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Short communication

Effect of electrolyte pH on the rate of the anodic and cathodic reactions in an air-cathode microbial fuel cell

Zhen He, Yuelong Huang, Aswin K. Manohar, Florian Mansfeld *

Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089, USA

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ABSTRACT

The measurement of electricity generation from an air-cathode microbial fuel cell (MFC) with a mixed bacteria culture at different pH showed that this MFC could tolerate an initial (feed solution) pH as high as 10. The optimal initial pH was between 8 and 10 with higher current generation compared to lower or higher pH. The bacterial metabolism exhibited a buffer effect and changed the electrolyte pH. The impedance spectra of the anode and cathode of the MFC at the open-circuit potential (OCP) revealed that the anodic microbial process preferred a neutral pH and microbial activities decreased at higher or lower pH; while the cathodic reaction was improved with increasing pH.

1. Introduction

In our energy-based society, the value of any energy-rich matters is increasing. Thus, the high organic load in wastewaters is no longer seen as waste, but instead as a valuable energy resource. Today, primarily methane is gained from the biogas of traditional anaerobic digesters, but its conversion into electricity via combustion is not very efficient [1]. Direct electricity generation from wastewater treatment using microbial fuel cells (MFCs) is advantageous, because a thermodynamic conversion step is not necessary [2]. In MFCs, oxygen is usually supplied into the cathode compartment by air sparging, which is energy intensive.

To reduce the cost of MFC operation, an air-cathode MFC using passive air supply has been developed by the researchers at Pennsylvania State University [3]. In such a device, one side of the cathode electrode was immersed in a solution (electrolyte), while the other side faced air. A cation exchange membrane (CEM) may or may not be placed between the anode and the cathode. Air-cathode MFCs have shown promising power production while simplifying the reactor configuration. It has been reported that an air-cathode MFC produced a power density of 1010 W/m^3, which is the highest power density reported from MFC studies so far [4]. In addition to high power output, air-cathode MFCs are capable of using various substrates as anodic fuels, such as short chain fatty acids, carbohydrates, and synthetic acid-mine drainage [5–7]. Other related studies include reactor configuration, electrode materials and catalysts, cathode structure and internal resistance [8–13].

The electrolyte pH is crucial to the MFCs power output. Generally, bacteria require a pH close to neutral for their optimal growth; while oxygen reduction on the cathode electrode results in an alkaline pH [14]. A traditional MFC can maintain two different pH conditions to optimize the anodic and cathodic reactions. It is, however, impossible to do so in air-cathode MFCs, because only one electrolyte is present. To our knowledge, no studies have examined the effect of electrolyte pH on the anodic and cathodic reactions in air-cathode MFCs. Therefore, it is necessary to investigate the optimal pH for air-cathode MFCs and understand how electrolyte pH affects the electricity generating process.

In this paper, electrochemical impedance spectroscopy (EIS) was employed to investigate the effect of electrolyte pH on the performance of an air-cathode MFC. EIS has been used to measure the internal resistance of MFCs [4,10,15–17] and analyze the characteristics of the individual electrode and biofilm formation on the electrode [17–19]. In the present experiments, EIS data of the anode and cathode electrodes were collected for different pH. The measured data were fitted to a one-time constant equivalent circuit. The solution resistance and the polarization resistance of the anode and the cathode were obtained. Meanwhile, the peak current density, peak power output, coulombic efficiency, open-circuit potential and the electrolyte pH (before and after the reaction) were monitored and compared.

2. Experimental

2.1. Air-cathode MFC setup and operation

The air-cathode MFC was designed and built according to a previous publication (Fig. 1) [3]. The anode and cathode electrodes

* Corresponding author. Tel.: +1 213 740 3016; fax: +1 213 740 7797.
E-mail address: mansfeld@usc.edu (F. Mansfeld).

