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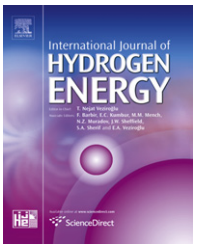

Photosynthetic cathodes for Microbial Fuel Cells

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ABSTRACT

One of the major limiting factors in the practical implementation of Microbial Fuel Cells is finding efficient and sustainable catalysts for the cathode half reaction, in an attempt to avoid expensive and/or toxic catalysts. The use of phototrophic organisms is one good option since they can act as efficient in-situ oxygenators thus facilitating the cathodic reaction. In the present study, the oxygen production by photosynthetic organisms was shown to be light dependant, which resulted in increasing the power generation by 42%. Furthermore, this study showed that a previously abiotic cathode that turned biotic showed a clear light response with an improved performance of 48%. Oxygen depletion in a water-based cathode can be avoided with the use of photosynthetic biocatalysts, thus providing sustainable operation for MFCs.

1. Introduction

The greatest challenges of present times are depletion of fossil fuels, environmental pollution and efficient development of renewable energy sources. One of the most promising approaches is the use of microorganisms to convert biomass into valuable energy. Microbial Fuel Cells (MFCs) represent a technology that directly converts energy found in organic matter into electricity, with a concomitant treatment of that organic fuel. This is facilitated through the metabolism of electroactive bacteria, which transfer electrons produced during biomass oxidation to the anode electrode [1,2]. The electrons flow around an external circuit and along with protons passing through a membrane, they combine to react with an oxidising agent, such as oxygen, at the cathode surface and 'close the circuit'. Although the MFC technology has already been implemented in small-scale practical applications [3,4], the possibility of large scale implementation requires further research. One of the major limiting factors influencing power generation, especially in the case of oxygen-diffusion cathodes, is the type and performance of the cathodic catalyst that drives the oxygen reduction. One of the most effective catalysts, and commonplace in MFC research, is platinum, which is nevertheless prohibitively expensive for scaling up MFC systems for real life applications. On the other hand, ferricyanide has also been widely used in lab scale MFC systems, and although not as expensive, requires replenishment and is toxic to the environment.

In a dual-chamber MFC with a non catalyst-based cathode, oxygen must be continuously supplied for the reaction; continuous use of fresh and oxygenated water has nonetheless obvious limitations because of its economic and environmental cost. Finding a solution that is analogous to the biocatalytic properties of microbes and the role of biofilm at the anode [5,6] has enabled research to focus on biotic cathodes (biocathodes), in recent years [7–12]. Algae are responsible for

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producing up to 75% of earth's oxygen, which is continuously produced as long as there is access to light using carbon dioxide from the environment for growth during photosynthesis. The algal biomass generation by fixing carbon dioxide during photosynthesis can be used for the production of biofuels [13], whilst microalgae also take part in wastewater treatment [14] since they can assimilate a significant amount of nutrients such as N and P [15]. Furthermore, the integration of photosynthesis with MFCs may be possible through various configurations facilitating numerous possibilities of sunlight to electricity conversion within an MFC system [16]. The Microbial Fuel Cell that is presented herewith is a complete biotic system that is able to degrade waste and produce electricity with the use of sunlight, and is aiming to demonstrate a way towards a more self-sustainable technology. This work focuses on the effect of naturally occurring photosynthetic organisms that were used in the MFC as active oxygenators for the cathode. The research also investigated the transformation – and resultant performance improvement – of abiotic cathodes into biotic half-cells.

