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The study of electrochemically active planktonic microbes in microbial fuel cells in relation to different carbon-based anode materials

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ABSTRACT

MFCs (Microbial fuel cells) are bio-electrochemical systems that convert chemical energy into electrical energy by utilizing electrochemically active bacteria.

rt-qPCR (Real-time quantitative polymerase chain reaction) assays were used to identify the planktonic bacteria present in the production of electricity in MFCs. The relationship between the bacterial communities with different carbon-based anode materials, such as C-FELT (carbon felt), carbon felt with C-PANI (polyaniline) and C-SADDLES (carbon-coated Berl saddles), were investigated.

The distribution of bacteria among the three different MFC anode materials was evaluated. Significant differences were observed for total bacteria ($p < 0.01$), *Geobacter* ($p < 0.05$) and *Shewanella* ($p < 0.05$). These differences were generally due to higher bacterial counts in the C-FELT anode MFC. Significant differences in maximum power density ($p < 0.001$) were also observed; the C-PANI MFC showed the highest maximum power density of 28.5 W/m^3 when compared with the C-FELT (4.7 W/m^3) and C-SADDLES (4.6 W/m^3) MFCs. The greatest number of electrochemically active planktonic microbes was observed in the C-FELT MFC, whereas the C-PANI MFC had the optimum carbon-based anode material.

1. Introduction

Due to the limited supply of fossil fuels and their environmental and economic influences, a major portion of world energy will be produced from sustainable sources. Sustainable energy production is one of the major concerns of the twenty-first century [1].

Evidence suggests that the next generation of sustainable energy could come from microorganisms, particularly from anaerobic digestion and MFCs (microbial fuel cells), which are gaining acceptance as an alternative “green” energy technology [2,3].

MFCs are a rapidly growing technology for the direct energy production [4] from raw materials, such as natural organic substrates, complex organic wastes and renewable biomass, through oxidation by electrochemically active microorganisms under ambient conditions [5].

A typical MFC device has two compartments, an anode and a cathode, which are separated by a CEM (cation exchange membrane).

In these bio-electrochemical systems, reduced compounds transfer electrons by EET (extracellular electron transfer) to the anode, which serves as an electron acceptor. The electrons then pass through an external circuit and combine with protons and a terminal electron acceptor at the cathode, where the process can be mediated by microorganisms [4].

Recent studies have expanded the number of microorganisms known to be electrochemically active in MFC systems. The most studied microorganisms include metal reducing bacteria, such as *Geobacter* spp. and *Shewanella* spp., and phototrophic bacteria, e.g., *Rhodopseudomonas* spp. [6].

Anodic communities can transfer electrons by either direct electron transfer, using membrane cytochromes or conductive pili, or indirect electron transfer, using shuttles are reduced on the cellular surface and subsequently diffuse to the anode where they transfer the electrons and are oxidized [4,6].

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Organic material generally act as electron donors, whereas many electron acceptor compounds (both organic and inorganic) are known.

Organic compounds commonly used as electron donors are easily biodegradable, including simple carbohydrates (e.g., glucose and saccharose), starch, low-molecular weight organic acids (e.g., acetate, oxalate, and fumarate), xylose and amino acids [5].

A variety of wastewaters have also been used as substrates in MFCs for generating electricity, including marine and river sediment, domestic wastewater, swine wastewater, food processing wastewater, fresh seawater, and activated sludge [1,7–9].

Numerous factors (e.g., microorganism type, MFC design, PEM (proton exchange membrane), and electrode type) can influence the performance of MFCs [1,5].

Over the last decade, a number of studies have attempted to improve the performance of MFCs by modifying a few factors, including MFC design, architecture, and configuration, electrolyte solutions, organic fuels, electrode material and surfaces, and electrogenic biofilms on the anode [4]. In particular, electron transfer efficiency from electrogens to the anode has been noted to be the most critical factor in affecting MFC current production [10–12].

Despite the numerous studies that have attempted to maximize power output of MFCs by modifying reactor designs and configurations, operational parameters, and electrode materials, microbes, which are a core element of an MFC, have not been well investigated [6].

Bacterial attachment to the anode surface and the subsequent formation of a biofilm are essential for the efficient biological transfer of electrons between microbes and anode [1]. The screening of potential microbial species is essential for optimizing bacteria development in the anodic chamber [5].

Over the past decade, the power output of MFCs has increased by several orders of magnitude. Significant developments and improvements have been reflected in increasing numbers of publications and patents [2]. However, this technology remains far from large-scale, real-world applications due to low power generation and high costs. As such, increasing the production capacity is one of the most important tasks for MFC development [1]. To achieve this goal, electrochemically active bacteria and the microbial community in an MFC need to be characterized [6].