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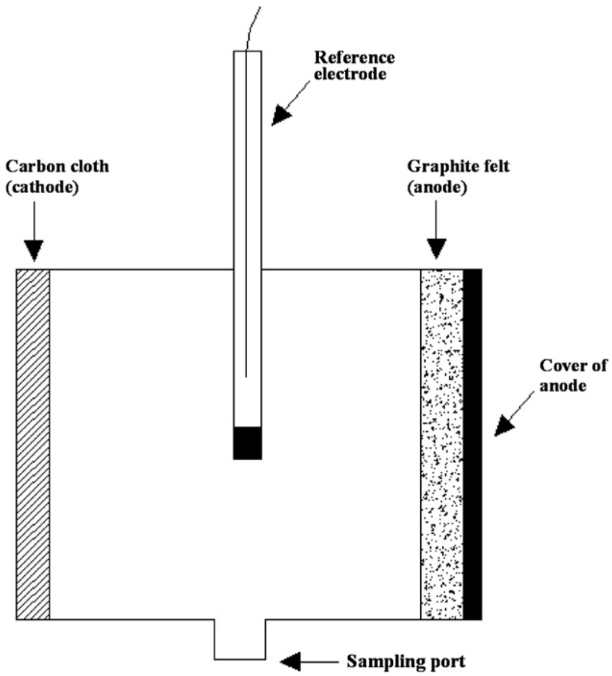

Fig. 1. The scheme of the air-cathode MFC.

were installed at two ends of a tubular chamber (10 mL), and connected by a 1000 Ω resistor. The distance between the anode and cathode electrodes was 2 cm. The outer side of the anode electrode (graphite felt, GF-S6-06, Electrolytica, USA) was capped by a plastic cover to prevent oxygen intrusion. The cathode electrode was prepared by electrodepositing platinum on carbon cloth (E-tek, Somerset, NJ, USA) with a loading of ~0.05 mg/cm^2 [20]. Two mL of 5% Nafion® solution (DuPont, USA) containing carbon particles (Sigma-Aldrich, St. Louis, USA) was applied on one side of the carbon cloth to form a water-proof layer. Both anode and cathode electrodes have an apparent surface area of 5 cm^2, respectively. A reference electrode (Ag/AgCl) was installed in the middle of the tubular chamber.

To start the MFC, 1 mL of inoculum (mixture of aerobic and anaerobic sludge from a local wastewater treatment plant, Los Angeles, USA) and 9 mL of the feed solution were injected into the chamber using a syringe. The feed solution contains (per L): sodium acetate, 2 g; yeast extract, 1 g; NH_4Cl, 0.3 g; $MgSO_4$, 0.03 g; $CaCl_2$, 0.015 g; KH_2PO_4, 5 g; K_2HPO_4, 10.7 g; and trace element 1 mL [21]. During the operation, when the current production decreased to less than 20% of its peak value, the electrolyte was completely replaced by 10 mL of the feed solution. The pH of the feed solution was adjusted by weak acid or base solution to the designed values (5, 6, 7, 8, 9, and 10). The concentration of phosphate buffer remained same at different pHs. The experiment started from the lowest pH of 5 and moved to next pH only after the electricity generation was stable and data collection was completed.

2.2. Measurement and calculation

The cell voltage was recorded every 30 s by a digital multimeter (DMM 2700, Keithley Instruments, Inc., Cleveland, OH, USA). The open-circuit potential and individual electrode potentials were measured using a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). The power density and coulombic efficiency were calculated according to He et al. [21]. Coulombic efficiency represents how many electrons available in the substrates are converted into electricity. The pH was measured using a Benchtop pH meter (UB-10, Denver Instrument, Denver, CO, USA). The data was presented with triplicate measurements of the same MFC.

