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Characterization and comparison of the performance of two different separator types in air–cathode microbial fuel cell treating synthetic wastewater

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HIGHLIGHTS

- First study to compare the performance of Zirfon® and Fumasep® as separator in MFC.
- Zirfon® performed better compared to Fumasep® in an air cathode MFC.
- The maximum power density obtained with Zirfon® was 424.50 mW/m^2.
- The maximum power density obtained with Fumasep® was 38.03 mW/m^2.
- SEM/EDX images showed a good biofilm formation on electrode surface.

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ABSTRACT

Bioelectricity production from microbial fuel cell (MFC), fed with synthetic wastewater can achieve both wastewater treatment and energy production. Two different types of separators were used in this study to compare their performance in an air cathode MFC. Power generation and substrate utilization from the wastewater was compared for these membranes. The maximum power density obtained with Zirfon® was 424.50 mW/m^2 and of 16.98 W/m^3 (volumetric) while with Fumasep® was 38.03 mW/m^2 and 1.52 W/m^3 (volumetric). The internal resistance obtained with Zirfon® increased from initial 0.38 Ω cm^2 to 1.72 Ω cm^2 while with Fumasep® increased from 2.57 Ω cm^2 to 10.92 Ω cm^{-2} at the end of the experiment. The results showed that the MFC with Zirfon® stabilized early and the anodic and cathodic cell potentials reached maximum earlier as compared to Fumasep®. Impedance spectra confirmed the lower resistance of the Zirfon® as compared to Fumasep® and this may be the reason for its better performance. Zirfon® might be a good option for the future scale up of MFCs because of its low cost and low internal resistance in comparison to other membranes.

1. Introduction

The microbial fuel cell (MFC) is a progressing sustainable technology that can produce direct electricity while performing wastewater treatment. This is a novel type of reactor that uses microbial electrocatalysis to achieve redox conversions of organic and inorganic substrates present in the waste streams [1–3]. A MFC consists of an anode and a cathode, normally separated by a proton exchange membrane (PEM). At the anode, electrochemically-active microbes (electrogenic bacteria) oxidize organic or inorganic substrates using the anode as the final electron acceptor. Pant et al. provided a comprehensive review of the different substrates that can be decomposed in MFCs, and recently it has been proved that even elevated levels of COD (e.g. in the order of 8–10 g/L) can be degraded in a MFC [4]. In the MFC, the anode potential (E_{an}) spontaneously evolves lower than the cathode potential (E_{cat}) [5]. Electrons are externally transported from anode to the cathode through an external electrically-conducting material (e.g. a resistor). Protons generated at the anode are transported through the anodic medium, across a separator (PEM), and through the cathodic medium to finally reach the cathode, where they combine with an equivalent reducible compounds and electrons [6–8].

For a better understanding of electron transfer mechanisms between bacteria and electrodes, as well as for characterizing material properties that ameliorate the performance of MFCs, various

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electrochemical methods have been used, such as linear sweep voltammetry [9], cyclic voltammetry [10,11] and chronoamperometry [11]. More recently, electrochemical impedance spectroscopy (EIS) has been primarily used to find the overall internal resistance and individual-component resistances in MFCs [12–16]. Dominguez-Benetton et al. [5] provided a detailed review on the accurate application and interpretation of EIS and its broader employability to study the electron transfer and reaction mechanisms, mass transfer phenomena and distribution of the heterogeneous properties of MFCs. Still, large-scale application of MFC for real wastewater treatment are not yet fully developed due to several constraints that have been detected through the aforementioned methods, including low power output, high internal resistance and high costs of the materials.

The internal resistance in a MFC is one of the limiting parameter that determines its energy efficiency. This total internal resistance consists of several partial resistances, comprising—in order of contribution to the total internal resistance—the cathode resistance, followed by the resistance for ion transport through the membrane, the anode, and the electrolyte resistance [17]. The research group authoring the present manuscript has addressed elsewhere the development and performance of improved carbon-based gas-diffusion electrodes as cathode materials that reduce the internal resistance, increase power density and cell efficiency [18–20] as compared to other existing cathodes for MFC and even for other types of fuel cells [21]. For this reason, the present investigation spotlights on the membrane component.