This study screened bacteria using rt-qPCR (real-time quantitative polymerase chain reaction). To evaluate their relationship with different carbon-based anode materials, different physical conditions and time were investigated. The three following anode materials of sodium acetate MFCs were studied: (1) commercial C-FELT (carbon felt), (2) C-PANI (polyaniline)-deposited carbon felt and (3) C-SADDLES (carbon-coated Berl saddles).

C-FELT is one of the most used electrode materials for MFCs. PANI (Polyaniline) can be easily deposited on carbon felt, thereby improving conductivity and bacteria adhesion [13]. Finally, the use of carbon-coated Berl saddles has been demonstrated to be a low-cost solution that satisfies electrical and bioreactor requirements, increasing the reliability of MFC processes [14,15].

2. Materials and methods

2.1. Materials

Carbon felt, commercial Berl saddles, α-D-glucose ($C_6H_{12}O_6$, 96%), sodium acetate (CH_3CO_2Na, 99%), peptone, sodium phosphate dibasic dihydrate ($Na_2HPO_4 \cdot 2H_2O$, 98%), sodium phosphate monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$, 98%) and potassium ferricyanide ($K_3Fe(CN)_6$, 99%) were purchased from Sigma Aldrich. Seawater was used as an inoculum for the active microorganisms.

The deposition of PANI on C-FELT was performed using a layer-by-layer technique. The details of the experimental procedure have been previously described by Hidalgo et al. [13].

The deposition of a conductive carbon layer on the Berl saddles was performed as reported by Hidalgo and co-workers [14].

2.2. MFC configuration and operation

The MFC devices each consisted of two circular chambers, i.e., the anode and the cathode. Both compartments were made from poly (methyl methacrylate) with internal diameters of 12 cm and 1.5 cm thickness (i.e., an internal chamber volume of approximately 170 mL) separated by a CEM (CMI 7000, Membranes International, Inc., Glen Rock, NJ, USA). Different conductive materials were used in the anode chambers: commercial C-FELT (soft felt SIGRATHERM GFA5, SGL Carbon, Germany) in MFC 1, C-PANI in MFC 2 and C-SADDLES in MFC 3. For all cathodes, C-FELT was the electrode material. Fig. 1 shows the experimental setup. The structural properties of the materials have been previously described [13–15]. Each conductive material was connected with a graphite rod (5 mm diameter) to ensure effective current transport. The MFCs were inoculated in the anode chamber using seawater from the same sample (Arma di Taggia, Italy) enriched under anaerobic conditions as previously described [15]. The first 3 days of tests were conducted under OCV (open circuit voltage) conditions so that the bacteria cultures could adapt to the MFCs. After this start-up period, the three MFCs were operated under an external resistance of 1000 Ω. During days 6 and 7, the resistance was briefly removed to evaluate the capacity of each system to recover to the initial operational conditions. All investigations were carried out under the same conditions, i.e., in fed-batch mode by using a multi-programmable syringe-pump (NE-1600, New Era Pump System) at 22 ± 2 °C. The anode and cathode chamber solutions were mixed by recirculating anolyte and catholyte from a 500 mL reservoir, respectively, at a high flow rate (30 mL/min) using multi-channel peristaltic pumps (Peri-Star Pro 4 and 8 channel, respectively, USA).

Evaluations were performed over a period of 5 weeks. Sodium acetate (1 g/L) and peptone (1.25 g/L) were provided respectively as synthetic substrate and nutrient source for microorganism growth in the anodic solution of the three MFCs each weekday.

The cathodic compartment used potassium ferricyanide (6.58 g/L) as an oxidant. To prepare the anodic and cathodic solutions, inorganic salt buffers, i.e., $Na_2HPO_4 \cdot 2H_2O$ (8.2 g/L) and $NaH_2PO_4 \cdot H_2O$ (5.2 g/L), were used.

2.3. Electrochemical measurements and analyses

The monitoring of the MFCs during the tests included measuring physiological and electrochemical parameters. Every 2 − 3 days of operation, the pH, rH (redox potential), conductivity and OD (optical density) at 600 nm were measured by taking planktonic samples from the MFC compartments. Moreover, electrochemical characterizations, including OCV (open circuit voltage), LSV (linear sweep voltammetry) and CI (current interrupt) methods, were conducted from day 3 to day 35 to biologically and electrically evaluate the system. Electrochemical experiments were performed on a multi-channel VSP potentiostat/galvanostat produced by BioLogic. Measurements were recorded by using EC-Lab software version 10.1× (BioLogic) for data acquisition. All tests were carried out using a two electrode setup; the working electrode was coupled to the anode, and the counter and reference electrodes were connected to the cathode. When a constant OCV was achieved, polarization curves were performed at a scan rate of 1 mV/s from the open-circuit cell voltage V_0 (where $I = 0$) to the short-circuit cell voltage $Vsc = 0$ (where $I = I_{max}$). From these I–V curves, the power