Impact of salinity on cathode catalyst performance in microbial fuel cells (MFCs)

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ABSTRACT

Several alternative cathode catalysts have been proposed for microbial fuel cells (MFCs), but effects of salinity (sodium chloride) on catalyst performance, separate from those of conductivity on internal resistance, have not been previously examined. Three different types of cathode materials were tested here with increasingly saline solutions using single-chamber, air-cathode MFCs. The best MFC performance was obtained using a Co catalyst (cobalt tetramethoxyphenyl porphyrin; CoTMPP), with power increasing by 24% to 1062 mW/m² (normalized to the projected cathode surface area) when 250 mM NaCl (final conductivity of 31.3 mS/cm) was added (initial conductivity of 7.5 mS/cm). This power density was 25% higher than that achieved with Pt on carbon cloth, and 27% more than that produced using an activated carbon/nickel mesh (AC) cathode in the highest salinity solution. Linear sweep voltammetry (LSV) was used to separate changes in performance due to solution conductivity from those produced by reductions in ohmic resistance with the higher conductivity solutions. The potential of the cathode with CoTMPP increased by 17 mV in LSVs when the NaCl addition was increased from 0 to 250 mM independent of solution conductivity changes. Increases in current were observed with salinity increases in LSVs for AC, but not for Pt cathodes. Cathodes with CoTMPP had increased catalytic activity at higher salt concentrations in cyclic voltammograms compared to Pt and AC. These results suggest that special consideration should be given to the type of catalyst used with more saline wastewaters. While Pt oxygen reduction activity is reduced, CoTMPP cathode performance will be improved at higher salt concentrations expected for wastewaters containing seawater.

1. Introduction

The shortage of freshwater in recent years in Hong Kong and other coastal cities has led to an increase in the use of seawater for domestic purposes. Seawater is used as an alternative water source for toilet flushing and cooling, resulting in sewage that has a much higher salt content than typical domestic wastewaters. The use of seawater for these...
applications not only reduces the freshwater demand of a city, but it also saves energy that would otherwise be used for seawater desalination. In Hong Kong, for example, seawater is used for toilet flushing in most urban areas, or about 80% of the population, providing 22% of the total water supply [1]. The resulting wastewater has a salinity of around 8% and a conductivity of more than 20 mS/cm, compared to typical wastewaters that have ~1 mS/cm [2]. This high conductivity of the wastewater could be very helpful in extracting energy from the wastewater using microbial fuel cells (MFCs).

MFCs are devices that use bacteria to convert organic and inorganic matter to electrical energy [3–6]. One application that is being explored for MFCs is wastewater treatment [6]. There are a variety of factors that affect the overall performance of an MFC, such as type of organic matter and concentration, solution conductivity, alkalinity, pH, temperature, and others [7,8]. The effects of the solution chemistry and the MFC architecture (such as electrode spacing) on the performance of these bio-electrochemical devices are usually evaluated in terms of internal resistance, Rint [9]. The internal resistance includes contributions from solution ohmic resistance as well as the polarization behavior of the anode and cathode [10]. In many MFCs, the electrolyte ohmic resistance accounts for a major portion of the total internal resistance [11]. Increasing the electrolyte conductivity decreases the ohmic resistance, and it has been shown that power density can be substantially increased by adding up to 300 mM of NaCl to the solution [7,12,13]. Further increases in salt concentration, however, reduce power production by inhibiting bacterial growth [7]. The effect of salt specifically on catalyst performance is a major concern, but it has not been previously examined in MFC studies.

In many MFCs Pt is used as a cathode catalyst for oxygen reduction. Not only is Pt an expensive and precious metal, but chloride can adversely affect Pt [14,15]. Alternatives to Pt are therefore needed, especially for MFCs treating saline (high chloride) wastewater. One alternative is the non-precious metal complex cobalt tetramethoxyphenyl porphyrin (CoTMPP) which has a high activity for oxygen reduction in direct methanol cells [16] and it has been used in MFCs [17–19]. Activated carbon (AC) cathodes have also recently shown great promise as a cathode material [20–22]. In this study, we investigated the performance of MFCs with CoTMPP or AC cathode catalysts at different salt concentrations, and compared their performance to the same systems using Pt catalysts. We show here that the cathode material is particularly important to performance when the salinity of the solution is increased.

