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# Ion exchange membranes as separators in microbial fuel cells for bioenergy conversion: A comprehensive review

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## ABSTRACT

The urgent need to address the twin problems of the modern world, energy insecurity caused by fossil fuel depletion and climate change caused by global warming from carbon dioxide emission and the greenhouse effect has led to among other things the emergence of fuel cell technology as a green energy technology that could generate cleaner and highly efficient energy. Microbial fuel cell (MFC), an emerging dual function, bioenergy conversion device, that not only treats wastewater but also generates electricity, has caught much attention of both fuel cell and bioenergy researchers. Until today, the commercialization of MFC has been restricted mainly due to its high cost and low power density. Many challenges still remain to be conquered, in order to improve the performance and commercialization of MFC. It is generally known that ion exchange membrane in MFC is one of the main factors that could significantly affect the cost and performance of MFC. This review provides an overview of several important membrane characteristics, which include membrane internal resistance, membrane biofouling, pH splitting, oxygen diffusion, and substrate loss across the membrane. The negative impact of these characteristics on MFC performance, are discussed. Moreover, this review concerns the types of membrane that have been applied in MFC systems, such as cation exchange membranes, anion exchange membranes, membraneless technology, polymer/composite membranes, and porous membranes. The future trend of membrane development for MFC applications is also discussed. © 2013 Elsevier Ltd. All rights reserved.

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Abbreviations: PEMFC, Proton Exchange Membrane Fuel Cells; AFC,, Alkaline Fuel Cells; PAFC, Phosphoric Acid Fuel Cells; MCFC, Molten Carbonate Fuel Cells; SOFC, Solid Oxide Fuel Cells; DMFC, Direct Methanol Fuel Cells; DFAFC, Direct Formic Acid Fuel Cells; MFC, Microbial Fuel Cells; Cl, Current Interruption; ElS, Electrochemical Impedance Spectroscopy; HFR, High Frequency Resistance; DO, Dissolved Oxygen; CEM, Cation Exchange Membrane; AEM, Anion Exchange Membrane; ORR, Oxygen Reduction Reaction; SEM, Scanning Electron Microscopy; PEM, Proton Exchange Membrane; MEA, Membrane Electrode Assembly; COD, Chemical Oxygen Demand; CE, Coulombic Efficiency; SPEEK, Sulfonated Polyether Ether Ketone; BPSH, Disulfonated poly (arylene ether sulfone); DS, Degrees of Sulfonation; PES, Poly(Ether Sulfone); CNF, Carbon Nanofiber; PECVD, Plasma Enhanced Chemical Vapor Deposition

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### 1. Introduction

Mankind's changing lifestyle, which has become more energy intensive, needs a secure, sustainable supply of energy to power homes, factories and offices, and more recently, to power increasing numbers of personal devices. Most of the energy comes from nonrenewable primary energy sources, namely fossil fuels such as coal, natural gas and oil, all which will run out in the near future. Coal, the first fossil fuel to be exploited, is expected to be depleted by the year 2112, while more recently used fossil fuels, oil and natural gas, will be exhausted even earlier (i.e., by year 2040 and 2042, respectively) [1]. In addition, extensive energy production from fossil fuel combustion has caused wide spread pollution of the atmosphere by  $NO_x$  and  $SO_x$ emissions, resulting in serious global environmental problems, such as global warming, due to carbon dioxide emissions and the greenhouse effect, which has led to climate change on a global scale. The emergence of clean. zero emission fuel cell technology in recent years has provided a sustainable and efficient means of reducing carbon emissions from electrical power generation and transportation. Many types of fuel cells have been developed over the years, including PEMFC, AFC, PAFC, MCFC, SOFC, DMFC, DFAFC, and MFC. AFCs are not only very well known for providing auxiliary power to NASA's Apollo spacecraft, but have also been used to provide auxiliary power in early hybrid vehicles [2]. PEMFCs have been applied mostly to power fuel cell vehicles because of their high power density and efficiency [3] whilst PAFC [4], SOFC [5] and MCFC [6] have been used mainly as stationary, distributed power generation plants in smart grids and in combined heat and power (CHP) applications because of their high operational temperatures. DMFCs are mainly applied to power portable electronic devices because of their high power density compared to lithium ion batteries and the ease of handling of liquid methanol compared to hydrogen [7]. MFC, an emerging fuel cell technology, has drawn great interests from fuel cell as well as bioenergy researchers in recent years because they have the potential to not only generate electricity like other fuel cells, but to simultaneously treat wastewater, a bioenergy resource [8,9].

MFCs are basically bioreactors that use bacteria as electrocatalysts to convert the bioenergy of biomass in wastewater into electrical energy [10]. MFCs commonly consist of an anode and a cathode, either separated by a proton exchange membrane that acts as a solid electrolyte bridge or connected directly via the wastewater substrate that also acts as an electrolyte bridge. At the anode, anaerobic microbes acting as biocatalysts oxidize the organic constituents of the wastewater, which is also called the substrate, to generate protons, electrons, and carbon dioxide gas. Protons migrate to the cathode from the anodic chamber through the membrane or directly across the wastewater in the case of membrane-less MFCs. In addition, electrons migrate to the cathode through the external circuit in order to complete the circuit and generate electrical power. They then combine with the protons to form water if the electron acceptor is oxygen, or ferrocyanide if the electron acceptor is ferricyanide [11].

Various configurations of MFCs have been developed: dual chamber MFCs, single chamber MFCs, tubular MFCs, plate MFCs and stacked MFCs. The anode and the cathode of a dual chamber MFC are placed in two distinct compartments that are separated by a proton exchange membrane. In contrast, the cathode of a single chamber MFC is not located in an aerated chamber but is directly exposed to the air, leaving the MFC with only a single anode chamber. The cathode and anode of this type of MFC are usually hot pressed together with the membrane to form a MEA [12]. Fig. 1 shows the schematic diagrams of the dual chamber and single chamber MFCs [13].

Tubular MFCs, as the name belies, have a cylindrical or tubular shape rather than a rectangular shape, where the MEA is wrapped around a central anode chamber and the cathode is exposed to the air, as shown in Fig. 2 [14]. Plate type MFCs have a flat rectangular shape, where the MEA is sandwiched between two non-conductive rectangular plates whose inner surfaces are engraved with flow channels that allow wastewater to flow on the anode side and air to flow on the cathode side in much the same way as the PEMFC, as shown in Fig. 3 [11]. MFCs can also be scaled up by arranging them in a stack, either in series or in parallel, like other fuel cells, in order to produce higher voltage or larger current densities respectively, as shown in Fig. 4 [15].

Although the MFC has the dual function advantage of simultaneous wastewater treatment and generating electricity over other low temperature fuel cells, such as the PEMFC and DMFC, its high cost [16] and low power density [17] still prohibit commercialization. The membrane separator is one of the main components of the MFC that could significantly affect its overall cost and power density. Hence, the main objectives of this review are to investigate how the membrane's internal resistance could affect MFC performance and how the membrane could act as a physical barrier to inhibit oxygen diffusion and substrate crossover between the two chambers of the MFC. Furthermore, the review will elucidate how biofouling on the



Fig. 1. (a) Dual chamber MFC, (b) Single chamber MFC [13].

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