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Effect of mode of operation, substrate and final electron acceptor on single-chamber membraneless microbial fuel cell operating with a mixed community

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ABSTRACT

Waste minimization and circular thinking are to be achieved in order to cope with the limited amount of resources of our planet. In this perspective, bio-electrochemical systems (BESs) can contribute to the global balance with their ability to extract chemical residual energy from wastewater and transform it directly into electrical current. BESs development has been limited by the cost connected to reactor design, in which membranes and cathode catalyst constituted a major drawback. In this paper we report the optimization process of a simple reactor without membranes or precious catalyst that produced 47.1 mW m^{-2}, which is more than what achieved with configurations including membranes, operating in similar conditions (glycerol as substrate and hydraulic retention times of 3 days). In opposition to what is usually reported for conventional divided microbial fuel cells (MFCs), we have found that in this kind of reactor fermenting substrates (mainly glycerol) can give higher current density than non-fermentable ones (acetate). Feeding modality and proper electrode orientation were confirmed to have a dramatic impact on power output. Finally, a possible niche for the exploitation of our single chamber membraneless MFC was pointed out to exist in bio-refinery industry.

1. Introduction

1.1. Bio-electrochemical systems for waste valorization

Global energy consumption was 1.5×10^9 MWh in 1850 ([1]) and global population was of about 1.26 billion people (*United Nations Population Division*) for a specific energy consumption of about 1.16 MWh $year^{-1}$ $person^{-1}$. The same calculation for the 7 billion people population of 2017 is of about 4.19 MWh $year^{-1}$ $person^{-1}$ (our estimate). This means that energy demand is not linearly related to the growth of population. The reason for this un-linearity has to be searched in our development model, based on the assumption that the pro-capita production has always to rise, against the natural concept of stationarity, which belongs to every eco-system [2]. In order to get closer to stationarity, wastes have to be avoided. It is calculated that annually 1.5×10^8 MWh are wasted as municipal, industrial, and animal wastewater [3]. Bio-Electrochemical Systems (BESs) are electrochemical devices developed for the direct conversion of the residual chemical energy of wastewater into electric current [3]. Exoelectrogens bacteria are employed, capable to close their respiratory electron chain on the surface of an electrode [4]. Up to know, BESs were used to extract energy from a multitude of wastes, such as distillery, food, animal carcass, brewery, biodiesel, manure, cheese, urine, feces, bad wine, old juices and composite vegetable [5]. In various cases, BES obtained relatively high energy conversion, but still their use is limited to the laboratory scale, since scale up seems to embed some major limitations. First of all, the ion-exchange membranes used for the separation of the two electrodic compartments are very expensive and brittle [6], making their use economically unsustainable. Sustainability can be improved by the integration of energy production with wastewater abatement in both compartments [7–9]. As an example, a water contaminated by acid orange 7, was first abiotically decolored in the cathodic compartment and, then, residual carboxylic acids were fed to the anodic bio-community [10]. Economics figures show that another constrain to BESs scale-up is represented by the cost of the catalyst that are used to improve the Oxygen Reduction Reaction (ORR) on cathode surface [11].

Many attempts to overcome these limitations were done; notable is the single chamber MFC implemented by Prof. Carlo Santoro and co-workers that showed how a membrane-free MFC without cathode catalyst can obtain the same results of an identical MFC operating with a Pt catalyst thanks to an efficient cathodic biofilm [27]. In authors opinion,

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Table 1
Comparison of single chamber membraneless (SCML) MFC without air cathode.

Cell-type	Inoculum	Peak power [mW m^{-2}]	Substrate	Size [L]	CE[b] [%]	Ref.
Sediment	Marine sediment	1.4	Sediment organic matter	–	–	[12]
Sediment	Polluted riverbank	7.5	Sediment organic matter	0.5441	–	[13]
Sediment	Farm manure	5	Manure	7	–	[14]
Sediment	Dairy wastewater	0.51[a]	Dairy wastewater	–	–	[15]
Solid phase	Composite food	4	Waste food	0.55	–	[16]
SCML	WWTP	220	Carbohydrates	0.2	–	[17]
SCML	*Shewanella putrefaciens*	37.5	Lysogeny broth	0.06	1.3	[18]
Baffled	Anaerobic paper sludge	74	Glucose	63	–	[19]
GAC-SCML[c]	WWTP	0.25[a]	Acetate	0.15	80-15	[20]
DF-SCML[d]	Anaerobic activated sludge	37.4	Glucose	0.85	–	[21]
SCML	WWTP	100	Municipal wastewater	45	10-24	[22]
SCML	*Bacillus subtilis*	19	Glucose	0.028	11	[23]
SCML	Previous MFC	58[a]	Urine	5	–	[24]
SCML	Previous MFC	64[a]	Urine	30	–	[25]
SCML	WWTP	22.7[a]	Acetate	1.1	4.4	[26]
SCML	WWTP	47.1	Glycerol	0.6	1.48	This study

