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Using a glass fiber separator in a single-chamber air-cathode microbial fuel cell shortens start-up time and improves anode performance at ambient and mesophilic temperatures

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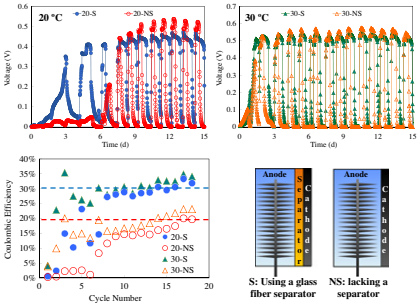
HIGHLIGHTS

- Using a separator in MFCs shortened start-up time at both 20 °C and 30 °C.
- Using a separator in MFCs enhanced anode performances at both 20 °C and 30 °C.
- MFC with a separator acclimated at 30 °C exhibited adaptability at 20 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

A shorter start-up time and highly negative anode potentials are needed to improve single-chamber air-cathode microbial fuel cells (MFCs). Using a glass fiber separator reduced the start-up time from 10 d to 8 d at 20 °C, and from 4 d to 2 d at 30 °C, and enhanced coulombic efficiency (CE) from <60% to 89% (20 °C) and 87% (30 °C). Separators also reduced anode potentials by 20–190 mV, charge transfer resistances by 76% (20 °C) and 19% (30 °C), and increased CV peak currents by 24% (20 °C) and 8% (30 °C) and the potential range for redox activity (−0.55 to 0.10 mV vs. −0.49 to −0.24 mV at 20 °C). Using a glass fiber separator in an air-cathode MFC, combined with inoculation at a mesophilic temperature, are excellent strategies to shorten start-up time and to enhance anode performance and CE.

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1. Introduction

Microbial fuel cells (MFCs) generate electricity from biomass using bacteria as catalysts, which can treat wastewater and simultaneously harvest electrical energy from waste (Logan, 2008; Logan and Rabaey, 2012; Lovley, 2008; Rabaey and Verstraete, 2005; Wang et al., 2012). The technical development of MFCs from small scale laboratory-based reactors, to larger-scale systems that can produce practical products faces inherent challenges to become an efficient and economical alternative to current commercialized wastewater treatment technologies (Logan, 2008). A number of factors have been found to influence MFC performances, including reactor materials and architectures (Cheng and Logan, 2007; Logan et al., 2006, 2007; Zhang et al., 2009a), substrate and solution chemistry (Fan et al., 2008; Feng et al., 2008; Huang and Logan, 2008; Liu et al., 2005), and operation mode (Ahn and Logan, 2010; Cheng et al., 2006b; Ren et al., 2011).

Temperature is an important operational parameter for MFCs (Ahn and Logan, 2010; Cheng et al., 2011; Michie et al., 2011; Patil et al., 2010). For half-cell experiments under potentiostatic control, biofilm formation required more than 40 days at 15 °C, decreased

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to 290 h (~12 d) at 22 °C, and further declined to 85 h (3.5 d) at 35 °C (Patil et al., 2010). For the MFC reactors studied by Cheng et al. (2011), a start-up time of ~210 h was needed to reach stable operation at 15 °C, but higher temperatures reduced start-up times to ~110 h at 20 °C, and ~50 h at 30 °C. Power production increased linearly with temperature at a rate of 33 ± 4 mW/°C (Cheng et al., 2011). The results of start-up time with temperature was not exactly the same in other studies but the trend was similar, for example, steady-state voltage generation using single chamber tubular MFCs with air-cathodes required 47 weeks at 10 °C, 41 weeks at 20 °C, and 10 weeks at 35 °C (Michie et al., 2011). Recent studies demonstrate that at higher temperatures MFCs required shorter start-up times to reach reproducible voltage generation, and also that they produced better anode performance since anodic biofilm formation could be faster and enzymes were more active (Ahn and Logan, 2010; Cheng et al., 2011; Patil et al., 2010). However, practical application of MFC such as wastewater treatment will require operation at ambient temperatures. Thus, shortening the MFC start-up time and improving the anode performance is needed at ambient temperature.

Inoculation at mesophilic temperatures provides one way to shorten the start-up time, and it was shown that an anode inoculated at 35 °C had better performance than anodes grown at 22 °C or 27 °C, over the operational temperature range from 15 °C to 45 °C (Patil et al., 2010). However, Michie et al. (2011) reported that an MFC acclimated at 35 °C produced only ~50 mV at 10 °C and ~200 to ~350 mV at 20 °C (originally ~500 mV at 35 °C) for reasons that were not explained.

