Journal of Power Sources 196 (2011) 3757–3760

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

A thermophilic microbial fuel cell design

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ARTICLE INFO

Article history:
Received 4 November 2010
Received in revised form
17 December 2010
Accepted 17 December 2010
Available online 7 January 2011

Keywords:
Air cathode
Cathode chamber
Cellulose
Microbial fuel cell
Thermophilic microorganisms

ABSTRACT

Microbial fuel cells (MFCs) are reactors able to generate electricity by capturing electrons from the anaerobic respiratory processes of microorganisms. While the majority of MFCs have been tested at ambient or mesophilic temperatures, thermophilic systems warrant evaluation because of the potential for increased microbial activity rates on the anode. MFC studies at elevated temperatures have been scattered, using designs that are already established, specifically air-cathode single chambers and two-chamber designs. This study was prompted by our previous attempts that showed an increased amount of evaporation in thermophilic MFCs, adding unnecessary technical difficulties and causing excessive maintenance. In this paper, we describe a thermophilic MFC design that prevents evaporation. The design was tested at 57 °C with an anaerobic, thermophilic consortium that respired with glucose to generate a power density of 375 mW m^{-2} after 590 h. Polarization and voltage data showed that the design works in the batch mode but the design allows for adoption to continuous operation.

1. Introduction

In the last few years, interest in alternative energy sources has increased greatly due to greenhouse gases and changes in fossil fuel-based policies and economics. Microbial fuel cells (MFCs) are one alternative that take advantage of the ability of microorganisms to couple anaerobic respiration to the reduction of external electron acceptors [1,2]. In MFCs the electrons travel through the anode and an external resistor, which generates a current, to the cathode where the circuit is completed by pairing with protons. Although these first-generation MFC systems are unable to support high power demand, they have been shown to run small electric devices such as light bulbs, calculators, clocks, and cell phones [1,2].

Thermophilic metabolism offers many advantages over its mesophilic counterparts and could prove the same for MFC technology. Thermophiles, while still vastly unknown, have great potential in bioprocesses for wastewater treatment and bioenergy production. For example, cellulose biodegradation occurs faster between 50 and 65 °C than at lower temperatures [3]. Arguments for thermophilic MFC applications are similar to the reasons for thermophilic anaerobic digestion: increased rates, improved efficiency, and the elimination of many human and animal pathogens [4]. Only scattered themophilic MFC studies have been reported, due to limitations in the reactor design. Our previous modular MFC design [5], shown to work under mesophilic conditions, 39 °C, was not usable at 60 °C. This design was not a closed system and permitted evaporation, specifically from the cathode chamber. As the catholyte evaporated anolyte diffused through the proton permeable membrane into the cathode compartment and evaporated. In addition to all of the catholyte, between 50% and 75% of the anode working volume was lost within 2 days. The concentrated anolyte could be detrimental to microbial metabolism and activity due to enrichment of metabolites and cell debris.

Thermophilic studies have not addressed these problems other than to note periodic anolyte or catholyte replacement [6,7]. Jong et al. [8] utilized continuous flow, rather than batch or fed-batch, which allowed for a constant replacement of anolyte and catholyte in their thermophilic MFC. The best MFC performance was with 338 cm^3 h^{-1} and 11 cm^3 h^{-1} for the catholyte and anolyte flow rates, respectively [8]. The catholyte required a higher flow rate likely due to the continuous evaporation of liquid from the open cathode chamber. While this prevents drastic liquid loss, electricity production then relies on the electrochemically active biofilm alone since suspended cells are removed with the continuous flow of the anolyte. Several MFC studies have tested a range of operation temperatures and demonstrated consistently higher power densities with higher temperatures, within the limits of the microbial populations [9–12].

The inadequacy of previous MFC designs at elevated temperatures prompted this study to develop an MFC design that prevents liquid evaporation. This technical problem has hindered research towards effective utilization of thermophilic MFC technology. The design in this study was tested successfully with a thermophilic consortium and glucose as a substrate.