[a] Recalculated and normalized on cathode surface.
[b] Coulombic efficiency (CE).
[c] Granular activated carbon (GAC).
[d] Down flow (DF).

a third constrain to BESs scale-up can be given by the utilization of air-cathodes which are gas-diffusion electrodes (GDEs) capable to enhance oxygen reduction [28–30], but increasing the complexity and the cost of the system. In order to limit these disadvantages, various researchers have investigated the utilization of single chamber membraneless (SCML) not equipped with air-cathodes (Table 1). In configurations derived from early sediment MFCs, anode is submerged into a detritic layer were oxygen is scavenged by microbes while cathode is in the overlying oxygenated water [12–16]. From an energetic point of view, these sediment-derived MFCs are currently regarded as the most realistic way for BES technology development [31]. SCML-MFC without an air cathode were developed also without any physical delimitation between the two environments [17–21]. Even if best results, in terms of power production, were achieved by Liu and co-workers [17] (see Table 1), the most promising approach to MFC scale-up seems to be the one adopted by the group of Ieropoulos that has conducted a successful systematic attempt to develop a system independent from any external peripherals and capable to power small electronic devices using the urine of a single individual [24,25]. The analysis of the performances of divided MFCs underlines that, as in any other biological reactor, substrate plays a fundamental role [32]. Pant research team has extensively reviewed the most of the substrate used in MFCs up to now in two different papers that can give to the reader a comprehensive understanding of the subject [5,33]. However, in the case of SCML-MFCs without an air cathode, scarce information on the effect of the substrate are present in literature. In particular, it would be very important to understand if the nature of the substrate has the same effects on both divided (i.e. with a membrane) and undivided MFCs (without any separator) exposed to air. Hence, in this paper, we have performed a detailed investigation on the effect of the substrate in both divided and undivided cells. The possibility of exploit the nitrogen cycle for biocathode functioning was taken into account. The effect of reactor feeding modality and electrode orientation on power production was also evaluated. It is worth to mention that we have found that the effect of the substrate in the case of undivided MFCs is different with respect to that achieved in divided cells.

2. Materials and methods

2.1. Reactor setup and operation

Single chamber membraneless microbial fuel cells (SCML-MFCs) with a total working volume of 60 mL were implemented into simple undivided electrochemical cell as described earlier [18]. Briefly, anode was a 10.5 cm^2 piece of carbon felt while cathode was a piece of compact graphite of the same surface. This last was rotated to get horizontality at the interphase between liquid and headspace in a specific set of experiments. Reactor were inoculated with 20 mL of aerobic sludge obtained from the aeration thank of a University of Cape Town Modified (UCTM) pilot plant available in our institution [34]. Three different way of feeding were compared:

- *Batch*. During batch tests 50 mL of solution were exchanged once total organic carbon (TOC) concentration was not changed appreciably. Batch averaged duration was of 2 weeks.
- *Semi-continuous*. Semi-continuous modality was implemented replacing every day 20 mL i.e. imposing a hydraulic retention time (HRT) of 3 days.
- *Continuous*. Continuous mode was implemented thanks to the use of two syringe pumps (NE-300, New Era Pumps Systems, Inc.) push/pulling two 60 mL syringe at a flow rate of 0.84 mL h^{-1} to obtain the same HRT of 3 days.

To test nitrate effect on bio-cathodic metabolism, 1 mL of 2 M NH_4NO_3 (Sigma-Aldrich) was poured every 60 mL of medium for selected experiments (final concentration 33 mM). Every cell was continuously stirred at 300 rpm with a magnetic stirrer (AREX, VELP Scientifica Srl). During normal operations, a 1 kΩ external resistor was used as cell load. Results obtained with SCML cells were also compared with H-type reactor assembled with two 100 mL glass bottles jointed by a horizontal glass tube housing a Nafion™ 117 (DuPont) membrane. Electrodes and load were exactly the same of the undivided reactor; compartments were opened to the atmosphere and stirred at 300 rpm. Catholyte consisted of pH 3 DM without carbon (sulfuric acid acidification). Experiments were performed at room temperature (25 ± 3 °C).

2.2. Media and analytics

Two defined media (DM) were prepared with a different Na_2HPO_4 and KH_2PO_4 ratio. When glucose or glycerol were used (fermenting substrates) 1.51 g L^{-1} of Na_2HPO_4 and 0.182 g L^{-1} of KH_2PO_4 were dosed, while 0.731 g L^{-1} of Na_2HPO_4 and 0.685 g L^{-1} of KH_2PO_4 were added in the case of lactate and acetate (non-fermenting substrates). The other components for liter of both solutions were: 8 g of NaCl, 0.5 g of NH_4Cl, 0.2 g of KCl, 0.1 g of $MgSO_4$, 0.133 g of $CaCl_2$, 10 mL of