2. Materials and methods

2.1. MFC design and operation

The MFCs comprised 25 mL anode chambers and 25 mL cathode chambers separated by a cation exchange membrane (VWR International). The chambers were made of Perspex® material and the internal dimensions were: 53 mm (h), 43 mm (w), and 13 mm (d). The chambers were assembled using rubber gaskets, 5 mm nylon washers, nuts and studding, and were sealed with a non-toxic aquarium sealant (Wet Water Sticky Stuff, Acquatrix, Witham, Essex, UK). The membrane window exposed to both half-cells was 18 cm^2. Both electrodes (anode and cathode) were made of carbon fibre veil with a carbon loading of 20 g/m^2 (PRF Composite Materials, Poole, Dorset, UK) and had a total surface area of 270 cm^2. Both electrodes were folded into 3D rectangular cuboids (geometric surface area of 17 cm^3) in order to fit into the chamber and be fully submerged in the anolyte fluid. The cathode electrodes were further modified as shown in Table 1, in order to support algal colonisation and current collection.

Nickel–chromium (0.45 mm thickness) wire was used to connect the two electrodes. Electrodes and wire were prepared without any chemical or physical pre-treatment and without any mediators or chemical catalysts. Electrode output was recorded in volts (V) against time using an ADC-16 Channel Data Logger (Pico Technology LTD., Cambridgeshire, UK). Each experimental condition (Table 1) was tested in triplicate thus resulting in a total of 15 – otherwise identical – MFCs.

Table 1 – Types of electrode in the cathode biotic and abiotic environment.

Electrode type	Catholyte type	Cathode type
Carbon veil (control)	Water	Abiotic
Carbon veil	Algae + pond water	Biotic
Carbon veil wrapped with cotton string	Algae + pond water	Biotic
Carbon veil with cellulose coating	Algae + pond water	Biotic
Carbon veil wrapped with stainless steel wire	Algae + pond water	Biotic

2.2. Inoculation and MFC operation

Anodes were inoculated with anaerobic activated sludge provided by the Wessex Water Scientific Laboratory (Saltford, UK). Sludge was mixed with 0.1 M acetate prior to use, resulting in an initial pH of 7.2. All biotic cathodes as well as being connected to the photo-reactors were filled with pond water (Frenchay, Bristol) and grown in a well-illuminated room for 2 months prior to the start of experiments. The cathode half-cells were operated in batch mode for 40 days to allow electrode colonisation. Subsequently, algae were re-suspended in fresh pond water (to ensure even distribution) and transferred to 0.5 L Schott bottles (Fig. 1). Autoclaved deionised water was used as the control. Continuous flow was maintained using a 16-channel peristaltic pump (205U, Watson Marlow, Falmouth, UK) with a flow rate of 123 mL/h. Marprene tubing was used within the pump manifold connected to the inflow tubes of the MFCs. The rest of the tubing was made of silicone; its length was 40 cm from the pump to the MFC, 60 cm from the MFC to the catholyte reservoir (0.5 L Schott bottle) and 30 cm from the reservoir to the pump. Only the catholyte was circulated, whereas the anode half-cell was operated in fed-batch mode, periodically supplied with fresh sludge mixed with 0.1 M acetate as a source of carbon, in order to maintain carbon-energy replete conditions and avoid having the anode as the limiting half-cell. Both photo-reactor bottles and MFCs were transferred to a temperature-controlled incubator (LMS Ltd., Kent, UK) using Cool White Daylight Tubes (Lm value of 2000 per tube) fitted in the cabinet. The temperature was set at 22° and the illumination cycle was set at 14 h light/10 h dark. Polarisation experiments were performed using a DR07 decade resistor box (ELC, France), and varying the external resistance from 30 kΩ to 10 Ω at 3 min time intervals after the MFCs were allowed 2 h to reach steady state open circuit voltage levels.

2.3. Calculations

The current (I) in Amperes (A) was calculated using Ohm's law, $I = V/R$, where V is the measured voltage in volts (V) and R is the known value of the external resistor expressed in ohms (Ω). Power (P) in Watts (W) was calculated by multiplying voltage with current; $P = I \times V$. Power density was calculated according to the electrode total surface area; $P_{Density} = P/\alpha$, where α is the total electrode macro surface area in square metres (m^2).

3. Results

3.1. Polarisation experiment

Polarisation curves represent the maximum actual power generation and power density of individual MFCs (per **total**

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