Bioelectrochemistry 106 (2015) 328–334

Contents lists available at ScienceDirect

Bioelectrochemistry

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

Conditions for high resistance to starvation periods in bioelectrochemical systems

Yolanda Ruiz, Edgar Ribot-Llobet, Juan Antonio Baeza *, Albert Guisasola

GENOCOV, Departament d'Enginyeria Química, Escola d'Enginyeria, Universitat Autònoma de Barcelona, 08193, Bellaterra, Barcelona, Spain

ARTICLE INFO

Article history:
Received 2 February 2015
Received in revised form 20 June 2015
Accepted 21 June 2015
Available online 28 June 2015

Keywords:
Microbial fuel cell
Microbial electrolysis cell
Starvation
Substrate accumulation
Exoelectrogenic bacteria

ABSTRACT

The present work aims at understanding the performance of bioelectrochemical systems when subjected to different starvation periods, which is very relevant in view of their industrial application or use as biosensor. The results show that both microbial fuel cells (MFC) and microbial electrolysis cells (MEC) could resist starvation periods up to 10–11 days without any significant decrease in their performance when endogenous consumption was enabled by closing the circuit in MFC or applying an external voltage in MEC. By contrast, starvation periods longer than 5 days in both MFC and MEC when the flow of electrons from the anode to the cathode was not permitted thereby avoiding endogenous consumption, led to a reversible decrease in the cells performance. A longer starvation period of 21-days under open-circuit caused an irreversible performance loss of the MFC.

1. Introduction

Bioelectrochemical systems (BES) comprise the biotechnological applications resulting from the ability of some microorganisms, known as exoelectrogens or anode respiring bacteria (ARB), to transfer electrons outside the cell. Extensive research has been conducted in the last decade on BES aiming at current generation or production of value added products, such as hydrogen [1]. In short, a BES consists of an anode, a cathode and an electrical circuit. Oxidation occurs in the anode, where exoelectrogenic bacteria convert organic matter into CO_2, protons and electrons. Microorganisms transfer these generated electrons to an anode and from there, electrons flow through an electrical circuit to the cathode, where a reduction reaction occurs. If oxygen is reduced to water, the process is thermodynamically favourable and then, electricity is generated (this device is known as microbial fuel cell, MFC). In contrast, if the generated protons are to be reduced to hydrogen, a certain potential has to be added to drive the system (in a device known as microbial electrolysis cell, MEC).

BES have been mainly applied for producing electricity from wastewaters. However, the enormous research conducted in the last years on this field has resulted in a plethora of alternative applications: from microbial electrosynthesis to bioremediation or biosensors development. With respect to the latter, different biosensors, in which anodic exoelectrogenic bacteria act as the biological sensing element, have been proposed so far for the measurement of biological oxygen demand [2–4], microbial activity [5], toxicity [6–9], dissolved oxygen [10] and single molecules such as glucose [11], lactate [12], volatile fatty acids [13,14] and arabinose [15].

However, when dealing with biological processes, one has to be aware of the need of maintaining bacterial activity. In this frame, starvation periods (i.e. periods in absence of substrate) may occur often in real systems due to technical plant stops. Under this scenario, it is very important to know i) how detrimental will this period be to the biomass activity and ii) which are the best conditions for biomass maintenance in case starvation is unavoidable. Regarding the particular case of biosensors, starvation periods will occur as part of their usual operation, during which the maintenance of an active ARB-enriched biomass must be ensured.

