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Selection of cheap electrodes for two-compartment microbial fuel cells

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ABSTRACT

This work compares the performance of four microbial fuel cells (MFCs) equipped with different cheap electrodic materials during two-month long tests, in which they were operated under the same operating conditions. Despite using sp^2 carbon materials (carbon felt, foam and cloth) as anode in the four MFCs, results demonstrates that there are important differences in the performance, pointing out the relevance of the surface area and other physical characteristics on the efficiency of MFCs. Differences were found not only in the production of electricity but also in the consumption of fuel (acetate) and even in the cathodic consumption of oxygen. Carbon felt was found to be the most efficient anode material whereas the worst results were obtained with carbon cloth. Performance seems to be in direct relationship with the specific area of the anode materials. In comparing the performance of the MFC equipped with carbon felt and stainless steel as cathodes, the later shows the worst performance, which clearly indicates how the cathodic process may become the bottleneck of the MFC performance.

1. Introduction

Microbial fuel cells (MFC) are energy conversion devices widely studied over the last decades [1,2]. Hundreds of papers have been published recently, pointing out the relevance of the topic for the scientific community [3]. Harvesting energy directly from organic matter as electricity is a promising concept, with very interesting results at small scales which, unfortunately, become difficult to be extrapolated in large facilities [4]. The clarification of the mechanisms involved, with a deeper understanding of the complex interactions between electrochemistry and biotechnology, is the more important handicap to be overcome in the near future and it justifies the research portfolios related to MFC currently carried out by many research groups [5].

In using mixed cultures in MFC, the microbial culture composition is expected to change and acclimate to the operation conditions applied [6,7]. In addition to the carbon source and nutrient composition (fuel of the MFC) [8,9], the values of the solid retention time and temperature [10] are known to be very important, as well as the organic loading rate used [11]. Initially, the electrochemical parameters are expected to show a lower relevance on the performance of the device and almost nil in the microbial composition. In fact, the most important electrochemical input is the choice of the electrode materials [12], because the electrocatalytic properties of these materials influence on the transfer of electrons required to harvest electricity from organic matter and their electric resistance on the voltage vs intensity performance [10]. Obviously, a cheap material exhibiting microbial-compatibility and suitable physical, chemical and electrochemical resistance is always the target, in particular for the anode. According to literature carbonaceous material are the best choice [13,14] and thus, most of the recent works use this type of anode material, which in addition to have high conductivity, they appear to be well suited for bacterial growth [15,16]. However, there are many types of carbonaceous materials with different physical characteristics associated to the sp^2-carbon [17] and it is important to determine the main differences between the performance of these materials in order to develop applications of MFC [18]. Within this context, carbon-based electrodes as foam and cloth are very common as electrode materials, exhibiting great advantages over the simpler carbon papers electrodes. Thus, carbon cloth is a flexible material with a greater porosity than carbon paper. It has been used as anode and cathode material with good results, achieving power densities near to 500 mW m^{-2} and 50% COD removal in single-chamber microbial fuel cell [19] and even higher when combined with activated carbon. Thus, in the treatment of fermented wastewater on a single chamber MFC, this combination achieves a power density of almost 3000 mW m^{-2} and 93% COD removal [11]. Its main drawback is its relative high cost, as compared to other carbonaceous materials [20]. Opposite to carbon cloth, carbon foams are much thicker and have more space for bacterial fixation, although the transfer of substrate typically limits the growth of microorganisms [12,21]. These materials have not been as extensively used in MFC studies as the paper and cloth materials. Carbon foam has been used as anode in marine benthic microbial fuel cells attaining a maximum power density of nearly 150 mW m^{-2} and higher values were obtained when carbon foam was modified with urea, attaining almost 260 mW m^{-2} of maximum power density [22]. Despite being very promising, carbon felt is less used although they have shown to be efficient 3D-electrodes in small mini-MFC [23] exhibiting good stability and fair robustness [24] [25].

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Regarding the cathode material, the complexity is even higher than that shown for MFC anode materials [26,27]. At this point, it is worth to take in mind that in abiotic cathode MFC, the electrochemical reduction of oxygen to water is sometimes the bottleneck of the electricity production in MFC. This fact explains the great effort made in the recent years in the search for efficient cathodes, which includes not only the use of platinum and other catalyst but also special cell design such as the air-cathode microbial fuel cells [26,28]. The main drawback of using catalyst on the cathode is the usual operation temperature of MFC, for which typical catalyst are not very efficient. Hence, more conventional materials are in focus nowadays and within this context, stainless steel have already proved to be efficient in MFC attaining very high current densities (20.5 A m^{-2}) have been achieved with a pure culture of an electrogenic bacteria. In addition, stainless steel cathodes exhibited high catalytic properties for oxygen reduction under this condition [29].

