



Microbial fuel cells meet with external resistance

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ABSTRACT

The influence of external load on the composition of the anodic biofilm microbial community and biomass yield was investigated in a microbial fuel cell fed with glucose and domestic wastewater was used as source of electrogens. Denaturing gradient gel electrophoresis (DGGE) of polymerase chain reaction (PCR) amplified 16S rRNA gene fragments revealed distinct differences in anodic bacterial communities formed at the anode of each MFC operated under a different external load. These results implied that in an MFC, electrogenic bacteria were enriched under higher current densities, i.e., low external load, and were able to sustain better current and effluent quality. The influence of the external resistance applied to the MFCs during formation of the bacterial communities from sewage wastewater was shown to have no significant effect on power performance of the MFCs nor to have a significant influence on their anodic activity with both glucose and brewery wastewater as fuel. As expected, current generation, COD removal and the biomass yield were all directly influenced by the external load. Significantly, when operated under lower external load, the biomass yield in the MFC was less than that in conventional anaerobic digestion (i.e., control).

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1. Introduction

Microbial fuel cell (MFC) technology is an emerging research field, in which electrons derived from the metabolism of biodegradable organic matter are converted to electricity (Logan et al., 2006). Barriers to the application of the technology include the use of expensive components (i.e., platinised cathode and proton exchange membrane) and low power densities, caused by poor electron transfer from the bacteria to the anode (Schröder, 2007; Torres et al., 2010). In recent years electricity generation using MFCs has received much attention as a potential source of renewable energy (Logan et al., 2006; Rozendal et al., 2008). In addition to generating electricity, the process can also treat wastewaters. However, in order for this technology to be a viable source of power or wastewater treatment method, further improvements in MFC performance are needed. Most studies have focused on how different MFC reactor configurations, substrates, operating parameters and different types of electrodes affect power generation. A number of potential rate limiting factors have been described and their influence on MFC performance, e.g., rates of substrate oxidation and electron transfer from bacteria to the anode, proton transport through the proton exchange membrane

(PEM), oxygen availability and reduction at cathode, have been documented (Jang et al., 2004; Rabaey et al., 2004).

In contrast to a classical fuel cell, MFC electrocatalysis takes place through bacterial metabolism. The effect of external resistance on MFC behaviour has been addressed, in a number of studies primarily focused on the relationship between external resistance, current and Coulombic yield (Gil et al., 2003; Jang et al., 2004; Liu et al., 2006). Liu et al. (2006) observed higher COD removal with the MFC operated under some external resistance when compared to open circuit systems. Menicucci et al. (2006) developed a procedure for selecting an optimal external resistance for maximum sustainable power. In their study, they considered the anode potential produced under different external resistances to determine conditions for the maximum sustainable power. Aelterman et al. (2008) studied the effect of different three-dimensional electrodes on electricity generation, electrochemical and microbial community structure of microbial fuel cells in relation to the applied loading rate and the external resistance. However, the effect of the external resistance on COD removal linked with changes in microbial community composition and influence on biomass growth have not been investigated to date.

Very recently Lyon et al. (2010) have reported the effect of external resistance on the performance of a MFC filled with primary clarifier effluent and fed with acetate as fuel. They found that differences in the external resistance were associated with changes in the bacterial community structure formed on the anode.

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However similar power production was observed regardless of community structure.

Current numerical models of MFCs predict that increased external resistance results in (i) higher biomass growth and (ii) a lowering of current generated at the anode (Picioreanu et al., 2007, 2008). It has also been suggested that increased electrical resistance favours methanogenic microbial growth as opposed to electroactive microbial growth (Picioreanu et al., 2008). In this study we have conducted a series of experiments in batch mode to evaluate the model predictions. We have therefore assessed the influence of external resistance on MFC performance, anodic microbial community composition, especially during the initial phase of anodic biofilm development, and factors of practical significance in wastewater treatment such as COD removal and biomass yield. These data were then compared with conventional anaerobic digestion and MFC operated at open circuit voltage (OCV), equivalent to an infinite external resistance.

2. Experimental

2.1. Feed

The MFC feed solution, which consisted of minimal salts medium with glucose as the electron donor, was prepared by dissolving 500 mg/L glucose and inorganic salts [$\text{NH}_4\text{-N}$ (NH_4Cl) – 40 mg/L; Mg (MgCl_2) – 10 mg/L; Cu (CuSO_4) – 0.1 mg/L; Ca (CaCl_2) – 5 mg/L; Mn (MnSO_4) – 0.1 g/L and Zn (ZnCl_2) – 0.1 g/L] in 950 mL of phosphate buffer (0.25 M, pH 7.0). Preceding experimental measurements, 50 mL of biomass inoculum was added, followed by vigorous purging with nitrogen gas for 30 min, at a rate of 40 mL/min, to create anaerobic conditions and uniform microbial distribution. The fuel and inoculum had a combined chemical oxygen demand (COD) of 550 mg/L and a biomass concentration of 56 mg/L as volatile suspended solids (VSS) and 7.9×10^8 cells/mL of bacteria.

