of such intriguing biofilms, which are able to ensure an anaerobic anode respiring process and catalysis of oxygen reduction alternately. No comprehensive description of the microbial population of reversible electroactive biofilms has been published so far.

The purpose of the present work was to assess the capability of garden compost to form such reversible microbial electrodes. This inoculum source has already led to very efficient microbial anodes (Ketep et al., 2014) and has also been shown to contain bacterial strains (members of *Enterobacter* and *Pseudomonas* genera) with the ability to catalyze the electrochemical reduction of oxygen (Parot et al., 2009). Consequently, this inoculum was a priori an excellent candidate to form reversible microbial electrodes and the results presented here confirm this hypothesis. The reversible microbial electrodes formed here were then used for the in-depth analysis of the microbial communities. From a practical point of view, reversible bioelectrodes made from a soil inoculum may also

open up interesting possibilities for designing plant-MFCs (Strik et al., 2008).

All experiments were performed in a 3-electrode set-up so as to accurately characterize the electrode behavior. Actually, in whole MFC set-ups, the potential of the working electrode vary considerably, which adds a source of deviation between one experimental device and another. Since the reversible bioelectrode concept was still in its infancy, it was chosen to work in well-controlled analytical conditions here, in order to focus on the electrode behavior, rather than repeating a proof of concept with a whole MFC set-up, as already reported (Freguia et al., 2008; Li et al., 2014). Following this line of thought, electrodes with small surface areas were implemented in large volumes of electrolyte to ensure experimental conditions that favored electrode performance (Rimboud et al., 2014). The bioelectrodes were formed under constant polarization at -0.2 V vs. SCE. Their electrochemical properties were characterized by cyclic voltammetry and their microbial communities were analyzed by 16S rRNA pyrosequencing.

2. Methods

2.1. Medium and inoculum: garden compost leachate

Commercial garden compost was used as a source of electroactive microorganisms. 1.5 L of an aqueous solution containing 60 mM KCl was mixed with 1 L of garden compost and stirred for 24 h at room temperature. The mixture was then percolated through a felt cloth to eliminate non-soluble macroparticles. The final leachate was used as the electrolyte in the electrochemical reactors after supplementation with 20 mM acetate. The initial pH was 7.8 and the experiments were performed at 40 °C as already optimized by Cercado-Quezada et al. (2010).

2.2. Electrochemical set-up

Experiments were performed in single compartment electrochemical reactors equipped with a 3-electrode system composed of an 8 cm² carbon cloth working electrode (PaxiTech, Grenoble) connected with a platinum wire, a saturated calomel reference electrode (SCE, Radiometer Analytical, +0.241 V vs. SHE) and an 8 cm² Pt grid as auxiliary electrode. The working electrode was located far (around 10 cm) from the auxiliary electrode but as close as possible (around 0.5 cm) to the reference electrode. Each reactor contained 600 mL of compost leachate. The working electrodes were polarized at -0.20 V vs. SCE using a multi-channel VSP potentiostat (Bio-Logic SA, software EC-Lab) and the current was recorded every 10 min. Chronoamperometry was sometimes interrupted to perform cyclic voltammetry at low scan rate (1 mV/s) in the range -0.6 to $+0.3$ V vs. SCE.

Coulombic efficiencies (CE) were calculated as the ratio of the experimental electric charge passing through the system, obtained by integrating the current over time, and the theoretical charge calculated by assuming that 1 mol of acetate produces 8 mol of electrons according to the oxidation reaction (1).

2.3. Development of the reversible bioelectrode

Two experiments were systematically carried out in parallel (duplicates) to validate the reproducibility of the results. In the running of the electrochemical reactors, periods of acetate supply alternate with periods of oxygen supply. Acetate was added as a pulse of 3 mL of 4 M sodium acetate solution. Oxygen was supplied by forced aeration of the solution.

Download English Version:

<https://daneshyari.com/en/article/7076200>

Download Persian Version:

<https://daneshyari.com/article/7076200>

[Daneshyari.com](https://daneshyari.com)