



## Short Communication

## Saline catholytes as alternatives to phosphate buffers in microbial fuel cells



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## HIGHLIGHTS

- ▶ High salinity solution used instead of phosphate buffer in two-chamber MFCs.
- ▶ Maximum power of 491 mW/m<sup>2</sup> was only 17% less than from MFCs with 50 mM PBS.
- ▶ The air-cathode was kept relatively free of a biofilm and CE was increased.
- ▶ Current production was reduced slightly due to pH changes.

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## ABSTRACT

Highly saline solutions were examined as alternatives to chemical buffers in microbial fuel cells (MFCs). The performance of two-chamber MFCs with different concentrations of saline solutions in the cathode chamber was compared to those with a buffered catholyte (50 mM PBS). The use of a NaCl catholyte improved the CE to 43–60% (28% with no membrane) due to a reduction in oxygen transfer into the anolyte. The saline catholyte also reduced the membrane and solution resistance to 23 Ω (41 Ω without a membrane). The maximum power density of 491 mW/m<sup>2</sup> (240 mM NaCl) was only 17% less than the MFC with 50 mM PBS. The decrease in power output with highest salinity was due to reduced proton transfer due to the ion exchange membrane, and pH changes in the two solutions. These results show that MFC performance can be improved by using a saline catholyte without pH control.

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## 1. Introduction

Microbial fuel cells (MFCs) are devices that convert chemical energy to electrical current using exoelectrogenic microorganisms (Logan, 2008). Microbes on the anode oxidize contaminants and release electrons and protons. Electrons are transferred through the circuit to the cathode where they combine with protons and oxygen to form water. Charged ions must be transported between the electrodes to maintain a charge balance (Logan, 2008; Logan et al., 2006). The relatively slow transport rate of protons compared to other cations such as K<sup>+</sup> and Na<sup>+</sup> can result in a reduction in the pH of the anode solution, and an increase in the pH of the catholyte in two-chamber MFCs (Rozendal et al., 2006). Buffered solutions are usually used to avoid large pH changes, and a pH below ~6 can inhibit current generation by exoelectrogenic bacteria on the anode (Gil et al., 2003).

Many different types of buffers have been used in MFCs to maintain suitable pH conditions and increase the solution conduc-

tivity, including phosphate, bicarbonate, and zwitterionic (Fan et al., 2007; Nam et al., 2010). Phosphate is the most commonly used buffer, with optimal performance produced in single-chamber, air-cathode MFCs at pHs in the range of 8–10 (He et al., 2008). Increasing the buffer concentration can improve power within certain concentration ranges. For example, increasing the phosphate buffer concentration from 50 to 100 mM increased the maximum power density by 45%, but a further increase to 200 mM increased power by only 11% (Fan et al., 2007). The use of high concentrations of phosphate in practice is not feasible due to its high cost, and the need to avoid phosphate releases into the environment. Bicarbonate buffers are more useful, but they can enhance the growth of methanogens (Fan et al., 2007). Zwitterionic buffers can be toxic to bacteria as metals tend to remain more bioavailable than with phosphate buffers (Mash et al., 2003). A more useful approach would be to avoid using buffers.

In a typical two-chamber MFC, the anode and cathode chambers are separated by an ion exchange membrane to allow ion transfer between two-chambers, and this also reduces oxygen diffusion into the anode chamber (Liu et al., 2005). The use of single-chamber MFCs that lack a membrane improves mass transfer and operating

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costs compared to two-chamber systems. Oxygen transfer from the cathode to the anode, however, reduces CEs in single-chamber systems due aerobic oxidation of substrate. For example, the CE decreased from 40–55% to 9–12% due to  $3.7\times$  more oxygen transfer into the anolyte (Liu and Logan, 2004).

Highly saline solutions of sodium chloride, in combination with a phosphate buffer, have been previously used in several studies (De Schampelaire et al., 2010; Kim et al., 2007; Lefebvre et al., 2012; Nam and Logan, 2011). The use of a saline solution in a single-chamber MFC increases solution conductivity, resulting in decreased internal resistance and higher power densities. For example, increasing the ionic strength from 100 to 400 mM using sodium chloride improved the maximum power density in an MFC by 85% (Kim et al., 2007). The use of saline solutions in microbial electrolysis cells (MECs) has also increased performance in terms of hydrogen gas production rate and energy efficiency (Nam and Logan, 2011). However, anodic microbial communities can be adversely affected by highly saline solutions. For example, the maximum power density decreased by 50% when the NaCl concentration increased from 342 to 684 mM, and the CE was lowered by using a lower NaCl concentration (171 mM) (Lefebvre et al., 2012). These results suggest that very saline solutions cannot be used in single-chamber MFCs, but the use of high salinity solutions has not been well explored in two-chamber MFCs.