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doi:10.1016/j.jpowsour.2010.12.088

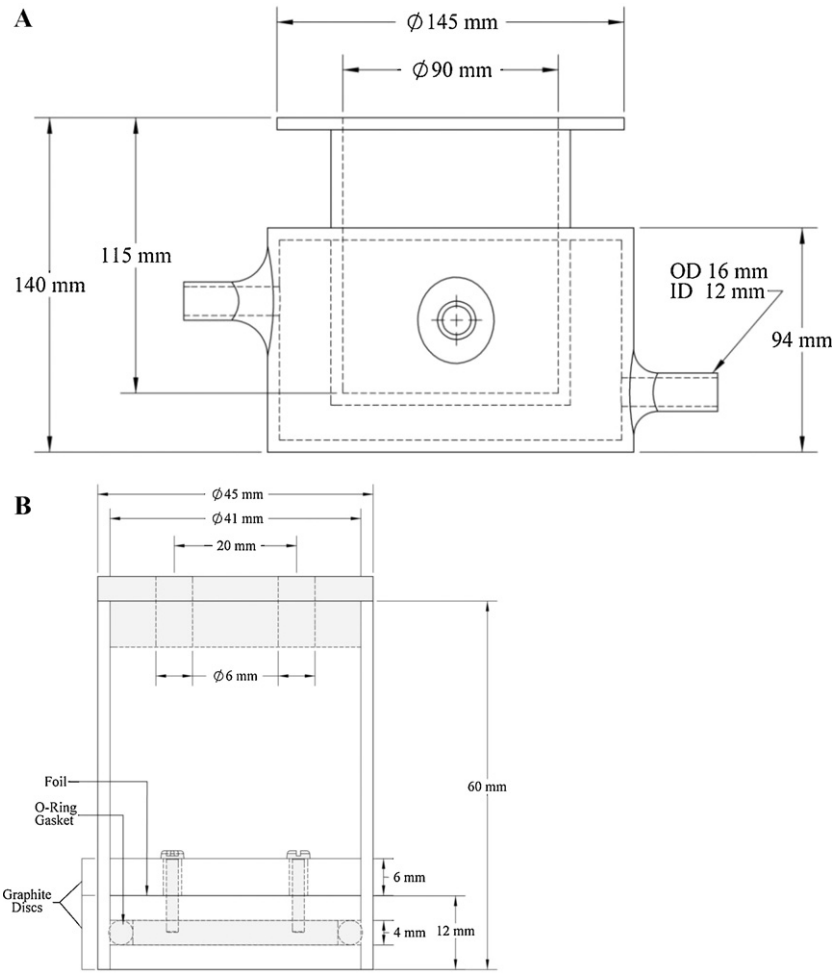

Fig. 1. Design of the thermophilic microbial fuel cell reactor (A) and the cathode assembly (B). Note the difference in scale.

2. Materials and methods

2.1. Thermophilic MFC design

The MFC design presented here is based on the original concept presented by Min and Angeladaki [13]. As shown in Fig. 1A, a custom designed glass reactor (158 mm OD × 137 mm height) with an inner chamber (90 mm ID × 115 mm height) was used as the anode chamber (Laborexin Oy, Helsinki, Finland). The reactor was closed with a glass lid with four access ports. The lid had a ground flange and was clamped to the reactor to ensure tight fit. The working volume was 450 cm^3 in this study. The reactor was surrounded by a glass water jacket (94 mm height) to maintain a constant temperature in the anode chamber. The glass lid and reactor were cleaned thoroughly with ethanol prior to MFC setup.