This study shows the influence of cheap anodic and cathodic materials on the performance of several MFCs operated over long periods. To do this, three carbonaceous materials (felt, foam and cloth) were evaluated as anodes in combination with two materials that were tested as cathodes (felt, stainless steel). No catalysts (such as platinum) were added because they may increase the prize and make the technology unfeasible from the view point of costs. The MFC were fed with a highly concentrated solution of acetate and nutrients, used as synthetic fuel and hydraulic retention time (HRT) was kept in 3.2 days over all the test. Two-compartment MFCs were used to evaluate the performance of the different electrode materials and a proton exchange membrane was placed to separate the anode and cathode compartments. The four cells monitored were seeded with the same mixed culture, fed with the same fuel solution and kept within the same operation conditions. Hence, changes are expected to depend only on the electrode material used.

2. Materials and methods

2.1. Microbial fuel cell set-up

The set-up used in this work consisted of a MFC with two chambers (4 cm^3 volume each one) separated by a proton exchange membrane, PEM (Sterion®), which has a high ionic conductivity (0.02–0.90 meq g^{-1}) and low electronic conductivity (8×10^{-2} S cm^{-1}) and has been used previously in PEMFCs with good results [30]. Each MFC is formed by two HDL (high pressure laminate) plates and two silicon plates to improve the mechanical properties and avoid liquid losses. The electrode spacing between the anode and the cathode (1.0 cm) was minimized in order to reduce as much as possible the internal electrical losses from the system. The two electrodes (3 cm^2 each) were connected by an external resistance (R_{ext}) of 120 Ω; this low value was chosen to prevent activation losses and facilitate electron transfer during the acclimation period [31]. A fishery compressor that can provide a flow rate of 1.6 L min^{-1} and a maximum pressure of 1.2 m of water-column was connected to the cathodic chamber to oxygenate the liquid. Each cell was equipped with two reservoirs (110 cm^3) connected, respectively, to its anodic and cathodic compartment. Peristaltic pumps were used to circulate an HCl solution (pH 3.5) from the cathodic reservoir through the cathode chamber of the MFC at 25 cm^3 min^{-1} and to circulate the analyte with a flow of 25 cm^3 min^{-1}. The experiments have been carry out at room temperature (23 ± 2 °C) which was kept constant by means of an air conditioning system.

2.2. Characterization techniques

A digital multimeter (Keithley 2000 Multimeter) was connected to the system to monitor continuously the value of the cell voltage at the value of the external load (120 Ω). Chemical oxygen demand (COD) was determined using a Velp ECO-16 digester and a Pharo 100 Merck spectrophotometer analyzer and pH, conductivity and dissolved oxygen were measured with a GLP22 Crison pH meter, a Crison Cm 35 conductivity meter and an Oxi538 WTW oxy meter, respectively. Polarization curves have been recorded periodically and obtained by replacing the external resistance with different loads. Three important parameters were evaluated: the open circuit voltage (OCV) or the maximum allowable MFC voltage, the maximum intensity and the maximum power density of the MFC. In addition, the shape of curves gives important information about the limiting processes, which control the performance of the cell (Fig. 1).

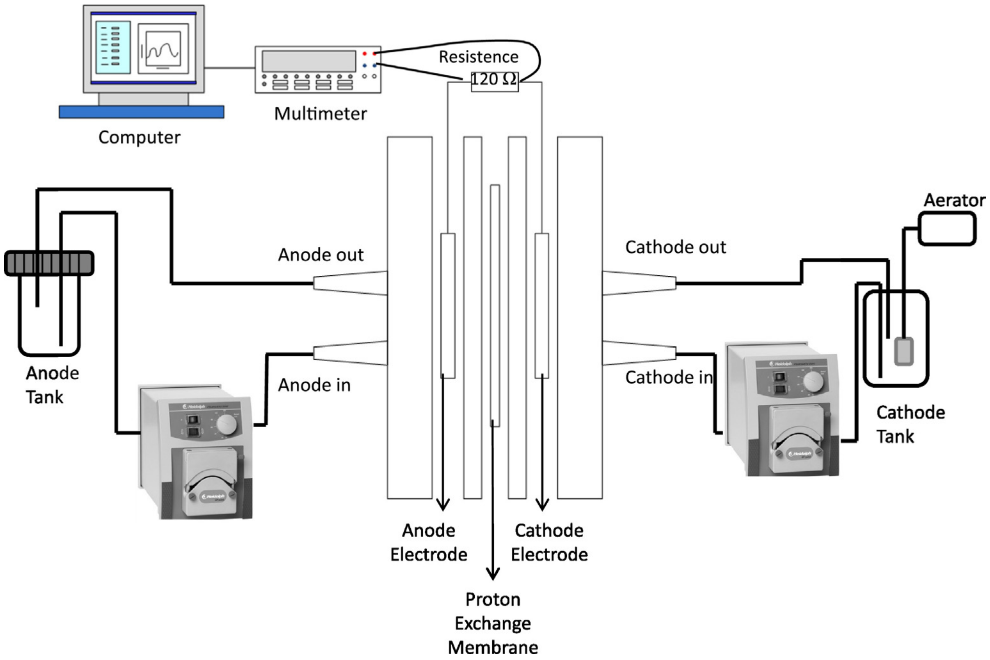

Fig. 1. Experimental setup used for each MFC.