In this study, we examined the use of higher salinity solutions in the catholyte of two-chamber MFCs, without any catholyte buffer, in order to improve CE and minimize the contribution of the membrane and solution to internal resistance. NaCl was added only to the catholyte in order to minimize inhibition on anodophilic microorganisms, although during operation of the MFC  $\text{Cl}^-$  ions will cross over from the cathode to anode chamber. While it was expected that there would be pH changes in the electrolyte solutions, it was also expected that the high pH of the catholyte would lead to  $\text{OH}^-$  crossover to the anolyte, and thus this might to sufficiently ameliorate larger changes in anolyte pH. As it was not possible to predict the outcome of these changes on MFC performance, we tested MFCs with catholytes containing several different NaCl concentrations, and compared performance of these systems to single-chamber MFCs lacking a membrane, and two-chamber MFCs with a phosphate buffer catholyte.

## 2. Methods

### 2.1. Construction and operation the MFCs

Two-chamber, air–cathode MFCs (28 mL) were constructed from two cylindrical chambers (7 cm<sup>2</sup> cross section) as previously described (Kim et al., 2007; Liu and Logan, 2004). The anode and cathode chambers were separated by anion exchange membrane (AEM) (AMI-7001, Membranes International Inc.). Each reactor contained a single air–cathode (30 wt.% wet-proofed carbon cloth, type B-1B, E-TEK) with a platinum catalyst (0.5 mg/cm<sup>2</sup>) on the water side, and four diffusion layers on the air side (Cheng et al., 2006a). The anodes were graphite fiber brushes (15 mm diameter  $\times$  25 mm length, 415 cm<sup>2</sup> surface area) (Mill-Rose, Mentor, OH) that were heat treated at 450 °C for 30 min. Single-chamber MFCs lacking AEMs with constructed with the same electrodes (Liu and Logan, 2004) and used as positive controls.

The MFCs were inoculated with domestic wastewater from the primary clarifier of the Pennsylvania State University Wastewater Treatment Plant, and operated in fed-batch mode (duplicate reactors) at 30 °C in a constant temperature room. For the first 5 days, the reactor was refilled with 50:50 mixture of PBS medium and fresh wastewater every day. Thereafter, the reactors were operated in fed-batch mode using only the medium, and they were refilled

when the cell voltage decreased to <10 mV. The PBS medium contained 1.5 g/L sodium acetate and 50 mM phosphorus buffer ( $\text{Na}_2\text{-HPO}_4$ , 4.58 g/L;  $\text{NaH}_2\text{PHO}_4\cdot\text{H}_2\text{O}$  2.45 g/L;  $\text{NH}_4\text{Cl}$  0.31 g/L; KCl 0.13 g/L; trace minerals and vitamins; conductivity of 6.8 mS/cm). After three batch cycles with a 50 mM PBS catholyte, cathode chambers were fed with 60 mM NaCl solution having a similar conductivity (6.3 mS/cm) with PBS buffer, and then the catholyte NaCl concentration was increased to 120 mM, and then to 240 mM. MFCs with 50 mM PBS catholyte were also used to as positive controls for testing the performance of MFCs with only saline solutions.