The cathode chamber was designed from a polyacrylamide tube (45 mm OD × 41 mm ID × 60 mm height) (Fig. 1B). The electrode consisted of two graphite discs, a disc of stainless steel foil between in order to facilitate charge transfer, and two stainless steel screws to hold the layers together. A high temperature graphite rod (50.8 mm diameter) was sliced and shaved for the electrode (McMaster-Carr, Elmhurst, IL). The first graphite disc was 6 mm height × 41 mm diameter with two holes of 3 mm diameter, 20 mm apart. The second graphite disc was 12 mm height × 41 mm diameter with an inset ring of 4 mm height and 3.75 mm depth. This disc had two threaded (3 mm × 0.5 mm thread) holes of 8 mm depth at 20 mm apart. Within the inset of the second disc, a rubber o-ring gasket (standard size AS568A-202) was placed to prevent leaks during operation. The three layers were held together with stainless steel screws to ensure a tight connection. With slight heating of the polyacrylamide tube, the three-layer electrode could be gently pushed up into the tube. The polyacrylamide lid was made from two pieces of polyacrylamide glued together containing two holes of 6 mm diameter, 20 mm apart. The holes allowed for norprene tubing (L/S 15, Masterflex, Vernon Hills, IL) to be used to enter the chamber. One of the tubes was connected to a fish tank pump while the other allowed for excess air to escape without contaminating the anodic headspace. A copper wire was connected to a wire terminal and surrounded one screw. The other end of the wire was extended through the outlet air tube to the potentiostat after the external resistor, 100 Ω, connection.

2.2. MFC setup

An anaerobic microbial consortium (TC60) was used as the inoculum for thermophilic MFCs. TC60 originated from the interior of thermophilic compost and subcultures had been maintained with cellulose at 60 °C. This anaerobic consortium has been previously used for the decomposition of cellulose and other biomass constituents [14,15]. The identification of the dominant members in the consortium is underway using culture-independent approaches. The culture was maintained anaerobically (N_2 headspace) in a medium previously described [14]. The TC60 inoculum had been grown at 60 °C for 48 h on 4 kg m^{-3} cellulose (Sigmacell Type 20, Sigma–Aldrich, St. Louis, MO). TC60 was added (10% (v/v)) to the anode chamber with a

combination of 1.66 mol m^{-3} acetate and 25 mol m^{-3} glucose as the substrate.

The anode and cathode graphite was prepared according to previous studies [5]. The anode (surface area of 40 cm^2) was suspended in the anolyte as the wire was threaded through a septum port in the reactor lid. The cathode chamber was positioned with the air inlet and outlet tubes threaded with o-rings through two separate ports. The fourth lid port was sealed during this study. At this point, assembly and manipulations to the MFC were completed in an anaerobic chamber with N_2/CO_2 head space. After adding the nutrient medium, inoculum, and substrate in the MFC, the lid was secured using silicon grease and a metal clamp. Silicon grease was also placed around cathode chamber connections exposed to the MFC headspace. Upon removal from the anaerobe chamber, ports on the lid were reinforced with additional silicon grease to prevent ingress of oxygen. The water jacket was connected to a water bath to maintain an internal MFC temperature of 57 ± 1 °C. The anolyte was continuously stirred using a magnetic stir plate and adjusted daily to approximately 6.5 pH using 1 M NaOH. Semi-batch feeding provided a final concentration of 25 or 50 mol m^{-3} glucose.

2.3. Performance analysis

The electrical output of the thermophilic MFC was monitored by measuring the potential difference (voltage) at 1 min intervals using a data acquisition unit (DATAQ Instruments, Akron, OH). The power density (W m^{-2}) was calculated according to the equation $P = I \times VA^{-1}$, where V is the voltage (V), I is the current (amps), and A is the surface area of the electrode (m^2). Polarization tests were completed as previously described [6].

3. Results and discussion

The thermophilic, cellulolytic consortium, TC60, with optimal growth at 60 °C was of interest for electrochemical analysis of the MFC design in this work. Initial attempts in two-chamber MFC modules [5] were unsuccessful because of rapid, extensive evaporation. Half of the anode working volume, 75 cm^3, was lost within two days, necessitating frequent interruptions because of anolyte and catholyte replacement in addition to pH adjustment and semi-batch feeding.

In a previous study conducted at 30 °C, Min and Angeladaki [13] utilized an anaerobic, glass reactor design in combination with a cathode chamber submersed in the anolyte. The design was a foundation for the thermophilic MFC reactor described in this study. The cathode chamber design was simplified to facilitate easy access and modular construction (Fig. 1B). Rather than extensive layers of gaskets, membrane, carbon paper, and polycarbonate as in the previous design [13], the cathode chamber had a single rubber o-ring able to prevent liquid or air crossover. The components of the cathode assembly, including the stainless steel screws, foil, and graphite discs, have all been shown to be conductive and were securely connected [16].