For this reason, it is essential to understand the behaviour of BES under different periods of starvation as well as to estimate how detrimental will these periods be to the biomass and, finally, which are the best conditions for the biomass in case starvation is unavoidable. To the best of our knowledge, there is little information about starvation in both MFC and MEC. In Oh and Logan [16] the relationship between starvation and voltage reversal in two MFC stacked together was studied and it was concluded that starvation periods were detrimental for the MFC performance. However, this detrimental effect could have been caused not only by starvation but also by the voltage reversal experienced by the cell. In contrast, Kaur et al. [17] evaluated starvation as strategy to avoid electron losses derived from methanogenesis and the results suggested that 12 days of starvation were not overly harmful for ARB in MFC. Nevertheless, only closed loop starvation conditions were tested and the causes of such high resistance to starvation were not

* Corresponding author.
E-mail addresses: yolanda.ruiz@uab.cat (Y. Ruiz), edgarribot@gmail.com (E. Ribot-Llobet), Juanantonio.baeza@uab.cat (J.A. Baeza), Albert.guisasola@uab.cat (A. Guisasola).

http://dx.doi.org/10.1016/j.bioelechem.2015.06.010
1567-5394/

addressed. Gao et al. [18] studied the syntrophy between biopolymer-accumulating bacteria and ARB both in MFC and MEC, which allowed current generation without the addition of an external substrate for several days. Moreover, the system recovered the initial current generation when external substrate was added. Experiments were conducted by operating both MFC and MEC in two chamber configuration and with a set anode potential at −0.4 vs Ag/AgCl, but no experiments were performed in open loop for MFC or without applied voltage in MEC. Therefore, considering the few works in the literature where BES starvation was studied and the lack of a systematic evaluation, the aim of this study is to shed light on the effect of starvation processes in MFC and MEC under a wider set of operating conditions. Open-circuit and closed-circuit conditions for MFC and the application or not of an electrical voltage for MEC were studied in order to know which condition is better to maintain ARB activity and where is the limit of starvation time for each case.

2. Materials and methods

2.1. Reactors set-up

Two different type of cells were used, MFC for electricity generation and MEC for hydrogen production. MFC consisted of a 30 mL cylindrical cell with a lateral 3 cm diameter aperture where the cathode was assembled (7.07 cm^2). The cathode was carbon cloth coated with carbon powder and platinum suspension on the inner side (0.5 mg/cm^2, ETEK C1-10 10% Pt on Vulcan XC-72, ElectroChem Inc.), whereas the outer side was coated with a polytetrafluoroethylene (PTFE) solution, which permitted oxygen diffusion into the cell while preventing water leakage [19,20]. The anode was a carbon fibre brush (PANEX®33 160 K, ZOLTEK) [21] of 20 mm diameter × 25 mm length wound into a titanium core. It was thermally treated at 450 °C for 30 min prior to its utilization to enhance biomass adhesion [22]. The two electrodes, spaced 2 cm apart, were connected through an external resistance (1000 Ω or 100 Ω). Current intensity was determined from the monitoring of the voltage drop across this resistance. A reference electrode (Ag/AgCl NaCl 3 M, model RE-1B, BAS Inc.) was placed inside the cell. The MEC was similar to the MFC but the cathode was not exposed to air and the cell was provided with a glass cylinder that enabled gas collection. The gas produced was further collected in a 0.1 L gas sample bag with a twist type valve (Cali-5-Bond, Ritter), connected to the glass cylinder. Both electrodes were connected to a power source (HQ Power, PS-23,023) applying a voltage of 0.8 V. Current intensity was determined from the monitoring of the voltage drop across a 12-Ω resistor connected in series to the circuit. A low external resistance was selected in MEC to minimize the voltage losses across the resistor, so that the voltage applied by the power supply was approximately the voltage between the anode and the cathode.

Voltage evolution for both MFC and MEC was monitored by means of a 16-bit data acquisition card (Advantech PCI-1716) connected to a personal computer with a software developed in LabWindows CVI 2013 for data acquisition.