### 2.2. Analyses and calculations

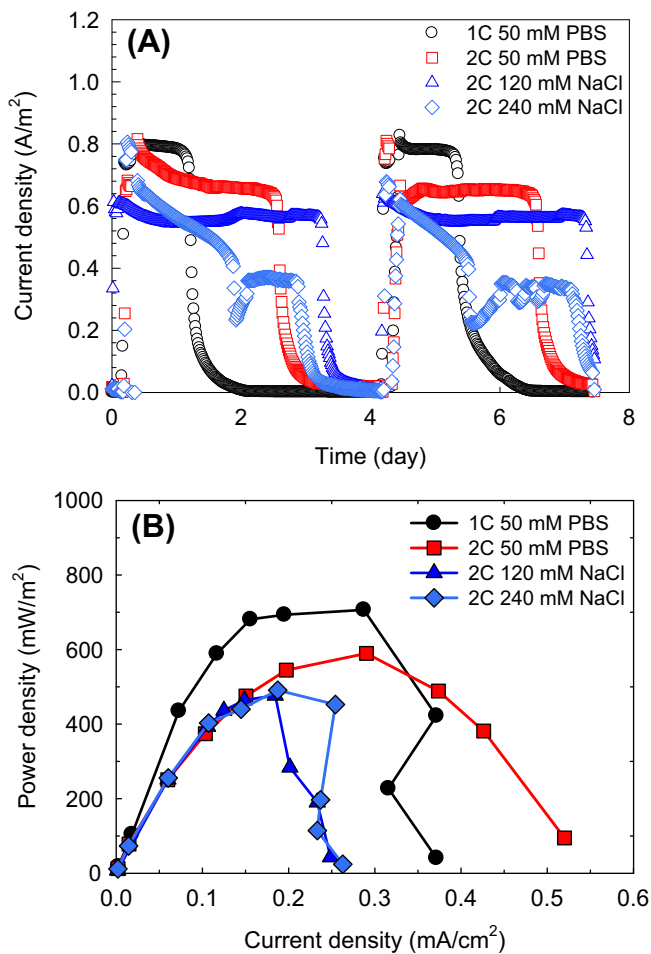
The voltage ( $E$ ) across an external resistor (1 k $\Omega$ ) was measured every 20 min using a data acquisition system (Model 2700, Keithley Instruments) connected to a computer. Current ( $I$ ) and power ( $P = IE$ ) were calculated as previously described (Logan et al., 2006) and normalized by the projected surface area of the cathode (7 cm<sup>2</sup>). Polarization and power density curves were obtained by varying the external resistance using in the circuit (20 min per resistor, single cycle method). During each polarization test, anode and cathode potentials were also recorded using reference electrodes (RE-5B; BASi, West Lafayette, IN). Coulombic efficiency (CE) was calculated using the ratio of the total coulombs produced during the experiment to the theoretical amount of coulombs available from the substrate as previously described (Logan et al., 2006). COD was measured using a low range (0–150 mg/L) HACH COD system (Hach Co., Loveland, CO) (Cheng et al., 2006b). Total COD removal was calculated as  $(\text{COD}_{\text{in}} - (\text{COD}_{\text{an}} + \text{COD}_{\text{cat}}))/\text{COD}_{\text{in}} \times 100\%$ , where  $\text{COD}_{\text{in}}$  is the input COD, and  $\text{COD}_{\text{an}}$  and  $\text{COD}_{\text{cat}}$  are the final anode and cathode chamber CODs. Ohmic resistance was characterized using electrochemical impedance spectroscopy (EIS) (He and Mansfeld, 2009). The impedance measurements were taken from 1 MHz to 10 mHz by applying a sine wave (10 mV) on top of the bias potentials with a potentiostat (BioLogic, VMP3). The electromotive force, generated by the diffusion of chloride ions across the AEM, was measured under abiotic conditions. Anode chambers were filled with 50 mM PBS, with and without 1.5 g/L sodium acetate. The cell potentials were recorded from each test with different catholyte NaCl concentrations (60, 120, 240, and 600 mM).

## 3. Results and discussion

### 3.1. Current and power production

Reproducible current was generated after 7 days of inoculation (Fig. S1) and representative current production from MFCs at each condition is plotted on one graph (Fig. 1A). MFCs with saline catholytes produced only slightly less current than that obtained using 50 mM PBS in a two-chamber MFC, as well as that from a single-chamber MFC (Fig. 1A). The maximum current of  $0.55 \pm 0.01$  mA ( $428 \pm 17$  mW/m<sup>2</sup>) was obtained in a single-chamber MFC over a fed batch cycle time of  $\sim 2$  days. Two-chamber systems had longer batch cycle times ( $\sim 4$  days) due to a greater conversion efficiency of the fuel to current, and a slightly lower maximum current densities which were  $0.48 \pm 0.03$  mA ( $328 \pm 45$  mW/m<sup>2</sup>) with 50 mM PBS, and  $0.40 \pm 0.01$  mA ( $230 \pm 10$  mW/m<sup>2</sup>) with 120 mM NaCl. The MFC with the highest catholyte salinity (240 mM NaCl) had a much different current output profile than the other reactors as the current sharply decreased from 0.24 to 0.16 mA within 1 h, and then gradually increased to 0.25 mA within the next 10 h.