2. Materials and methods

2.1. MFC reactors

MFCs were fabricated from solid blocks of Lexan bored to contain a cylindrical chamber 2 cm long by 3 cm in diameter (empty bed volume of 14 mL), containing an anode and a cathode (projected surface area of 7 cm²) on opposite sides of the chamber, as previously described in Reference [23]. The anodes were made of ammonia treated flat non-wet proof carbon cloth (type A, E-TEK, 3 cm diameter).

Cathodes were made of either wet-proofed (30% Pt) carbon cloth (type B; E-TEK) coated with Pt or CoTMPP (water facing side) or from AC and nickel mesh. Pt was applied to the cathode as a Pt/C paste (10 wt% Pt/C, E-TEK) prepared by mixing the chemical binder (5% NaFion solution) and the catalyst (20% Pt; E-TEK) to a final Pt content of 0.5 mg/cm² [24]. CoTMPP was prepared as previously described [25], and applied to the cathode using the same procedure used for Pt (0.5 mg/cm², CoTMPP). AC cathodes were made from powdered AC and a PtTE binder (water side), nickel mesh, and a PTFE diffusion layer (air side) as described elsewhere [20].

2.2. MFC tests

All MFC tests were operated at a fixed external circuit resistance (1000 Ω). MFCs were inoculated using a bacterial suspension obtained from an MFC that had been operating for 4 months at 30 °C. Initially, the MFCs were fed a 50:50 mixture of the inoculum and a nutrient buffer solution containing sodium acetate (1 g/L), a phosphate buffer solution (PBS, 50 mM, Na2HPO4, 4.58 g/L and NaH2PO4·H2O, 2.45 g/L, pH = 7.0), NH4Cl (0.31 g/L), KCl (0.13 g/L), and trace mineral (12.5 mL/L) and vitamin (5 mL/L) solutions [19]. After replacing this feed solution twice over three days, the reactors were then fed only nutrient buffer solution and acetate. When a reproducible maximum voltage (~2% change) was obtained for at least three batch cycles, the MFC was considered fully acclimated.

Four MFCs were initially acclimated to the medium without salt addition in a solution with a conductivity of 7.5 mS/cm. Feed solution salinities (duplicate reactors) were then increased by adding 100 mM, 150 mM, 200 mM, and 250 mM NaCl to the medium to produce a linear increase from 11.5 mS/cm (100 mM NaCl, conductivity comparable to that of a typical saline wastewater), to a maximum of 31.3 mS/cm (250 mM NaCl, conductivity comparable to that of seawater). Controls (duplicate MFCs) were operated only with the unamended feed solution.

2.3. MFC performance

Each MFC system was monitored using a precision multimeter and a data acquisition system (2700, Keithley, OH) with a voltage across a resistor recorded every 20 min. An Ag/AgCl reference electrode (0.195 V; corrected to a normal hydrogen electrode, NHE) was placed in the middle of the cell and the potentials of individual electrodes were determined using a multimeter. In order to minimize well known effects of the biofilm on cathode performance after long term MFC operation [26], polarization curves were measured after removal of the cathode biofilm. The cathodes were cleaned as previously described by gentle rinsing with deionized water [26]. This restored on average of 92% of the original cathode performance, and minimized changes in cathode performance by biofilms on the cathode surface. A power density curve was obtained by measuring the voltages obtained with five or six different external resistors (100–1000 Ω). Power (P) was
calculated using $P = IE$ ($I = E/R$), where $I$ is the current (A), $E$ the voltage (V), and $R$ the external resistance.