Brewery wastewater diluted with domestic wastewater (1:100 by volume) was used as feed in the anodic chamber (anolyte) for some of the experiments in this study. Domestic wastewater was collected from the primary clarifier overflow at a local municipal sewage treatment works (Northumbrian Water, Newcastle upon Tyne, UK) and brewery wastewater was provided by the Federation Brewery (Newcastle upon Tyne, UK). For the MFC tests, brewery wastewater was added to the domestic wastewater followed by vigorous nitrogen gas purging for 15 min, at a rate of 55 mL/min to create anoxic conditions and a uniform microbial distribution. The feed prepared in this way had a soluble chemical oxygen demand (COD) of 700 mg/L.

2.2. Inoculum preparation

Sewage wastewater, collected from the primary clarifier overflow at a local municipal sewage treatment works (Northumbrian Water, Newcastle upon Tyne, UK), was used as inoculum. The biomass was collected by centrifugation (10,000 g, 10 min) from sewage wastewater and washed twice with sterile saline solution (0.9% NaCl solution) to remove organic compounds adhered to the microbial cells. The biomass was then re-suspended in 50 mL of sterile phosphate buffer (0.25 M, pH 7.0) and mixed with the anolyte feed medium (inoculum/anolyte ratio, 1:20 [v/v]) to initiate the experiments.

2.3. MFC configuration and operation

Experiments were conducted in a two-chambered fuel cell (150 mL capacity chambers made of borosilicate glass). A 6 cm^2 Nafion 117 proton exchange membrane (PEM) (Sigma, UK), was

used to separate the anodic and cathodic chambers. The top of the anode chamber was equipped with sample ports for liquids and gases and for an electrical connection to the anode, which was suspended in the anolyte. The anode consisted of a graphite plate (projected area 12 cm^2), which was sterilised by boiling in 0.1 M H_2SO_4 for 1 h, and washed with distilled water, followed by boiling in distilled water (30 min). A 20 cm^2 (projected area) platinised titanium mesh with 0.30 mg of Pt/ cm^2 was used as a cathode. Electrical contacts to the electrodes were made with titanium wire. About 125 mL of feed solution was added to the anodic chamber followed by purging with oxygen free nitrogen gas for 15 min to maintain an anaerobic environment in the reactor. The cathode chamber contained 125 mL of oxygen saturated potassium phosphate buffer (0.25 M, pH 7.0) containing 100 mM potassium ferricyanide.

Duplicate MFCs were operated with different external resistances (0.1 k Ω , 1 k Ω , 10 k Ω , 25 k Ω and 50 k Ω) between the anode and cathode. Additional cells were operated under open circuit conditions, i.e., bioreactors with the same construction as the MFCs except anode and cathode were not connected to an electrical circuit. Conventional anaerobic biofilm reactors (closed bottle with dummy anode) were used as controls to compare organic removal efficiency and microbial community composition with MFCs. All the reactors were monitored for 7 days and samples (3 mL) were withdrawn daily under a stream of oxygen free nitrogen, filtered through 0.2 μm filter membranes (Polyvinylidene fluoride, PVDF, VWR, UK) and analysed.

2.4. Analysis

2.4.1. Electrochemical measurements

The change in fuel cell voltage under different external resistance was recorded hourly using a data acquisition system (ADC 16, Pico Technology Ltd., UK) connected to a personal computer via a BS 232 Pico high resolution analog cable. Energy (mWh) was calculated by integrating power over time. The anode and cathode potentials were monitored using a Ag/AgCl (3 M NaCl, 0.209 V vs. NHE) reference electrode placed in the catholyte solution.

Cell polarizations were obtained by connecting each cell to different external resistances and measuring the voltage. The external resistance was then decreased and voltage measured again after stabilization. From the corresponding voltage values, current densities and power densities were determined using Ohms law. The Coulombic efficiency (%) was calculated according to Logan et al. (2006).

2.4.2. Chemical measurements

At the end of the batch experiment, the total biomass concentration of bulk liquid and the biofilm was estimated using the volatile suspended solids (VSS) method (APHA, 1998) by taking uniformly mixed samples. The attached biofilm around the anode was extracted into a separate container and a sub-sample of 250 μL of the biomass suspension was preserved for DGGE analysis. The remaining extracted anodic biomass was returned to the corresponding reactor anodic solution (i.e., anolyte) to determine the total bacterial biomass.

2.4.3. Microbial measurements

2.4.3.1. Bacterial samples. For microbial community analysis at the end of the experiment, the anodes with attached biofilms were transferred to sterile containers with 5 mL of sterile saline phosphate buffer (3.2 mM Na_2HPO_4 , 0.5 mM KH_2PO_4 , 1.3 mM KCl, 135 mM NaCl, pH 7.4) and glass beads. The entire biofilm from the anode was suspended in the buffer by shaking followed by sonication (five periods of 30 s separated by 2 min of cooling in order to disturb biofilm structure; 120 W, 40 kHz, Model FS 200b

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