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Bio-electrochemical characterization of air-cathode microbial fuel cells with microporous polyethylene/silica membrane as separator

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ABSTRACT

The aim of this work was to study the behavior over time of a separator made of a low-cost and non-selective microporous polyethylene membrane (RhinoHide®) in an air-cathode microbial fuel cell with a reticulated vitreous carbon foam bioanode. Performances of the microporous polyethylene membrane (RhinoHide®) were compared with Nafion®-117 as a cationic exchange membrane. A non-parametric test (Mann–Whitney) done on the different sets of coulombic or energy efficiency data showed no significant difference between the two types of tested membrane ($p < 0.05$). Volumetric power densities were ranging from 30 to 90 $W \cdot m^{-3}$ of RVC foam for both membranes. Similar amounts of biomass were observed on both sides of the polyethylene membrane illustrating bacterial permeability of this type of separator. A monospecific denitrifying population on cathodic side of RhinoHide® membrane has been identified. Electrochemical impedance spectroscopy (EIS) was used at OCV conditions to characterize electrochemical behavior of MFCs by equivalent electrical circuit fitted on both Nyquist and Bode plots. Resistances and pseudo-capacitances from EIS analyses do not differ in such a way that the nature of the membrane could be considered as responsible.

1. Introduction

The research and development of microbial fuel cells (MFCs) have become important parts of the "green" energy domain, due to their double functions — water purification and energy production. MFCs are devices that use bacteria as catalysts to oxidize organic and inorganic matter and to generate electrical current. The main components of the MFCs are the anode and the cathode with a separator as an optional component to prevent oxygen and substrate crossover [1]. At the cathode, electrons and protons react with oxygen with the help of catalysts such as platinum, and form water. In a MFC bacteria are the anodic catalysts for oxidation of an electron donor, often glucose or acetate in laboratory scale studies. A lot of designs and electrode materials have been tested in order to understand the involved phenomena and to improve efficiency of both organic charge removal in wastewater and electricity generation [1,2]. The generation of electrical energy by MFC systems is significantly limited by the properties of individual components such as electrodes, electrolyte and membrane. A membrane acts as a proton conductor with a certain electrical resistance; therefore, the membrane should be analyzed carefully [3]. In order to achieve high voltage and power density; it is essential to optimize factors influencing the internal resistance of MFCs. For example electrodes with high surface area and low resistance cation-exchange membranes could greatly improve the power density [4]. Separating membranes, that are necessary for preventing oxygen to reach the anode as well as substrate crossover, can be the source for power limitations coming from pH gradients [5,6], from biological and chemical fouling [6] or from mechanical deformations [7]. Cation (CEM) or Anion (AEM) Exchange Membranes are the most used in MFCs, with better efficiencies claimed for CEMs [7–9]. But electrochemical reactions on the cathode can be significantly limited due to high concentrations of cations that inhibit the migration of protons through the sulfonated membranes [5,10]. Moreover Ion Exchange Membranes (IEMs) are expensive [10]. To overcome these problems, various materials have been studied, including glass fiber, J-cloth and various polymers [11–16]. Such separators generally showed a higher proton migration capability and a better applicability than IEMs. However, these materials should be considered in terms of sustainability and longevity before being used for field applications [17].

Large-scale production polyethylene separators are of common use in lead–acid batteries. Such membranes can be mechanically reinforced by a glass fiber mat and are especially surface-designed for acid stratification [18]. Burkitt and Yu [19] recently included such a separator in their comparative study of AEM and CEM in MFCs.

The aim of this work was to study the behavior over time of a separator made of a non-selective microporous membrane in an air-cathode MFC with a bioanode in reticulated vitreous carbon (RVC) foam. The

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behavior was characterized by monitoring the degradation of the substrate (acetate), by chronoamperometry with calculations of coulombic and energy yields and by electrochemical impedance spectrometry (EIS). Performances of the microporous polyethylene (PE) membrane were compared with Nafion®-117 as a cationic exchange membrane in a similar MFC. EIS coupled with other electrochemical and biochemical measurements helps to provide a better understanding of the different limiting factors in MFCs and allows optimizing design and operation of MFCs for power production [20]. In order to better understand biofouling on membranes, bacterial and archeal community analyses were carried out.