2.4. Electrochemical characterization of electrodes

The electrochemical properties of the anode and cathodes were characterized by linear sweep voltammetry (LSV) in a two-chambered electrochemical cell designed to obtain a controlled chemical reaction at the cathode. Both chambers of the cell were filled with buffer solution (50 mM PBS) and NaCl (100–250 mM). The test cell was constructed from two cylindrical chambers (2 cm long by 3 cm in diameter) like those used for the MFC, except that two chambers were separated by a cation exchange membrane (Nafion 117) (Supporting information, Fig. S1). The working electrode was the cathode (with a project area of 7 cm$^2$), with the catalyst-coated side facing the solution, and the uncoated side exposing directly to air. The counter electrode made of a Pt mesh (30 cm$^2$ surface area) was placed in the middle of the anode chamber, and the reference electrode was an Ag/AgCl electrode (RE-5B, Bioanalytical Systems, IN) put in the middle of the cathode chamber 1 cm from the working electrode. LSV was performed using a potentiostat (PC4/750, Gamry Instruments, PA) by sweeping the voltage between the working and reference electrodes from 0.3 V to −0.2 V at a rate of 1 mV/s. Current interrupt was used to compensate for the drop in potential due to the decrease in the electrolyte resistance, allowing determination of the catalytic activity separately from that caused by NaCl on the solution conductivity.

Cyclic voltammetry (CV) was performed at a scan rate of 10 mV/s with the electrodes exposed to water degassed with $N_2$ gas for 30 min. The same two-chamber system used for LSV tests was used in CV tests with air. A three-chamber system was used for tests with $N_2$ gas on the other side of the cathode (Supporting information, Fig. S1) in order to evaluate catalytic effects in the absence of oxygen. AC cathodes were degassed by applying a vacuum and then exposed to $N_2$ gas in order to try to minimize trace oxygen in the highly porous carbon structure. All LSV and CV tests were performed on new cathodes (no biofilm).

3. Results

3.1. Effect of NaCl addition on MFC performance and power density

Based on the polarization data for the acclimated MFCs, the maximum power densities for the three cathodes in the nutrient buffer medium (no NaCl addition) decreased in the order: CoTMPP, 827 mW/m$^2$; Pt, 798 mW/m$^2$; and AC, 745 mW/m$^2$ (Summary in Fig. 1; complete polarization curves in Supporting information, Fig. S4). It was expected that Pt cathode MFC would produce slightly more power than the MFC with AC based on previous tests in this nutrient buffer medium [20], but the MFC with CoTMPP had not previously been compared to the AC cathodes under otherwise identical conditions. Power densities obtained with the AC here are different than those previously obtained [20] due to differences in these two studies in electrode spacing, anode materials and anode construction.

The NaCl concentration in the feed solution was gradually increased (over two weeks at each concentration) to the next concentration level to minimize possible inhibitory effects of NaCl on the microorganisms [27,28]. The measured power densities reflect changes of both solution conductivity and performance of the catalyst. Power densities increased for all electrodes with the first increase in NaCl concentration (50 mM), but power did not consistently increase for the different cathodes at all higher NaCl concentrations despite the increase in solution conductivity (Fig. 1). The largest overall increase in maximum power was obtained for the MFC with the CoTMPP catalyst. Power increased by 24 ± 1% compared to the base nutrient solution to 1062 ± 9 mW/m$^2$ at the maximum salt concentration of 250 mM. Only the CoTMPP cathode maintained consistent performance in the more saline waters.

MFCs with a Pt catalyst cathode increased in power by 15 ± 1% to 921 ± 48 mW/m$^2$ when the NaCl concentration was increased from 0 to 100 mM (Fig. 1). However, there was no further increase in power when the NaCl concentration was increased from 100 to 250 mM, and power decreased to 850 ± 27 mW/m$^2$ at the highest NaCl concentration of 250 mM. A lack of increase in power density suggests the Pt catalyst was adversely affected by salinity, but the effects on the anode must also be considered (see effects on electrode potentials below).

Although the power density produced by the AC catalyst was lower than that for the other two cathodes, power consistently increased with salt addition, with an overall increase of 15 ± 1% for the AC cathode to 857 ± 7 mW/m$^2$ at 200 mM NaCl (Fig. 2). There was no further change in power at the highest salinity (250 mM).

