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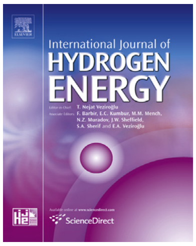

Comparison of alternative membranes to replace high cost Nafion ones in microbial fuel cells

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ABSTRACT

The aim of this work was to compare the performance of microbial fuel cell (*MFC*) fitted with alternative, low cost membranes (*AMs*). Lab scale single chamber *MFCs* were loaded with sulphate-reducing inocula as biocatalyst and leachate from dark fermentation of organic wastes as substrate. The *MFCs* were fitted with either hybrid membrane made of agar and Nafion *MH*, agar membrane *M6* (6% agar), agar membrane *M2* (2% agar) or the control Nafion 117 membrane (*NF-117*).

We found that the internal resistances (R_{int}) were generally low for all the cells. The lowest R_{int} corresponded to alternative membranes *M6* and *MH* with a value *ca.* 90 Ω. So, results of R_{int} tend to favour the AMs. The costs of these membranes were only 2.5–6% of the cost of the *NF-117* one. However, the powers delivered by *MFC* fitted with AMs were 4–40% (weighed average 28%) of the power of the cell fitted with the conventional *NF-117*. In spite of the reduced power, the AMs still exhibited a higher Power/Cost ratio (0.9–4.4. mW/US$) than that of the *NF* membrane (0.23 mW/US$.)

We should highlight that the AMs do not require the conditioning treatment with hazardous chemicals typical of *NF-117*. Therefore, there is another competitive edge of AMs in the form of avoided costs of chemicals and hazardous waste disposal.

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Introduction

Water pollution challenges the existence of humankind and effective, sustainable actions and solutions for wastewater treatment and water pollution prevention should be found and implemented in the short term [1]. In this regard, microbial fuel cells (*MFCs*), that are one type of the denominated Bioelectrochemical systems, constitute a promising technology whereby is possible the energy generation from and bioremediation of effluents, as well as other applications through bio-electrochemical reactions using microorganisms as biocatalysts [2–5].

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In the last years, renewable energy sources have attracted increasing attention due to current and future outlook of fossil fuels [6–8]. The *MFCs* represent an interesting alternative to produce electrical energy and provide wastewater treatment simultaneously. A wide range of soluble substrates (organics or inorganics) can be used as fuel to feed the *MFCs*. Furthermore, the fuel to *MFCs* in the form of effluents is typically a renewable source, cheaper or free and available around the world [9–13].

However, it has been reported that the scale up of *MFCs* is hindered by the typical high costs of membrane or separator used in the design of *MFCs*, among other things [3,14]. It has been shown that the membrane represents approximately 40% of the cost of *MFCs* [14–16] considering Nafion 117 membrane (*NF-117*) as proton exchange membrane (*PEM*). Rozendal et al. [14] predicted a fall in the separator cost till 20% of the total cost of the cell in the medium term. So far, Nafion is the material most often used for membranes in *MFCs*; it has become a non-official standard [17–23]. Furthermore, the use of a separator such as membranes, may affect negatively the *MFC* performance increasing the internal resistance (R_{int}) of *MFCs*, the pH splitting, retard in the transfer of protons, among others issues [24–26].

Yet, a membrane is necessary as component in the *MFCs* to ensure a good performance and stability along the operation time due to other properties and features [24,27–29]. For instance, membranes act as separator between anodic and cathodic electrodes avoiding the electric short circuit, as a barrier to the transfer of other ions between the chambers, reducing the substrate flux from the anodic to cathodic chamber. Membranes also prevent the backdiffusion of the oxygen increasing the coulombic efficiency (*CE*), isolate the catalyst from the cathode in single-chamber *MFCs* and ensures that the cells exhibit efficient and sustained operation [24,27,30].