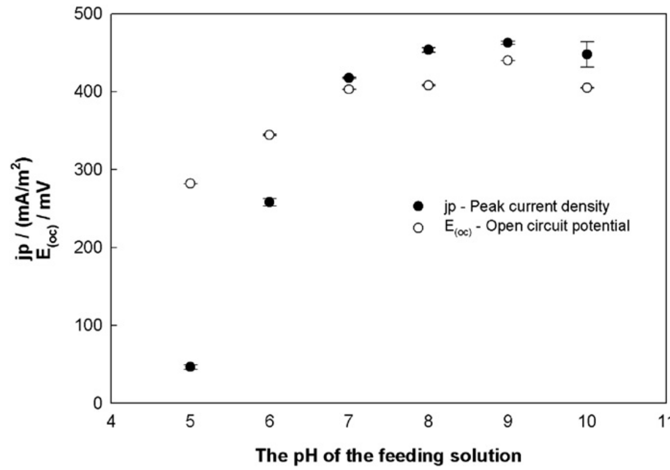

Fig. 2. The peak current density and open-circuit potential are presented as a function of the feed solution pH. Error bars represent standard deviation from triplicate measurements of the same MFC.

2.3. Electrochemical impedance spectroscopy (EIS)

EIS measurements were conducted using a Gamry Reference 600 potentiostat in a frequency range from 100 kHz to 5 mHz. An ac signal of 10 mV amplitude was applied during the measurement. The experimental data were fitted to a one-time constant equivalent circuit using the ANALEIS software [22], and the values of the solution resistance (R_s), polarization resistance (R_p) and capacitance (C) of the anode and the cathode were determined.

3. Results and discussion

3.1. Effect of pH on electricity generation

The experimental results clearly showed the influence of the feed solution (electrolyte) pH on the performance of this air-cathode MFC. With each injection of the feed solution, the electric current increased at the beginning and decreased after reaching a peak value (data not shown). This process took 1–2 days, depending on the feed solution pH. The peak current density increased with increasing pH and

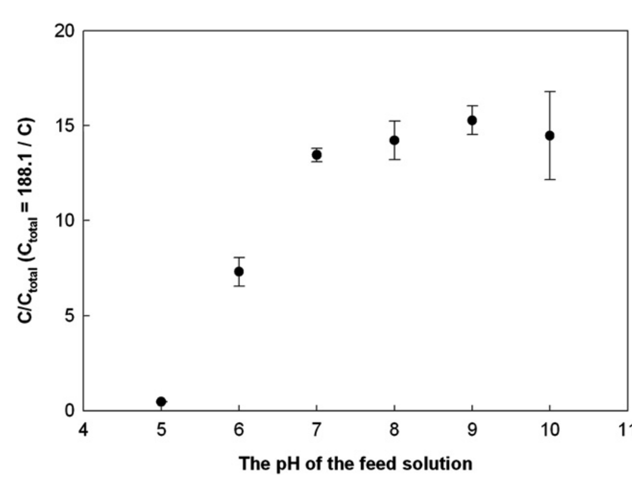

Fig. 3. The coulombic efficiency is presented as a function of the feed solution pH. Error bars represent standard deviation from triplicate measurements of the same MFC.

reached the highest value at pH 9 (Fig. 2). The lowest peak current density of 46.5±2.9 mA/m^2 occurred at the lowest pH of 5. Between pH 8 and 10, the peak current was relatively stable, varying between 223.8±8.1 mA/m^2 and 231.3±1.1 mA/m^2 corresponding to values between 87.2±0.4 mW/m^2 and 107.1±1.0 mW/m^2 in terms of the peak power density. The open-circuit potential exhibited a similar trend as the peak current density with the highest value of 439.7±0.1 mV at pH 9 (Fig. 2). Since the peak values (current and power) only showed a point of the current generating progress, instead of reflecting the whole current profile, current values and time were integrated to calculate coulombic efficiency (CE). Likewise, CE increased from 0.5±0.0 to 16.5±2.6% when the feed solution pH increased from 5 to 10, with the highest value of 17.5±0.8% at pH 9 (Fig. 3).