2. Materials and methods

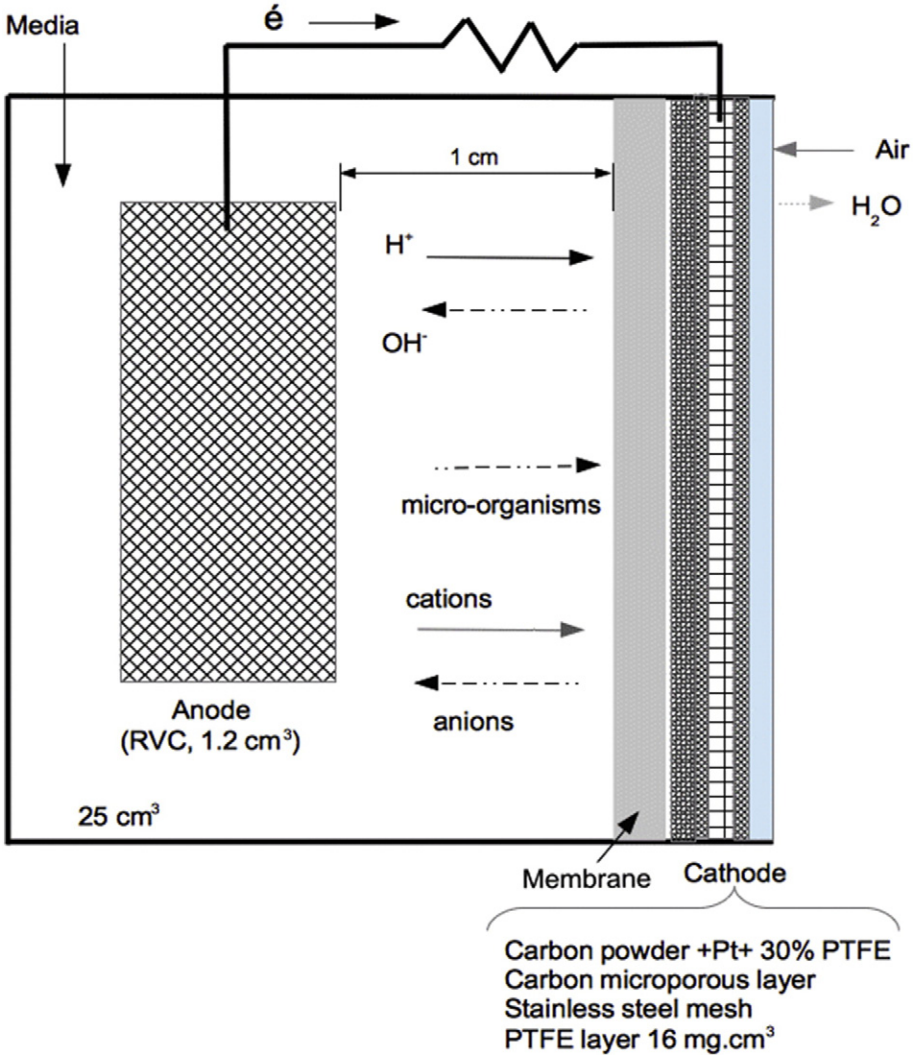
2.1. MFC construction

The cell's external dimensions were $60 \times 60 \times 20$ mm^3, giving a working liquid volume of 25 cm^3. The anode was built using a small stainless steel nut and carbon cloth pieces which sandwich the Carbon Foam (CF) piece ($20 \times 20 \times 5$ mm^3, 3750 m^{-2} m^{-3}, 24 pores per cm, Goodfellow). The cathode was a specific multi-layered air-cathode based on a carbon-supported catalyst, supplied by Paxitech (Grenoble, France), (Scheme 1). The electrolyte-exposed active face (40×40 mm^2) was a 0.5 mg·cm^{-2} Pt-catalyzed carbon powder bound by PTFE in proportion 70/30 w/w. The other side was a 70 μm-PTFE gas diffusion layer exposed to air. A stainless steel mesh maintained the assembly and served as a current collector, connected by a crocodile clip to the external circuit. A rubber seal ensured waterproofness.

Two different membranes have been studied, a 0.18 mm-Nafion® N-117 (Ion Power) and a 0.60 mm RhinoHide® polyethylene (ENTEK), both 40×40 mm^2. Both membranes were treated before use, aiming at eliminating any substance that could interfere and impair ion transport, as well as to saturate it with positive ions. For this purpose the Nafion® cationic membrane requires an immersion in a H_2SO_4 1 M solution for 1 h at 110 °C, followed by a thorough rinsing out and immersion in a H_2O_2 3 wt.% solution for 1 h at 110 °C. Finally, the membrane was rinsed again and stored in distilled water. For its part, the microporous polyethylene membrane was immersed in absolute ethanol for 16 h at ambient temperature followed by rinsing in distilled water.

2.2. MFC operation

Two experiments were conducted in time with similar conditions except for acetate concentration and number of replicates. In the first experiment two reactors were operated in parallel, each with one type of membrane; 50 mM acetate and a duration of 123 days. For the second experiment two additional reactors were run in parallel giving two reactors for each type of membrane; 10 mM acetate and a duration of 60 days. The values of the state variables of the bioelectrochemical system (pressure, temperature, conductivity, pH) and inoculum corresponded to stable



Scheme 1. Schematic representation of the air-cathode microbial fuel cell used in this study.