The membrane or separator has the main intentions of facilitating diffusion and migration of protons towards the cathodic compartment, as well as impeding the counter flow diffusion of oxygen to the cathodic compartment [22]. Membrane-less MFC have been employed, but they have demonstrated to be less efficient than those containing them [22]. A variety of separators have been used in MFCs, including salt-bridge [23], anion exchange membrane (AEM) [24–26], cation exchange membrane (CEM) [24,27–30], bipolar membrane [26,31,32] and ultrafiltration membranes [26,33]. Li et al. [34] summarized various separators used in MFCs with their detailed characterization with respect to their advantages and disadvantages. CEM are generally preferred in MFC, contrary to Microbial Electrolysis Cells (MECs), in which AEM have improved performance of the system [17]. Nafion® (Dupont) and Fumasep® (FuMA-Tech GmbH) are the most popularly used membranes, due to their recommended high proton selectivity; several studies have been carried out to find cation-exchange materials as replacements t, but in terms of proton selectivity they continue being the preferred option. Nonetheless, membranes fabricated with these materials have prohibitive costs for practical use and, besides, in batch operation they cannot prevent transport of other cations such as Na^+, K^+, NH_4^+, Ca^{2+} Mg^{2+}, making them cation and not proton-specific [22,35]. The Zirfon® separator has been proposed as replacement for conventional ion exchange membranes in MFC; this material proved to reduce oxygen flux towards the anode compartment, and no reduction in electrode performance for oxygen reduction at the cathode and acetate oxidation at the anode was observed [18]. However, the dynamic response of such materials has not been revealed previously, during power generation in continuous closed-circuit mode. Furthermore, although these membranes have been anticipated to be used in systems where substrates other than acetate are present, experimental results have not been yet exposed. So, to provide further evidence of Zirfon® as an efficient separator with reduced cost and improved MFC performance, it was compared to a commonly used CEM in this work.

Thus, the objective of this study was therefore to examine the power production and simultaneous wastewater treatment achieved by using air–cathode MFCs with two different types of separator (PEM) and their effects on anode and cathode potentials. The MFCs used were (i) with Zirfon® membrane (MFC-1), (ii) with Fumasep® membrane (MFC-2).

2. Materials and methods

2.1. MFC configuration and operation

Two identical air–cathode MFCs were constructed from plexiglass with a total working volume of 25 mL each. Zirfon® and Fumasep® were used as separator in MFC-1 and MFC-2 respectively. Prior to use, the membranes were pre-treated and characterized according to Pant et al. [27]. All the electrodes and membranes used in these two MFCs had cross sectional area of 10 cm^2. Ag/AgCl–3 M KCl (+199 mV vs. Standard Hydrogen Electrode) was the reference electrode (Radiometer Analytical, France); all potentials reported in this article are referred to such reference electrode. A Pt disc laser-welded on a titanium (Ti) plate served as the counter electrode (CE). To prevent interference of gases (O_2 or H_2) which can be produced at the counter electrode during the polarization measurements, the ion permeable separator was placed between the working electrode and the CE. Air (21% O_2) was fed to the air compartment at the PTFE side of the electrode at an overpressure of 5 m bar (g). All MFCs were operated at 23–27 °C (room temperature). Phosphate buffer solution (PBS) treated (70 °C, 4 h) activated carbon cloth (Ballard, USA) was used as the anode. Non-platinized, gas diffusion electrodes were used as air cathodes and were constructed at VITO (Belgium) as described previously [18,19]. Both anode and cathode included a stainless-steel mesh current collector, which has been previously described [18,19].

2.2. Synthetic wastewater composition

In all the experiments the synthetic wastewater (glucose 2 g/l, yeast extract 0.34 g/l, ammonium chloride 0.84 g/l, potassium di hydrogen phosphate 0.136 g/l, di potassium hydrogen phosphate 0.234 g/l, magnesium chloride hexa hydrate 0.084 g/l, ferric chloride 0.05 g/l, sodium thioglycolate 0.1 g/l) was used.

2.3. Inoculation

The anode chambers were inoculated from another previously running MFC in the lab that has been in operation for 28 months with acetate (10 mM) and PBS. The inoculum enrichment was done according to Sevda et al. [4]. The final medium was flushed with N_2/CO_2 (80:20) for 30 min prior to use. The pH was adjusted to 7.0. The microbial diversity of these inocula has been evaluated to be stable over 30 months, with a high predominance of *Geobacter sulfurreducens*.

2.4. Analytical measurement and calculations

Parameters like pH, electrical conductivity (EC), dissolved oxygen (DO) concentration, open circuit voltage (OCV), internal resistance and chemical oxygen demand (COD) were monitored on a regular basis, allowing an understanding of the evolution of the system during the bioelectrochemical process. DO and pH were measured using a purpose-built multimeter (wtw 340i). The EC was measured using a conductivity meter (Knick SE204). The resistance between the electrodes (internal resistance) was measured using a milliohm resistance meter (HIOKI 3560 AC mOHiTester). For analysis of volatile fatty acids (VFAs), filtered samples were acidified with 0.5 ml of a 50% H_2SO_4 solution and then extracted with diethyl ether. VFAs were analyzed in a gas chromatograph (GC) (CE Instruments-Thermoquest) equipped with a flame ionization detector (FID) and a 15 m AT-1000 filled capillary column