Compared with a previous study [23], we found similarity and difference. Both studies observed that low pH (pH 5 and 6) resulted in lower electricity generation. However, in our case pH 5 showed a more severe inhibition on electricity generation that obtained only 10% of the highest peak current and 3% of the highest CE (at pH 9); while Gil et al. [23] reported that at pH 5, the MFC generated 85% of the highest current and 44% of the highest CE. In addition, the optimal pH for their MFC was between 7 and 8 while in the present study, this range was from 8 to10. Gil's results reflected the effect of pH on anodic process only, because they performed experiments in a two-chamber MFC [23]. In the present MFC (one-chamber MFC), the pH of the electrolyte affects both anodic and cathodic reactions in which a high pH (8–10) inhibited the anodic bacterial activities to some extent, but might be favorable to the cathodic reaction, thus improving the overall performance.

Besides the studies discussed above, other researchers have also found that the acidic pH reduces electricity production. In a two-chamber MFC study, similarly to our study the power density at pH 5 was about 10% of the highest value [7]. Ren et al. [24] found that the power production decreased significantly when the final pH dropped to 5.2 due to the acidic products of fermentation and resumed quickly when the pH was recovered to 7.0. In contrast, few studies have investigated electricity generation under an alkaline condition, except for one paper published about 20 years ago. In that study, a pure culture from a range of *Bacillus* strains was tested at pH 9–11 and the maximum current and coulombic yields were found at pH 10.5 [25]. The authors reported that the current output at this pH was about one order of magnitude less than that harvested from neutral organisms, which is different from the present finding that the peak current at pH 10 was 7.23% higher than that at pH 7, indicating that a mixed bacterial culture is more resistant to high pH than a pure culture.

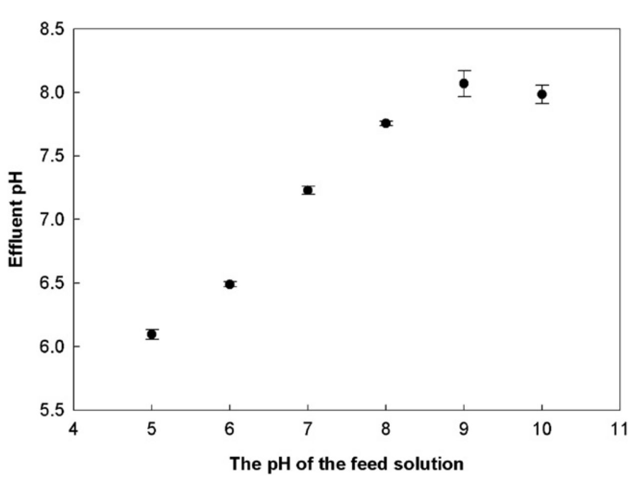

Fig. 4. The effluent pH is presented as a function of the feed solution pH. Error bars represent standard deviation from triplicate measurements of the same MFC.

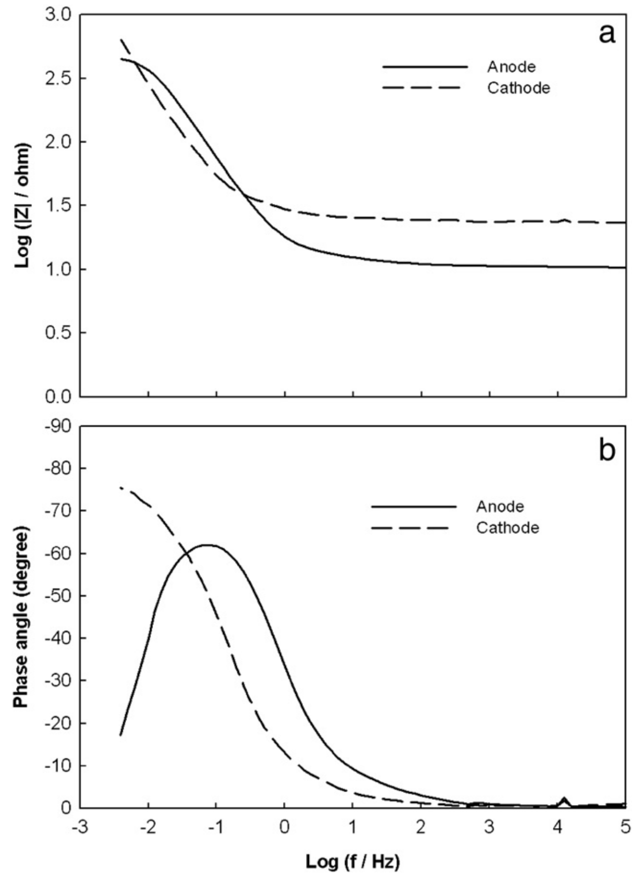

Fig. 5. Bode plots for the anode and cathode electrodes at pH 8: a) impedance; b) phase angle.