Suitable separator application in MFCs can shorten the electrode spacing, limit oxygen intrusion, and prevent short circuiting (Harnisch and Schröder, 2009; Li et al., 2011; Zhang et al., 2009a, 2009b). Separator characteristics impact MFC performances (Zhang et al., 2009a, 2010b, 2011a). Cation (CEMs) and anion exchange membranes (AEMs) (Liu and Logan, 2004; Kim et al., 2007, 2009; Zhang et al., 2009a, 2009b, 2010a) are commonly used as separators in MFCs; however, CEMs and AEMs have relatively large internal resistances and create pH gradients, resulting in a reduction of power compared to systems without a membrane (Kim et al., 2007; Rozendal et al., 2007). During long-term operation of membrane electrode assembly MFCs, the CEMs and AEMs can deform, causing water and gas becoming trapped between the membrane and cathode, reducing performance (Zhang et al., 2010a). Glass fiber mats showed excellent separator characteristics for MFCs, as they have a high proton but low oxygen transfer coefficient, a low ohmic resistance, and are non-biodegradable (Zhang et al., 2009a, 2011a). However, in previous studies, MFCs were inoculated in absence of a separator with 2 cm of space between anode and cathode in order to achieve parallel anodic performances (Zhang et al., 2009a, 2010b) and separator effects on MFC start-up and anode performance were not investigated.

In the present study, start-up characteristics of single-chamber air-cathode MFCs with and without glass fiber separators were examined at ambient (20 ± 3 °C) and mesophilic (30 ± 1 °C) temperatures. Anode performance was evaluated in polarization, electrochemical impedance spectroscopy, and cyclic voltammetry tests. MFCs started up at mesophilic temperature were also subsequently operated at ambient temperatures. Oxygen diffusion through cathode and separator was studied to explore the possible mechanism of enhanced anode performance when using a separator.

2. Methods

2.1. MFC reactors

MFCs were cubic-shaped reactors with a single chamber (2 cm length, 12 mL liquid volume), constructed as previously described (Zhang et al., 2011a). The anode was a graphite fiber brush with a core of two twisted titanium wires as the current collector. The brush anode was ammonia gas treated (Logan et al., 2007) and placed in the middle of the cylindrical chamber. The cathode was made of 30% wet-proofed carbon cloth (Type B, BASF Fuel Cell, Inc., USA) with platinum (0.5 mg/cm^2, 7 cm^2 projected area) catalyst layer and four polytetrafluoroethylene (PTFE) diffusion layers to prevent water loss (Cheng et al., 2006a). The cathode was on one side of the reactor, with the catalyst layer facing the solution, and the diffusion layers facing air. The "control" MFCs (NS) lacked a separator, with a distance of ~2 mm between the brush anode and the air-cathode to avoid short circuiting. This design was modified by placing a glass fiber mat separator (DC1.0, Jiafu Co., China; termed "S") against the cathode to investigate the effects of the separator on start-up and anodic performance.

Four conditions for MFC start-up and operation were examined: (1) with a separator at an ambient temperature of 20 ± 3 °C (on laboratory bench; 20-S); (2) without a separator at 20 ± 3 °C (20-NS); (3) with a separator at a mesophilic temperature of 30 ± 1 °C (in temperature control box; 30-S); and (4) without a separator at 30 ± 1 °C (30-NS). All anodes were acclimated in MFCs with a 1000-Ω resistor except as noted, using a bacterial suspension obtained from single chamber air-cathode MFCs operated in fed batch mode at 20 ± 3 °C for over one year. All MFCs were fed with acetate (1 g/L) as substrate in a sodium phosphate buffer solution (PBS, 50 mM) containing mineral (12.5 mL/L) and vitamin (5 mL/L) solutions (Cheng and Logan, 2007).

2.2. Analysis

Voltage (E) across an external resistor in the MFC circuit was monitored at 20-min intervals using a data acquisition system (2700, Keithley Instrument, USA) connected to a personal computer. Current ($I = E/R$, R: external resistance) and power ($P = IE$) were calculated as previously described (Logan, 2008), and then normalized by the cathode projected area (7 cm^2).

Coulombic efficiency (CE, recovery of electrons from the substrate) was calculated as (Logan et al., 2006)

$$CE = \frac{M \int_0^t Itdt}{nVF(COD_0 - COD_t)} \quad (1)$$

where M is the molecular weight of oxygen, F is Faraday's constant, $n = 4$ is the number of electrons exchanged per mole of oxygen, V is the volume of anode chamber, COD_0 is chemical oxygen demand (COD) of influent, COD_t is COD of effluent over time (t). The CEs at different current densities were obtained by varying the external resistance from 1000 Ω to 20 Ω, with a single resistor used per fed-batch cycle.

Polarization curves were obtained by varying resistance in the MFC circuit in decreasing order at 20-min intervals at each resistance. Anode potential was measured during polarization tests and reported versus a Ag/AgCl reference electrode (+0.211 V vs. a standard hydrogen electrode).

Ohmic and charge transfer resistances were determined by electrochemical impedance spectroscopy (EIS) using a potentiostat (PGSTAT 128N, Metrohm Autolab, Netherlands) (He et al., 2006; Hutchinson et al., 2011). Impedance measurements were conducted with a 1000-Ω resistor over a frequency range of 10,000–0.01 Hz using a sinusoidal perturbation with a 10-mV amplitude. Three electrode experiments were performed for anode impedance analysis, with the anode as working electrode, the cathode as counter electrode, and Ag/AgCl as the reference electrode. Two electrode experiments were conducted for MFC ohmic internal resistance analysis. The anode and total ohmic resistances were determined at high frequencies where the impedance data cross

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