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Original Research Article

Small-scale microbial fuel cells utilising uric salts

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ABSTRACT

With exhausting fossil fuels and increasing greenhouse gas emissions, numerous attempts, to overcome future energy challenges, are being pursued. In this study, small-scale microbial fuel cells (MFCs, 0.7 mL anodic chamber volume) were built to investigate their electrical performance with uric salts as fuel for power generation. When uric salts were added to other substrates such as urine or sewage sludge, results showed improved power generation and longevity. The small-scale MFCs produced a comparable amount of power output (P_{MAX}: 11.09 mW/m^2; 44.36 W/m^3) to that produced by larger MFCs, which suggests that MFC miniaturisation and multiplication is a sound approach for scale-up and practical implementation.

Introduction

Organic waste is an abundant source of energy, which if fully utilised, could help alleviate some of the global energy problems. At present, treatment and disposal of organic waste and wastewater comes at a high cost, and it therefore becomes very important to explore and promote technologies that can utilise organic matter for the production of useful energy. Taking wastewater as a good example for the North East England, it has been reported that the calorific value of this waste product is 7.6 kJ/L [1]. In this respect microbial fuel cells (MFCs), that generate electricity directly by the breakdown of this *energiferous* organic fuel, have a great potential for future energy challenges.

One of the main advantages of MFCs is their environmentally friendly nature and operation. Instead of using refined expensive fuel, MFCs can utilise a wide range of substrates, and produce useful amounts of energy without the need for high-cost catalysts or special operational conditions. Their primary disadvantage, however, is the relatively low power output compared to chemical fuel cells. In order to obtain a sufficient amount of power for practical applications, scale-up of MFC systems, through connecting individual small-scale cells in series or parallel (or both) as a stack, has been suggested [2]. When the size of a MFC device is enlarged, the system tends to lose power due to a higher internal resistance [2]. Therefore it appears that one viable method for scale-up is the miniaturisation of individual units and their multiplication in stacks.

Various substrates – including urine – have been reported as efficient fuels in MFCs for electricity generation [3–10]. Urine is an abundant waste product and the main source of nitrogen and phosphorous in wastewater [11], which are difficult and expensive to remove in treatment systems. Previous work has already suggested that the early break down of urine for electricity generation can help remove and lock-away, (in the form of new biomass), some of the nitrogen, phosphorous and potassium content in urine, thus having a positive impact on wastewater treatment [9]. However, urine tends to accumulate in the form of uric salts (uric sludge) especially in communal drainage systems, requiring frequent removal and maintenance. Usually strong alkaline solutions are used to remove the uric salts, which are not environmentally friendly and bring further problems such as drainage corrosion. With this in mind, this study investigated the feasibility of utilising uric salts mixed with urine or sludge in MFCs for direct electricity generation.

The specific aims of this study were; (i) to investigate whether uric salts can be utilised for power generation by MFCs; (ii) to demonstrate whether useful levels of electricity can be produced from miniature MFCs fed with uric salts.

Methods

Type I (Batch mode medium-scale MFCs)

The Type I MFCs comprised single 25 mL anodic chambers. The open side of the chamber was sealed with a cation exchange mem-

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brane (VWR, Leicestershire, UK). Cathodes were attached onto the membrane by a plastic paraffin film and one side of them was exposed to air (open-to-air type). They were made of acrylic material with dimensions h = 6 cm, w = 5 cm, l = 1 cm and a membrane window with 30 cm^2 surface area. Carbon fibre veil electrodes (PRF Composite Materials Poole, Dorset, UK) with a total surface area of 270 cm^2 were folded several times along the length and width before being placed in the chambers and used as the anode and cathode electrodes. Nickel-chrome wire (thickness: 0.45 mm, length: 6 cm) was used to connect the electrodes to the external circuit and data logging equipment. After inoculation and maturing using activated sewage sludge (Wessex Water, Cam Valley Works, UK) for at least 3 weeks, 5 mL of neat (unprocessed) urine (pH 5.56) or uric salts (pH 8.45, 100 times diluted with deionised water) was fed into MFCs for the purpose of substrate comparison. The resultant pH of the anolyte, especially after 48 h of operation, was between 8.78–8.81. Tap water (7.5 mL) was used for hydrating cathodes on a daily basis.

Type II (Re-circulating medium-scale MFCs)

The Type II MFCs consisted of 25 mL anode and cathode chambers (50 mL in total) separated by the same membrane and having the same electrode type, size and conformation, as above. Unlike the open-to-air cathodes of the type I MFCs, cathodes were placed in the closed cathode chambers on one side of the membrane. Maturing of these MFCs was as described above. Neat urine stored in 1L bottles was recirculated through MFCs by single channel peristaltic pump (WELCO Co. Ltd, Japan) with a flow rate of 4 mL/min. In order to test uric salts in MFCs as a substrate, 5 mL of diluted uric salts (in deionised water) was added directly into the anodes of these MFCs. Tap water (700 mL) was recirculated at a rate of 30 mL/min using a single channel diaphragm pump (KNF Neuberger, Germany). Anolyte in the reservoirs was replaced with fresh urine when the power output of the MFCs reached the pre-set baseline, which was 50 mV.