3.2. pH change

The biological and electrochemical reactions in the air-cathode MFC changed the electrolyte pH (Fig. 4). When the feed solution pH (initial pH) was lower than 8, the electrolyte pH after 1–2 days' reaction (called "effluent pH") was increased. The opposite results were found at the pH values equal to or higher than 8. The increase of pH is due to proton consumption by the cathodic reactions [26]. Meanwhile, bacterial metabolism constantly produces weak acid compounds and maintains their intracellular pH [27]. As a result, the high pH was decreased over the current generation process by uptaking protons. Both proton consumption and generation occur at the same time, but a balance was established based on the initial pH. These results demonstrated that the air-cathode MFC can tolerate an initial pH impact as high as 10, which does not significantly affect electricity generation due to a buffer effect possibly from bacterial activities. It should be noted that the present MFC is a batch-operated system. In a continuously operated MFC, the buffering effect via bacterial metabolism may not be as important as that in a batch system, because a constant flux of high pH solution may overwhelm the proton generation. Fig. 4 shows that the effluent pH values at high currents output are within a relatively small range, varying between 7.23±0.03 and 8.07±0.10, indicating that the anodic bacteria prefer a pH close to neutral for their growth.

3.3. EIS analysis of the anode and cathode electrodes

EIS measurements provide information on solution resistance (R_s) as well as polarization resistance (R_p) and capacitance (C) of the anode and cathode, respectively. Fig. 5 shows Bode plots at pH 8 and Fig. 6 shows the values obtained by analysis of the impedance spectra at