In the open literature, it has been reported at least 20 different materials used as membrane or separator in *MFCs* [20,24,31] e.g. ultrafiltration and microfiltration membranes [24], sulphonated polyether ether ketone membranes [22,32], anion and cation exchange membranes e.g. AMI 7001 [33], CMI-7000 [25,26], Nafion 117 [7,26,27,31,34,35], bipolar membranes [36], forward osmosis membranes [37], glass fibre mats [38], glass wool [39,40], cloth separators (J-Cloth and canvas) [41,42], salt-agar slab [43], salt bridge [44], agar membranes [29,45], Zirfon membrane [46], ceramic membranes [47], nylon mesh [24], polyvinylidene fluoride (PVDF)/Nafion composite membranes [16], uncharged and sulfonated porous poly(vinylidene fluoride) membranes [25]. In general, the purpose of all of them is to reduce the cost of *MFC* by choosing more economic separators, to increase the *MFC* performance and decrease the overall R_{int} [24]. A survey of the costs of membranes/separators indicate the following ranges, depending on the type (in USD/m^2): anion exchange membranes AMI 7001, 80–83; cation exchange membranes such as CMI-7000, 200; Nafion 117, 1400–2200; plastic (polypropylene) mesh, 13–26; stainless steel mesh, 80–135; ultrafiltration membranes, 350, and J-cloth, 400 [24,38].

The aim of this work was to compare the performance of *MFC* fitted with alternative, low cost membranes (*AMs*) and compare their performance with the classical Nafion membrane as well as other types of separators.

Materials and methods

Experimental design

The experiment consisted of testing *MFC* performance equipped with several *AMs* as separators: hybrid membrane made of agar and Nafion *MH*, agar membrane *M6* (6% agar), agar membrane *M2* (2% agar). The *NF-117* was used as reference membrane to compare the results. Graphite flakes (*GF*) with a surface area of 0.28 m^2 were used as anodic material [5,15]. Membrane materials and fabrication procedure are explained in the section ‘Preparation of membranes’.

The liquid fed to the *MFCs* was a mixture of sulphate-reducing inocula (*SR-In*) and leachate from dark fermentation of organic wastes as substrate. The experiments were carried out without using any extra source of energy to mechanical mixing or heating. All microbial fuel cells were operated at room temperature (22 ± 1 °C).

The main response variables determined in the electrochemical characterizations were the maximum volumetric power ($P_{V,max}$) and the internal resistance (R_{int}), among others.

Microbial fuel cells

Single compartment, air-cathode *MFCs* were used to carry out all the experiments. The *MFCs* were horizontal cylinders built in Plexiglas 80 mm long and 57 mm internal diameter (Fig. 1). The anodic chambers were packed with *GF* with a total surface area of 0.28 m^2. On the air side, the cathode was limited by a perforated plate of stainless steel 1 mm thickness. In the liquid side, the cathode was in contact with each of the *AMs* or *NF-117* tested as membranes. The cathode of the *MFCs* was a flexible carbon-cloth containing 0.5 mg/cm^2 platinum catalyst (Pt 10 wt%/C-ETEK).

NF-117 was pretreated to activate and remove impurities using H_2O_2, deionized water and H_2SO_4 before to use in the *MFC* [48].

Preparation of membranes

M6 (6% agar)

Membranes of 6% agar (*M6*) were fabricated based on easily accessible, low cost agar. A solution of agar (agar/agar, from red algae *Gelidium* genus; purchased from Labcitec S.A. de C.V., Mexico City, Mexico) at 6% w/v was made by dissolving 1.92 g of agar in 32 mL of warm distilled water. Afterwards, while still warm, the solution was poured in a Petri dish of 8.37 cm diameter. The Petri dish was placed in an oven at 70 °C for 9 h. With this treatment, the membrane achieved a dehydration extent of 94.27 ± 0.03% (Fig. 2). Typical thickness of the dry membrane was 1010 ± 19 μm. Thickness was measured with an ultrasonic thickness gauge Minitest brand model 2100 from the company ElektroPhysik. Finally, before use in the cell, the dry membrane was painted with 0.5 mg/cm^2 platinum catalyst (Pt 10 wt%/C-ETEK) [4,49].

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