2.2. MFC and MEC operation

The cells operated with acetate as substrate (1.5 g/L) in batch mode. The medium contained per litre: Na_2HPO_4 (12.04 g) and KH_2PO_4 (2.06 g), so that the final phosphate buffer saline (PBS) concentration was 100 mM, NH_4Cl (0.2 g), $FeCl_2$ (4 mg), Na_2S (6 mg) and mineral media (5 mL). The mineral media stock solution contained (g/L): EDTA (1), $CoCl_2 \cdot 6H_2O$ (0.164), $CaCl_2 \cdot 2H_2O$ (0.228), H_3BO_3 (0.02), $Na_2MoO_4 \cdot 2H_2O$ (0.04), Na_2SeO_3 (0.002), $Na_2WO_4 \cdot 2H_2O$ (0.02), $NiCl_2 \cdot 6H_2O$ (0.04), $MgCl_2$ (2.32), $MnCl_2 \cdot 4H_2O$ (1.18), $ZnCl_2$ (0.1), $CuSO_4 \cdot 5H_2O$ (0.02) and $AlK(SO_4)_2$ (0.02). A 50 mM 2-bromoethanesulfonate concentration was used to selectively inhibit methanogenic activity [23]. Anodes were inoculated from the effluent of an existing MFC. Both MFCs and MECs were working with substrate for 15 days prior to starvation experiments.

Starvation tests were conducted in two MFCs and two MECs. The effects of different starvation periods in MFCs were studied by maintaining the cell in closed-circuit (MFC_{CC}) and in open-circuit (MFC_{OC}) during these periods. The external resistance was 1000 Ω and 100 Ω for MFC_{CC} and MFC_{OC}, respectively. In the case of MFC_{OC}, the external resistance was only connected under feast conditions (i.e. substrate presence). Starvation tests in MECs were studied while maintaining the applied voltage (MEC_{AV}) and without it (MEC_{WV}).

The cell was filled with medium without acetate before each starvation period to ensure fully starvation conditions. The medium was replaced with fresh medium with substrate for one batch cycle after each starvation period. Cycles after starvation periods were monitored to evaluate the effects of each starvation period on the cell performance. The cell was filled again with medium without acetate once current density started to decrease, provided that the performance was similar previous to any starvation period and a recovery time with substrate was not required. MECs were sparged with nitrogen for 10 min after replacing the medium to guarantee anaerobic conditions. All experiments were conducted at room temperature (T = 25 °C).

2.3. Chemical analyses

Acetate concentration was analysed with gas chromatography (Agilent Technologies, 7820-A) using a flame ionization detector (FID) and helium as carrier gas. Gas composition was analysed with the same gas chromatograph using a thermal conductivity detector (TCD) [24]. Hydrogen production was calculated as proposed in Ambler and Logan [25].

2.4. Electrochemical analyses

Power and polarization curves were obtained with a multi-resistance board which allowed changing the external resistance between 470,000 and 25 Ω. The cell was left in open circuit (OC) for 1 h previous to any measurement. A 10 min period was used for voltage stabilization at each resistance. The voltage drop across each resistance was measured by means of a multimeter. Medium was renewed previous to polarization curves recording.

2.5. System performance indexes

Coulombic efficiency (CE) (i.e. the fraction of electrons recovered as current intensity versus that theoretically generated from substrate oxidation) was evaluated as described in equation 1.

$$CE = \frac{\int_{t_0}^{t_F} I\,dt}{F \cdot b \cdot \Delta S \cdot V_R} \quad (1)$$

where t_0 and t_F are the initial and final times of a batch experiment (s), F is the Faraday's constant (96,485 C/mol e^-), b is the stoichiometric number of electrons produced per mol of substrate (8 mol e^-/mol acetate), ΔS is the substrate consumption (mol/L) and V_R the liquid volume (L).

The cathodic gas recovery (r_{CAT}), the ratio of coulombs recovered as hydrogen compared to those recovered as current intensity, was calculated as in equation 2.

$$r_{CAT} = \frac{V_{H2} \cdot 2 \cdot F \cdot V_m^{-1}}{\int_{t_0}^{t_F} I\,dt} \quad (2)$$

where V_{H2} is the volume of produced hydrogen and V_m is the molar gas volume (24.03 L/mol) at 20 °C.