The maximum power density, based on polarization data, was determined to be affected by catholyte type and concentration



**Fig. 1.** (A) Current generation and (B) power density curves for two-chamber MFCs (2C) with different catholyte solutions (120 mM, 240 mM NaCl, and 50 mM PBS) and single-chamber MFC (1C).

(Fig. 1B). Two-chamber MFCs produced a maximum power density of 491 mW/m<sup>2</sup> with 240 mM NaCl, and 477 mW/m<sup>2</sup> with a less saline solution (120 mM). These values are lower than that obtained with a buffered catholyte (50 mM PBS). As expected, single-chamber MFCs produced the highest maximum power density of 706 mW/m<sup>2</sup>, while the two-chamber MFC produced 590 mW/m<sup>2</sup> with 50 mM PBS.

### 3.2. Total COD removal and Coulombic efficiency

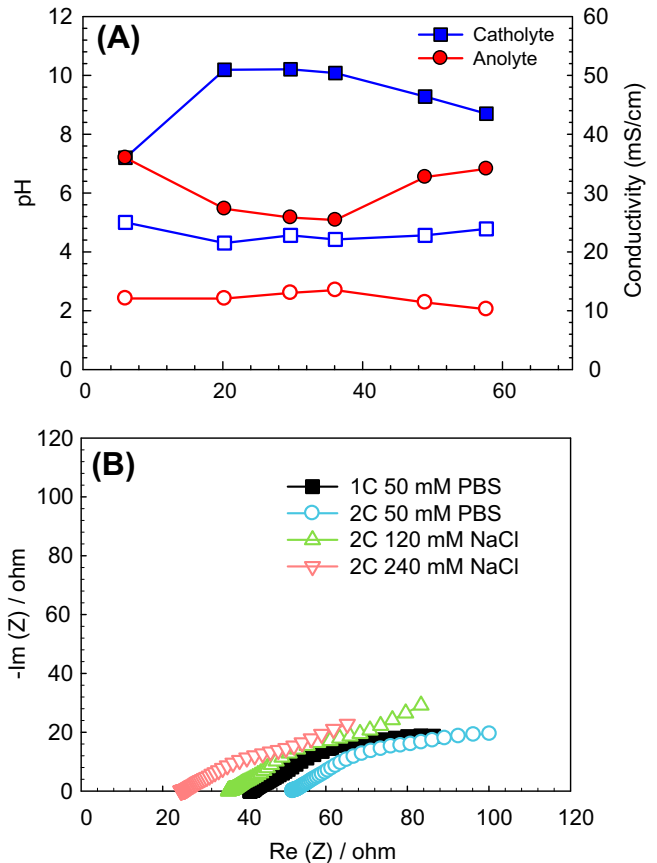
Total COD removal using the 50 mM PBS solution was 95 ± 4% with a single-chamber MFC, and 95 ± 4% with the two-chamber MFC. The use of a saline catholyte decreased total COD removal to 87 ± 2% (60 mM), 88 ± 3% (120 mM), and 94 ± 3% (240 mM) (Fig. S2). These lower total COD removals were due in part to acetate ion (CH<sub>3</sub>COO<sup>-</sup>) diffusion into cathode chamber through the AEM to balance charge. The final COD remaining in the cathode chamber was 101 ± 32 mg/L for 60 mM NaCl, and 35 ± 23 mg/L for 240 mM NaCl.

The CE was successfully increased by using two-chamber MFCs and highly saline solutions, without large reductions in power densities and COD removal as noted above. While the single-chamber MFC with 50 mM PBS produced the highest power density, the CE for this reactor was only 28 ± 5%. The CE was much higher (49 ± 3%) using the two-chamber MFC with the same buffer solution. The MFCs with non-buffered saline solutions achieved the highest

recoveries of fuel as electrical current, with a CE = 60 ± 5% using 60 mM NaCl, and 56 ± 4% (120 mM) and 43 ± 2% (240 mM) for the other two solutions. While it was previously observed that a highly saline solution could improve power production through decreased internal resistance (Lefebvre et al., 2012), the saline solution in that study was continuously fed first to the anode chamber, and then from there to the cathode chamber. The flow of the anolyte into the cathode chamber will promote biofilm growth on the cathode, which can decrease power and foul the cathode (Kiely et al., 2011). Here the saline solution was only used in the cathode chamber resulting in an increase in CE from 28% to 43–60% (54–114% increase). The use of an AEM improved CE by inhibition of oxygen cross-over from cathode to anode chamber (Zhang et al., 2009). Additionally, the high NaCl concentration in the cathode chamber might be another possible reason for increased CE as it will decrease the solubility of oxygen in water.