Type III (Re-circulating small-scale MFCs)

Type III MFCs consisted of two 0.7 mL hemispherical chambers, anode and cathode chambers, and they were 3D printed in Nanocure® resin material. Each chamber had an inlet and outlet (d = 2 mm) for continuous feeding. Between the two chambers, a circular cation exchange membrane with 15 mm diameter was placed. The same carbon veil folded electrode as described above was used, but with a total surface area of 28 cm^2 (w = 7 cm, l = 4 cm). Subsequent to inoculation and maturing, (as described above) MFCs were fed with uric salts mixed with activated sludge in batch mode for the first 9 days, in order to let microbial consortia settle and colonise the anode, and then 500 mL of uric salts and sludge mix was re-circulated. Uric salts were mixed with sludge at a 1:100 ratio (pH 9.27) and then this mixture was diluted with tap water with different ratios of 1:9, 1:4 and 1:1 (10%, 20% and 50% in percentage volume respectively). Tap water was recirculated with a flow rate of 0.5 mL/min as a catholyte and replaced on a daily basis.

Initially all three types of MFC were inoculated with activated sludge, collected from the Wessex Water's Cam Valley wastewater treatment plant. Design and operational conditions of the three different types of MFC are shown below in Table 1. The initial resistor loads used in the experiments were 2.7 kΩ for MFC Type I and II, and 12 kΩ for the Type III MFCs. These were chosen to match the initial internal resistances of the different MFC types, and were determined by periodic monitoring of the open-circuit voltage.

Composition of uric salts

Typically urine consists of 96% of water and 4% of various solutes [12]. When urine is saturated as a result of evaporation or microbial urea degradation occurring in urinary systems, these solutes precipitate and build up in the systems. This is insoluble thus often causes maintenance problems such as bad odours and blockages. Uric salts consist of mainly calcium carbonate ($CaCO_3$), hydroxyapatite (HAP, $Ca_5(PO_4)_3(OH)$) and struvite ($MgNH_4PO_4 \cdot 6H_2O$) [13]. Uric salts used in this study were provided by Whiff-Away Ltd, Slough, UK. Since the samples were provided from an operating communal urinal facility, they naturally consisted of a mixture of uric salts and sludge, which would have been high in impurities and organic carbon.

Data capture and calculation of power output

The MFC output was recorded in real time in millivolts (mV) using an ADC-24 A/D converter computer interface (Pico Technology Ltd, Cambridgeshire, UK). The current (I) in amperes (A) was determined using Ohm's law, $I = V/R$, where V is the measured voltage in volts (V) and R is the external load resistance value in ohms (Ω). Power (P) in watts (W) was calculated by multiplying voltage with current; $P = I \times V$. Power density (P_D) was calculated in terms of electrode total macro surface area; $P_D = P/\alpha$, where α is the total anode electrode surface area in square-metres (m^2) before folding the electrode to fit inside the MFC chambers. Type I and II MFCs employed 270 cm^2 of electrode, whereas the Type III MFCs employed 28 cm^2 of the same carbon veil electrode. The internal resistance of each type of cells was calculated according to the Physics method of measuring internal resistance in any physical power supply, i.e. $R_{int} = (V_{o/c}/I_{load}) - R_{load}$.

Results and discussion

Feasibility of uric salts as a substrate

Figure 1 shows the temporal profile of power production from the Type I MFCs. When MFCs were fed with urine, the power output reached up to 0.5 mW/m^2, and then continuously decreased as urine was depleted. After approximately 12 days, the MFCs produced only 0.03 mW/m^2, which was the pre-set baseline. At this point, the uric salts solution was injected into the anodes and the power output increased by 0.39 mW/m^2 before beginning to decrease over the next 3 days. Unlike after the urine feed, this decline did not continue as the power output reached a plateau and remained constant at approximately 0.2 mW/m^2 for the next 9 days. This suggests that uric salts improved the longevity of continuous power generation, although the peak power was lower than that with urine.

Adding uric salts to the Type II MFC, which were being fed with urine from the re-circulating reservoirs, has shown an even more marked improvement in terms of power generation (Fig. 2). When the uric salts substrate was added to the MFC anode directly, the power output increased significantly. The average power output of the MFC after being fed with uric salts and urine was 1.92 mW/m^2, which is approximately 51.2% higher than the average power output of the same MFC when it was fed only with urine (1.27 mW/m^2), and as in the previous case, the power output remained constant at the elevated level for 3.5 days (5000 min). The power output in terms of area under curve (AUC) analysis was 100% higher as a result of simply adding 5 mL of diluted uric salts to urine (Fig. 2 inset).

These findings suggest that uric salts can be used as a substrate for direct electricity production by MFCs. Moreover uric salts could