Variation of power generation at different buffer types and conductivities in single chamber microbial fuel cells

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ABSTRACT

Microbial fuel cells (MFCs) are operated with solutions containing various chemical species required for the growth of electrochemically active microorganisms including nutrients and vitamins, substrates, and chemical buffers. Many different buffers are used in laboratory media, but the effects of these buffers and their inherent electrolyte conductivities have not been examined relative to current generation in MFCs. We investigated the effect of several common buffers (phosphate, MES, HEPES, and PIPES) on power production in single chambered MFCs compared to a non-buffered control. At the same concentrations the buffers produced different solution conductivities which resulted in different ohmic resistances and power densities. Increasing the solution conductivities to the same values using NaCl produced comparable power densities for all buffers. Very large increases in conductivity resulted in a rapid voltage drop at high current densities. Our results suggest that solution conductivity at a specific pH for each buffer is more important in MFC studies than the buffer itself given relatively constant pH conditions. Based on our analysis of internal resistance and a set neutral pH, phosphate and PIPES are the most useful buffers of those examined here because pH was maintained close to the pK_a of the buffer, maximizing the ability of the buffer to contribute to increase current generation at high power densities.

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1. Introduction

Microbial fuel cells (MFCs) are increasingly being investigated as a method for renewable bioenergy production. Much research has focused on methods to reduce the MFC internal resistance as this is the main limitation for increasing power generation. Factors that affect internal resistance include system architecture and electrode spacing (He et al., 2006; Hu, 2008; Liu and Logan, 2004), electrode materials (Qiao et al., 2007; ter Heijne et al., 2008), electrode surface area (Logan et al., 2007), and catalysts (HaoYu et al., 2007). Limited proton transfer to and from the electrodes in MFCs can result in high ohmic resistance and energy losses (Kim et al., 2007a). Protons produced at the anode and consumed at the cathode must be balanced by charge transfer within the solution, although charge can be balanced by ionic species other than protons in solution (Kim et al., 2007b).

Reducing electrode spacing (Cheng et al., 2006), increasing solution conductivity through the addition of salts (Gil et al., 2003; Huang and Logan, 2008; Liu et al., 2005) or using higher buffer concentrations (Min et al., 2008) enhances MFC performance through reduction of ohmic resistance. The buffer affects MFC performance in several ways due to its chemical composition and interaction with the electrodes, bacteria, and membrane (if present). In addition, the buffer helps to reduce changes in pH in the bulk solution and in the biofilm, and therefore it maintains the pH in the range suitable for the growth of microorganisms (Gil et al., 2003). An ideal buffer should be able to maintain constant pH without interfering with chemical reactions or microbial physiology, and facilitate proton transfer to the electrode for high power densities in MFCs.

Phosphate buffers are widely used in MFC research (Kim et al., 2008; Liu et al., 2005; Logan et al., 2007), and it has been shown that increasing phosphate concentration within certain ranges will increase power output (Min et al., 2008). Bicarbonate buffer is another useful low-cost and effective pH buffer, although high concentrations of carbonate can enhance the growth of methanogens (Chang et al., 1998; Fan et al., 2007). Several synthetic zwitterionic buffers, such as MES (2-[N-morpholino]ethane sulfonate), HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), and PIPES (piperazine-N, N′-bis[2-ethanesulfonate]) are often used in routine microbiological studies (Good et al., 1966). These zwitterionic buffers have advantages compared with conventional buffers such as phosphate and carbonate buffers in biological studies as their pK_a

values are in the range of pH 6.0 and 8.0 (the pH of the midpoint of the buffering range), they are chemically stable and non-toxic, and do not interfere with biochemical reactions. Although these zwitterionic buffers have served well in biological studies (Somkuti and Gilbreth, 2007), their characteristics for power generation in laboratory MFCs have not been previously reported. In this study we therefore compared the effects of these buffers on the performances of single chamber air-cathode MFCs. We used MFCs lacking a membrane in order to focus on the effects of the buffers on the bacteria and electrodes, rather possible side interactions of buffers with a membrane.

2. Materials and methods

2.1. MFC set-up

Single chamber MFCs were designed using media bottles with a working volume of 250 mL. Air-cathodes (projected surface area = 5.9 cm^2) consisting of wet-proofed carbon cloth (Type B, E-TEK) and 0.5 mg Pt/cm^2 were prepared as described in the literature (Cheng et al., 2006). The anode was non-wet-proofed carbon cloth (12.5 cm^2) placed at the center of the bottles. The cathodes and anodes were connected with titanium wire and an external resistor (1000 Ω). Voltage across the resistor was recorded using a digital multimeter (Model 2700, Keithley).

2.2. Inoculum, medium and substrates

MFCs (duplicate reactors) were inoculated using activated sludge from a wastewater treatment plant that had a volatile suspended solid (VSS) concentration of 2.3 g/L. The initial solutions contained acetate (16.2 mM, 1 g COD/L), 50 mM buffer, 5.8 mM of NH_4Cl, 1.7 mM of KCl, and a trace metal salt and vitamin solution (Lovley and Phillips, 1988). For a control, we used same medium composition prepared for other MFCs without adding buffer. The initial pH was adjusted to 7.