### 3.3. Effects of using a highly saline catholyte on pH and internal resistance

In order to better understand the reasons for these changes in current production for the 240 mM saline catholyte MFC (Fig. 1A), the pH and conductivities of the solutions were measured during a fed-batch cycle (Fig. 2A). The pH of anolyte decreased from 7.2 to 5.5 during the initial 20 h, and then further decreased to 5.3 over the next 20 h. A pH below 6 is known to inhibit current generation, consistent with that observed here. However, after these rapid changes in current (at around 40 h), the pH recovered to a nearly neutral condition (6.5–6.8). The opposite trend was



**Fig. 2.** (A) Changes of pH (filled symbols) and conductivity (open symbols) during a fed-batch cycle (240 mM NaCl). (B) Nyquist plots of EIS spectra by single-chamber MFC and two-chamber MFCs with different buffer solutions.

observed in the cathode chamber. The catholyte pH increased from 7.2 to 10.2, and then decreased to 8.6. In contrast to these pH changes, there were no significant changes in solution conductivity with current output. The conductivity changed by <14% for the catholyte and <12% for the anolyte. Relatively stable conductivity shows that the ions are balanced between the anode and cathode chamber mainly due to the transfer of ion species other than H<sup>+</sup> and OH<sup>-</sup> ions.

Gil et al. (2003) showed that the pH decreases in the anode chamber and increases in the cathode chamber were due to less charge transfer by protons compared to other ions. The flux  $J_i$  of an ionic substance  $i$  through the ion exchange membrane can be described by the Nernst–Planck flux equation, which combines the diffusion due to a concentration gradient with that from a potential gradient:

$$J_i = -D_i \nabla c_i + \frac{D_i z_i e E c_i}{kT}$$

where  $D_i$  is the diffusion coefficient for the ion,  $z_i$  the charge,  $c_i$  the concentration of the ion in solution,  $k$  Boltzmann's constant,  $e$  the elementary charge,  $E$  the electric field strength, and  $T$  the absolute temperature. The diffusion coefficient of hydroxide ion ( $5.3 \times 10^{-9} \text{ m}^2/\text{s}$ ) is larger than that of the chloride ion ( $2.0 \times 10^{-9} \text{ m}^2/\text{s}$ ) in water, but the chloride concentration in the cathode chamber is much higher than the hydroxide concentration. Thus, chloride ions were preferentially transported into the anode chamber through the membrane compared to hydroxide ions, resulting in increased catholyte pH.

Junction potentials across an ion-exchange membrane were measured under abiotic conditions to measure additional voltages that could be generated by adding NaCl solutions to the cathode chamber (i.e. to evaluate possible salinity gradient energy added to the system by much different anolyte and catholyte salinities). Increased catholyte salt concentrations increased the junction potential, with the maximum potential of 67 mV using 600 mM NaCl solution. However, these voltage contributions by the saline solution were less than 5% of the OCP for all salinity conditions. This shows that the additional power generation by adding NaCl catholyte is negligible.

The internal ohmic cell resistances were determined from the high frequency real axis intercept of the EIS spectrum (Fig. 2B). The two-chamber MFC with 50 mM PBS had the largest ohmic resistance of 52  $\Omega$  due to the lower conductivity of the solution, and the presence of a membrane. This value was much larger than that of single-chamber MFC (41  $\Omega$ ) which lacked a membrane. The ohmic resistances of the two-chamber MFCs decreased to 36  $\Omega$  with 120 mM NaCl, and to 23  $\Omega$  with 240 mM NaCl. Thus, the use of highly saline catholytes successfully reduced the internal resistance below that of the single-chamber MFC.

These results demonstrate that it is important to avoid highly saline concentration in the cathode chamber. The air–cathode can be kept relatively free of a biofilm using the high salt concentration, and CE will be increased. However, current production is slightly reduced due pH changes and there is slightly less COD removal.

#### 4. Conclusions

The use of saline catholyte improved the CE from 28% to 43–60% and decreased the sum of membrane and solution resistance (from 41 to 23  $\Omega$ ), with only a 17% decrease in maximum power density. These results show that a high concentration of NaCl can offset the internal resistances produced by the use of a membrane, although

power is still slightly less than that of a single-chamber system. The increased CE due to the saline catholyte, however, may make the use of this type of system desirable in some cases where high fuel to current conversion is desired.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2013.01.113>.

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