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New prototypes for the isolation of the anodic chambers in microbial fuel cells

C. Prestigiacomo [a], C.M. Fernandez-Marchante [b], F.J. Fernández-Morales [b], P. Cañizares [b], O. Scialdone [a], M.A. Rodrigo [b,*]

[a] Università degli Studi di Palermo, Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Palermo, Italy
[b] Universidad de Castilla-La Mancha, Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies, Ciudad Real, Spain

HIGHLIGHTS

- The influence of the cell construction over the performance of a MFC was studied.
- A cathode, facing both MFC compartments, isolated anodic and cathodic reactions.
- The cathode facing both compartments keeps ionic and electric conductivity.
- Anodic and cathodic separation with a PEM membrane yielded the highest efficiency.
- Unbalanced electron exchanges indicate the existence of complex processes.

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ABSTRACT

This work has been focused on the assessment of new prototypes of MFC in which a more strict separation of the anode and cathode compartments is looked for, in order to attain strict anaerobic conditions in the anode chamber and hence, avoid lack of efficiency due to the prevalence of non-electrogenic competing microorganisms and to optimize composition of the anolyte and catholyte. A cylinder reactor with an inner chamber with graphite bars acting as anodes and the outer one with a stainless steel tube acting as cathode was used in three different configurations and results obtained during lifetests are compared in terms of electricity production, cathode oxygen consumption and anode COD depletion. Separation between compartments was obtained by (a) a two faces cathode (prototype R1, in which the cathode faces both compartments of the MFC), (b) a single cathode (prototype R2, in which the surface facing the anode compartment is electrically isolated and the ionic circuit is virtually detached) and (c) a conventional PEM membrane (prototype R3). Results show that the three prototypes perform as MFC from the electric point of view and they are efficient in the degradation of the COD contained in wastewater. However, the efficiencies in the production of electricity are very different and the greater the isolation of the anodic compartment, the lower are the current intensities produced. These results are explained because of the higher resulting ohmic loses. This large increase in the cell potential mask the potential benefits searched for with the isolation of the anode chamber but, at the same time, it gives significant information about performance of MFC that can be used for future MFC miniaturization studies.

1. Introduction

With the increasing concern for alternative more sustainable energy sources, global climate change and waste management, the search for novel technological solutions becomes a crucial necessity [1]. Amongst other technologies, microbial fuel cells stand up as an alternative and sustainable energy technology that nowadays is under development [2–5].

A microbial fuel cell (MFC) is an electrochemical reactor that converts the chemical energy contained in organic substrates directly into electricity, by means of the metabolic abilities of microorganisms [6–8]. This conversion can produce different types of metabolites and it may progress up to the formation of carbon dioxide. In the anodic chamber, microorganisms oxidize substrates releasing electrons which are transported to the anode. In this way, the anode acts as a solid external electron acceptor for the

* Corresponding author at: University of Castilla-La Mancha, Chemical Engineering Dept., Avda. Camilo José Cela S/N, 13071 Ciudad Real, Spain.
E-mail address: Manuel.Rodrigo@uclm.es (M.A. Rodrigo).

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microorganisms. The electrons released in the oxidation of the organic matter are transported by an external electrical circuit to the cathode. While the electrons travel through the circuit, in conventional divided MFC the corresponding protons migrate to the cathodic compartment through a proton exchange membrane to maintain charge neutrality [9]. At the cathode, an electron acceptor is reduced by the electrons transported from the anode via the external electrical circuit and the protons via the membrane. The kinetics of electrochemical reactions in MFC are comparable and they may vary depending on physical, chemical and biological operating condition [10–12]. In literature, different MFC configurations have been proposed, all of them aiming to reach the highest performances, usually measured as exerted power or potential and coulombic efficiencies [13].

The theoretical ideal potential, E_{thermo} (V), attainable from a MFC can be thermodynamically predicted by the Nernst equation as shown in Eq. (1), where E° is the standard cell potential (V), R the ideal gas constant (8.314 J mol^{-1} K^{-1}), T the temperature (K), n the number of electrons transferred in the reaction (dimensionless), F the Faraday's constant (96,485 C mol^{-1}), and Π the chemical activity of products divided by those of reactant (dimensionless).

$$E_{thermo} = E^{\circ} - RT/nF \ln(\Pi) \quad (1)$$

However, the actual potential exerted by a MFC is always lower than the thermodynamic one due to irreversible loses. The three major irreversibilities are related to activation, ohmic and mass transport loses [14]. Moreover, other irreversibilities such as the presence of oxidants in the anaerobic compartment usually exist [15]. The extent of these inefficiencies depends also on adopted materials and configuration. Thus, MFCs are being constructed using a variety of materials and configurations.