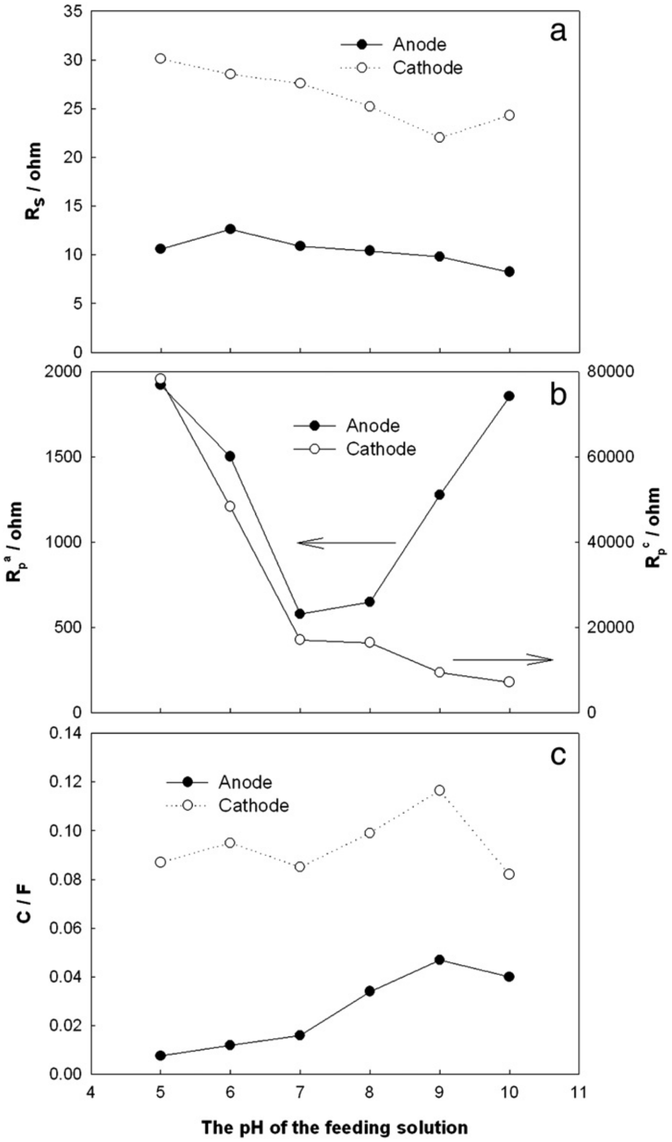

Fig. 6. The fitting results of EIS measurements of the individual electrode are presented as a function of the feed solution pH: a) solution resistances; b) polarization resistance; and c) capacitance.

different pH. Comparing Fig. 6a and b shows that polarization resistance of the anode and the cathode dominated over solution resistance restricting the power output. The cathodic R_s was slightly higher than the anodic R_s possibly due to a high ohmic resistance caused by a water-proof layer.

The polarization resistances of the anode and cathode electrodes differed by one to two orders of magnitude (Fig. 6b), suggesting that the cathodic reaction is the limiting factor. They also exhibited completely different dependence on pH: the anodic polarization resistance (R_p^a) decreased first and then increased after reaching a minimum at pH 7, while the cathodic polarization resistance (R_p^c) continuously decreased from pH 5 to 10. R_p^a is related to bacterial activities and thus its variation trend reflects the anodic microbial catalysis of the fuel. A low R_p^a revealed a stronger anodic bacterial activity involved in electricity generation. The lowest R_p^a occurred at the pH 7 verifying that a neutral pH is beneficial to bacterial activity. The pH values higher or lower than 7, on the other hand, restricted bacterial activity by affecting their energy generation that may be through influencing proton motive force during energy producing process [27] and resulted in a higher R_p^a. R_p^c decreased with increasing pH, indicating that the oxygen reaction rate increased at a higher pH, which has also been shown by a previous study [28]. Because of the negative effect of high pH on bacterial metabolism, this increased rate of the cathodic reaction at a higher pH is most likely an abiotic result instead of the development of a biocathode, although biofilm may be established on the cathode [29,30].

To understand the variation of the peak current at the different pH, the pH values were grouped into two stages. First, the increase in current generation between pH 5 and 7 is due to the increase of the rate of both the anodic and cathodic reaction (both R_p^a and R_p^c decreased). Second, the increase of electric current between pH 7 and 10 is a result of the decreased R_p^c. Although the R_p^a increased from 578 to 1855 Ω in this pH range, the cathodic reaction is a limiting factor and thus the decreased R_p^c from 17 to 7.2 kΩ determined the overall electricity production (Fig. 6b).

The capacitances of both anode and cathode electrodes did not appreciably change with pH (Fig. 6c). The cathodic capacitance is larger than that of the anode, possible due to the higher surface area of the cathode electrode due to platinum deposition [31].

4. Conclusion

Air-cathode MFCs are advantageous due to their high power output and simplified reactor configuration. A better understanding of the factors affecting their performance will help to apply this technology in practice. The electrolyte pH affects both anodic microbial activities and cathodic reaction, and thus is a very important factor. In this study, the electricity generation from an air-cathode MFC was evaluated at a feed solution pH between 5 and 10. The EIS of the anode and cathode electrodes were obtained under these conditions. It was found that the air-cathode MFC can tolerate an electrolyte pH as high as 10 with optimal conditions between pH 8 and 10. The anodic bacterial activity and cathode oxygen reduction were not only affected by the pH, but also changed the electrolyte pH by supplying or consuming protons. The EIS data demonstrated that the polarization resistance of the cathode was the dominant factor limiting power output. The low polarization resistance of the anode at the neutral pH confirmed that the anodic bacterial activity is optimal at a neutral pH, while the decreased polarization resistance of the cathode with the increasing pH indicated that the cathodic reaction was improved at a higher pH. The dependence of the cathodic reaction on the high pH requires further investigation. In conclusion, the performance of an air-cathode MFC is determined by the mixed effects of the electrolyte pH on both anodic and cathodic reactions.

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