The design was tested in two MFCs runs, each over 500 h and without liquid loss. Thus, this design eliminated evaporation. The first system was operated with 4 kg m^{-3} cellulose as a substrate at 60 °C. The glass reactor achieved and maintained anaerobiosis within 30 min of inoculation as shown by no color change following resazurin addition. While it is possible that some trace amount of O_2 was momentarily present in the headspace and exchanged at the gas–liquid interface, this would have been quickly consumed by facultative anaerobes and was therefore considered to have an insignificant effect on the overall MFC performance.

TC60 did not produce a stable, reproducible current in the MFC with cellulose as the substrate. Following a power density at

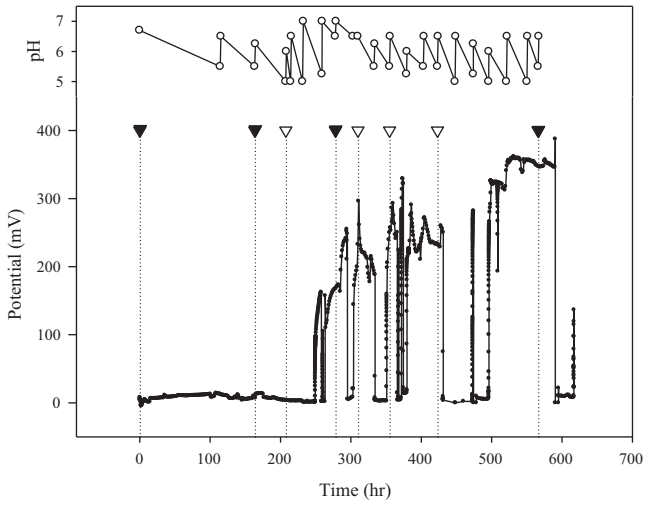

Fig. 2. Potential over time generated in the thermophilic MFC. Glucose additions to a final concentration of 25 mol m^{-3} (▼) or 50 mol m^{-3} (▽) are marked with dotted lines. Changes in the pH are indicated with open circles.

250 h of 337 mW m^{-2}, the current dropped rapidly and recovery was not achieved even after 800 h of operation (data not shown). The system failure was considered to be due to biological constraints of the consortium; the cellulose degraders present were likely fermentative and unable to complete electron transfer with the anode. Thus a build-up of metabolites, such as volatile fatty acids, would have prevented the utilization of glucose for anode-coupled respiration. In addition, the accumulation of glucose and cellobiose could have triggered feedback inhibition of cellulase activity [17].

The second MFC was run with TC60 and used glucose as a substrate. This run was successful as indicated by spiking power outputs following pH adjustment and five consecutive substrate additions (Fig. 2). The lag time was 250 h with the highest potential recorded prior the second performance analysis at 590 h, 387 mV. This potential is comparable to the range of values, 300–500 mV, obtained with glucose-fed mesophilic MFCs [18]. However, the range is usually broad because each MFC study differs in experimental parameters such as the glucose concentration, inoculum, MFC design, and external resistance, which all affect the power density. The system was successfully run for approximately 600 h at which point the experiment was terminated. It should be noted that that extensive acid formation and inadequate buffering in the medium required pH adjustment daily.

Two performance analyses of the glucose-fed thermophilic MFC showed improved performance over the 120 h difference with an increased maximum power of 3.3–4.5 mW m^{-2} (Fig. 3A). The polarization curve has three distinct sections of irreversible voltage losses: activation loss, ohmic loss, and mass transfer loss [19]. The typical initial and drastic voltage drop was not apparent, indicating lower than normal activation losses (Fig. 3B). This is attributed to increased reaction rates at thermophilic temperatures that lowered the activation energy and therefore the voltage necessary to maintain active, anaerobic metabolism. Ohmic loss can be observed in the center of the polarization curve with the gradual decrease of voltage as current density increases (Fig. 3B). The slope of this overpotential section, equivalent to voltage over current, yielded an internal resistance of 9.25 ± 0.15 Ω. This value is in the general range reported for other MFCs, although the experimental conditions are not comparable among the studies reviewed in the literature [20,21].