Regarding to MFC configuration, an ever increasing diversity of configurations is shown in literature ranging from the simple batch H-shape systems used for preliminary lab-scale tests to the continuous single chamber MFC [16]. In relation to configuration of the systems in one or two chambers, it must be stated that single-chamber MFCs design avoids the need for a membrane, thus avoiding the ohmic loses given by the separator [17]. However the spacing of the electrodes is a critical factor for achieving high performance MFCs. Indeed, decreasing the distance between the electrodes can improve power output because it reduces the ohmic loses [16]. Close electrode spacing could be especially important for domestic wastewater treatment as its conductivity is very low (1 mS cm^{-1}), and therefore widely spaced electrodes would result in high ohmic loses. Unfortunately, when electrodes are very close the presence of electron acceptors near the anode reduce the efficiency in the electron transfer and therefore the performances of the MFC [18,19]. In literature, it has been reported that very closely spaced flat electrodes have been shown to decrease MFCs performance, despite a reduction in ohmic resistance, due to oxygen crossover from the cathode to the anode [20]. Very close spacing of the electrodes can be obtained by placing a separator between the electrodes to avoid electrode contact and short-circuiting. This membrane electrode assembly (MEA) configuration also enables both more compact packing of electrodes and reduces oxygen crossovers into the anodic compartment. Adding a separator, however, increases ohmic resistance [21], which can decrease power generation as well as create pH gradients, due to the limitations imposed to the protons transfer to the cathode, that can decrease performance. The effect of ohmic resistance on the performance becomes more important when solutions with low conductivity, such as wastewater, are used as fuels, and the importance of the pH gradients became important when a significant amount of protons are generated in the system but not consumed.

Because of that, it is clear that the possibility of a stricter separation of the anodic and cathodic processes could enhance the performance of the MFC, because it may help to optimize both compartments separately and hence to obtain higher efficiencies [22,23]. This is particularly important in miniaturization of MFC, which for sure will become a challenge for the next years. In this context, the aim of this work was to assess three prototypes based on the same primary reactor design, in order to study the feasibility of an effective separation of the anodic and the cathodic chambers of a MFC in order to prevent oxygen transfer and to help to optimize composition of the anolyte and catholyte.

2. Experimental

2.1. Setup and MFC configuration

A schematic view of the setup used in this work is shown in Fig. 1. The main element of the setup is the biological reactor, the MFC, which presents a special design with two concentric chambers: the inner chamber with graphite bars acting as anodes and the outer one with a stainless steel tube, acting as cathode, which separates the two chambers.

The anode chamber included 40 graphite bars, each with a diameter of 0.2 cm and length of 10 cm. The graphite bars were fixed to two perforated plastic plugs with a metal adhesive (Silver Loaded Epoxy Adhesive RS). Copper wires and the conductive metal adhesive were used to connect the graphite bars with the electrical circuit. The anodic compartment (113 cm^3) was connected to a reservoir of 600 cm^3.

The cathode was a stainless steel tube. The external side of the cathodic chamber was made with a concentric plastic tube, being the cathodic volume 74 cm^3. This chamber was also connected to a reservoir, 600 cm^3, from which an aqueous solution of HCl was fed. During operation, the anode and cathode were connected by means of copper wires and a resistance (120 Ω).

In this work, three different prototypes were taken from this base design. They were the following:

- R1: base design with no modifications; the stainless steel cylinder is in direct contact with the anodic (inner surface) and cathodic (outer surface) chambers but no electrolyte flow is allowed between the two compartments.
- R2: inner surface of the stainless steel (in contact with the anodic chamber) is isolated with a polymeric layer coating (previously painted) preventing, or at least strongly limiting, the exchange of electrons between the steel tube and the anodic solution. Initially, this prototype is not expected to perform as a MFC because the ionic circuit is virtually detached.
- R3: holes made in the surface of the stainless steel and a cationic exchange membrane (Sterion) separating the anodic and cathodic compartments and preventing the mixture of both electrolytes.

To start-up the process, the anodic compartment was inoculated with 300 cm^3 of activated sludge from the biological reactors of a conventional municipal wastewater treatment plant (WWTP) located in Ciudad Real (Spain). More information about this facility can be found elsewhere [23,24]. The characteristics of the actual wastewater and of the activated sludge employed in this work in terms of chemical oxygen demand (COD), pH, phosfates (P_T), nitrates (N_T) and total suspended solids (TSS) are given in Table 1.

A peristaltic pump was used to recirculate the activated sludge and actual wastewater from the reservoir through the anodic chamber at 0.5 cm^3 s^{-1}. Once the anodic chamber was completely filled, 125 cm^3 of actual wastewater were added to the reservoir. In