2.3. Buffers and operating procedures

Phosphate buffer (PBS, pK_a = 7.20) and three types of organic buffers were tested. MES (pK_a = 6.15) was purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA), and HEPES (pK_a = 7.55) and PIPES (pK_a = 6.76) were purchased from Sigma–Aldrich Chemicals, Inc. (St. Louis, MO, USA).

Tests using these different buffers were conducted in three separate phases. In Phase I, all reactors solutions except the control MFC (CMFC, no buffer) contained a buffer at a concentration of 50 mM. In Phase II, the solution conductivity was adjusted to match that of the buffer with the highest conductivity (8.2 mS/cm; PBS) using NaCl. In Phase III, the conductivity of all solutions was further increased to 20 mS/cm to increase power output. Each phase is composed of two or three consecutive fed-batch experiments. When the substrates were depleted, medium in the MFC was completely replaced with a fresh solution to verify the reproducibility of electricity generation over time by achieving steady-state performance over successive batches. For each fed-batch, final solution pH was measured at the end of the period.

2.4. Analytical methods

The current (I, A) was calculated by I = E/R where R is resistance (Ω) and E is voltage (V). The power output of the cells (P, W) was calculated as P = IV. Variable external resistance (10–10^6 Ω) was used to obtain polarization curves and each resistor was changed every 20 min. Power density (mW/m^2) and current density (mA/m^2) were based on the cathode surface area (m^2).

The ohmic and charge transfer resistances were measured using electrochemical impedance spectroscopy (EIS) with a potentiostat (CompactStat, HS Technologies). EIS was performed under open circuit voltage (OCV) conditions over a frequency range of 10^5–0.005 Hz with sinusoidal perturbation of 10 mV amplitude. A Nyquist plot with one semicircle was obtained and the first x-intercept (lower value of x) at high frequency was determined as ohmic resistance. The second x-intercept (higher x value) at low frequency was regarded as the sum of ohmic and charge transfer resistances. Diffusion resistance was obtained by subtracting ohmic and charge transfer resistance components from the total impedance resistance obtained from the slope of the polarization curve (Rezaei et al., 2007). Volatile fatty acids (VFAs) were analyzed by a high performance liquid chromatograph (HPLC, SpectraSYSTEM P2000) equipped with an ultraviolet (210 nm) detector and a 300 m × 7.8 mm Aminex HPX-97H column after pretreatment with a 0.45 μm membrane filter. Sulfuric acid (0.005 M) was used as a mobile phase at a flow rate of 0.6 mL/min. pH and conductivity were measured using pH meter (Orion model 720A, Thermo scientific) and conductivity meter (HI8633, Hanna).

3. Results and discussion

3.1. Effect of different buffers on voltage and power density

During the reactor start-up in Phase I, there was a lag in voltage generation for all buffers that lasted 42–47 h. After that, there was a rapid acclimation of the electrochemically active microorganisms as evidenced by a large increase in voltage in all the MFCs. The average voltages in Phase I that were produced in the MFCs with different buffers at a fixed resistance (consistently over several fed-batches) were: 504 ± 19 mV, PBS; 480 ± 15 mV, PIPES; 448 ± 32 mV, HEPES; 461 ± 9 mV, MES; and 402 ± 25 mV for CMFC. Variations among the duplicate reactors in the voltage produced in each fed-batch of this and the other two phases are shown in Table 1.

Polarization data were obtained to characterize the performance of the system at different current densities, with stable performance based on reproducible power density curves over multiple cycles. We observed that power production depended on the buffer type, with the highest power density in Phase I produced with the PBS buffer (410 mW/m^2). Maximum power densities produced with the other buffers were reduced in comparison to PBS by 6.3% for PIPES (385 mW/m^2), 28% for MES (295 mW/m^2), and 50% for HEPES (205 mW/m^2) (Fig. 1A and D). CMFC with no buffer was 50% lower (204 mW/m^2) than that of the PBS reactor. These results demonstrate that a buffer was needed to optimize power production, and that the type of buffer at the same added concentrations substantially affected power production.

The reason for the differences in power generation was primarily the different solution conductivities produced by each buffer. The conductivity of the solution in the PBS-MFC was 8.2 mS/cm compared to 3.0 mS/cm for CMFC, with corresponding ohmic resistances of 8.6 Ω/cm^2 and 25.1 Ω/cm^2 (Fig. 2A). To demonstrate this effect of conductivity with the different buffers, in Phase II we set the conductivity of all reactors to approximately the same as that of PBS at a 50 mM concentration (8.2 mS/cm) using NaCl and then ran the reactors until stable and reproducible power densities were obtained (Table 1).

Polarization data were then obtained to compare the performance of these reactors over a range of current densities (Fig. 1B and E) at this constant conductivity in Phase II. The power densities did not substantially vary among reactors, with the HEPES-MFC producing a slightly larger power density (459 mW/m^2) than that obtained using PBS -MFC (449 mW/m^2) and PIPES-MFC (437 mW/m^2). There was some difference in power production