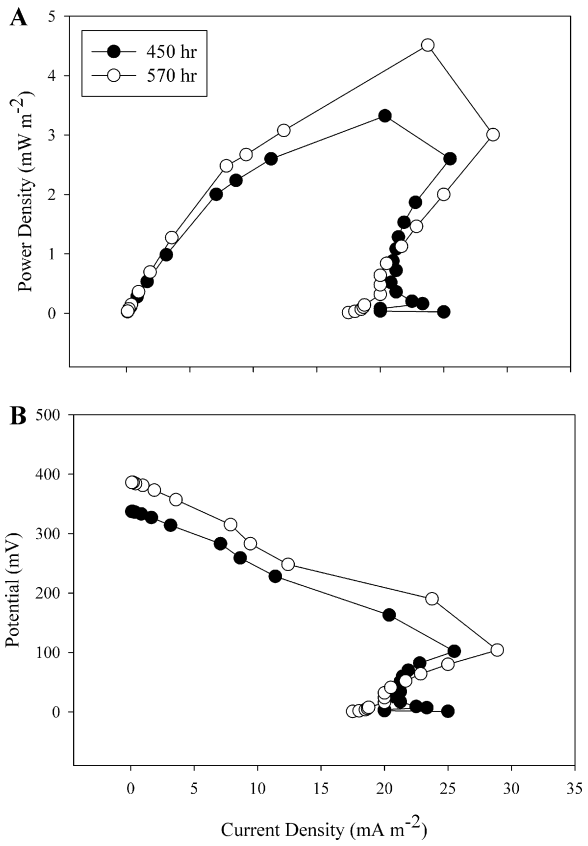

Fig. 3. Power (A) and polarization (B) curves at 450 h and 570 h for thermophilic MFC fed glucose.

The voltage overpotential resulting from mass transfer processes could not be assessed due to a power overshoot curve [11,22–24]. Initially, Min et al. [11] suggested that the overshoot effect was related to mass transfer, but increased agitation of the anolyte and catholyte did not modify the unusual curve. Ieropoulos et al. [22] hypothesized that the phenomenon was a result of overwhelming the anodic microorganisms, temporarily slowing their ability to transfer electrons. The most recent research [23,24] confirms that the overshoot is a limitation of the microbially mediated electron transfer at the anode. Watson and Logan [24] eliminated power overshoot by utilizing a polarization method with a multicycle technique. In this method, the MFC is left at an individual resistance until the substrate is depleted, between 1 and 2 days. At that time, the system is switched to a new resistance and fed substrate again. Whether the power overshoot is exaggerated under thermophilic conditions or with the present design requires further research. The overshoot in this study is probably due to limitations of the biofilm at the anodic surface. It should be noted that the anodic biofilm was not enriched completely as indicated by the increased overshoot current density from 25.5 to 28.9 mA m^{-2} after 120 h (Fig. 3). Testing of the further enrichment of TC60 was outside of the scope of this study.

This study provides the first step towards studying thermophilic MFCs by supplying a design for stable current while eliminating evaporation at elevated temperatures. Although this study describes an initial design for R&D, the results suggest the potential for stable, thermophilic MFC operation. The optimization of biological and engineering components is necessary prior to application of the design. In comparison to the mesophilic counterparts, the thermophilic MFCs could demonstrate increased metabolic and current production rates as indicated by other complex bioprocesses at elevated temperatures.

Acknowledgements

We acknowledge with thanks T. Bower for assistance in producing Fig. 1 and inspiring discussions on design development with C.J. Morobito, A. Yost, and A.D. Christy. This work is part of a project supported by the Finnish Agency of Technology and Innovation (Finland Distinguished Professor Program 402/2006). The study was also funded, in part, by the USDA National Needs Graduate Fellowship Program (S.M.C.).

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