Tests were conducted over a period of ~800 h. Although cell voltages of the treatment cells were different than the controls (no change in salt concentration) there was no apparent appreciable degradation in cell voltage at high salt concentration and all results were reproducible (Supporting information, Fig. S2). In addition, COD removals were stable...
and consistently >90%. Coulombic efficiencies increased over time to ~20% (250 mM NaCl; Supporting information, Fig. S3).

3.2. Effect of NaCl concentration on the electrode potentials

NaCl addition consistently decreased the overall $R_{\text{int}}$ of the MFCs. $R_{\text{int}}$ can be separated into electrolyte, anode, and cathode resistances. Electrolyte resistance is directly related to the solution conductivity, and decreases when adding NaCl. Anode resistance arises from the bio-electrochemical reaction at anode, and thus the activity of the electricity-generating bacteria. Salt addition did not produce appreciable changes in anode potentials except at the very highest salt concentration (Figs. 2B, 3B and 4B). The anode potentials in the MFCs with different cathode materials were also consistent with each other at the same NaCl concentration, showing that differences in reactors with the different cathodes was not due to changes in anode potentials.

Increased NaCl concentrations produced considerable changes in cathode potentials (Figs. 2A, 3A and 4A), particularly for the CoTMPP and AC cathodes. The working potential of the CoTMPP cathode increased with NaCl concentration, producing higher overall circuit voltages at a given current density (Fig. 2A). For example, at 3 A/m², the potential of cathode CoTMPP increased by 0.1 V (77%) with 250 mM of salt compared to the base case (0 NaCl addition) (Fig. 2A). This increase in cathode potential was due in part to the decrease in $R_{\text{int}}$ resulting from the NaCl addition. The working potential of the AC cathode at 3 A/m² increased by 42% for the NaCl addition of 250 mM (Fig. 4A). In contrast, NaCl addition had very little impact on the working potential of the Pt cathode (Fig. 3A), but there was a decrease in power density due to the reduced performance of anode at the highest salt concentration. The different effects of NaCl on the cathode potentials suggest that the NaCl produced changes other than just those due to a lower electrolyte resistance. In a previous study [18], current densities of plain carbon cloth cathodes (no catalyst) were shown to produce much less power (70% lower than that with Pt catalyst). Thus, the different performance of the cathodes resulted from the effects of the salt on the cathode catalysts as shown below in the LSV and CV analyses.

3.3. LSV and CV analysis of the electrodes

LSV tests were performed to further investigate the impact of NaCl on the electrochemical behavior of the cathode materials. The current interrupt procedure was needed to observe the effects of the salt on the catalytic activity of the cathode.
separate from those caused by changes in solution conductivity. When current interrupt was not applied, the performance of the Pt cathode increased with salt concentration (Fig. 5A). However, when current interrupt was applied (Fig. 5B) there was little change in the LSV curves at the different NaCl concentrations. This suggests that for Pt, the main impact on MFC performance with NaCl addition was increased electrolyte conductivity. There was no apparent change in anode performance in MFC tests with NaCl addition of 100 mM–200 mM, however, suggesting that there may have been some small adverse impact on the Pt catalyst cathodes under more steady operation conditions that could not be detected in our LSV tests.

LSV measurements on the CoTMPP and AC cathodes (with current interrupt) both showed improvement in current densities at the applied voltages. The CoTMPP catalyst potentials increased by 17–20 mV as the NaCl concentration increased to 250 mM (Fig. 5C). At a potential of 0.1 V (vs. Ag/AgCl), the CoTMPP cathode produced the highest current, which indicated that greatest oxygen reduction rate was achieved at this potential range. This increase of the CoTMPP potential with the NaCl addition suggests that the oxygen reduction activity of CoTMPP was improved by the higher salinity content. Thus, for the MFC with CoTMPP catalyst, the observed improvement with salt addition was likely due to the combined effect of increased solution conductivity and enhanced catalyst activity.

![Graph A](image1.png)

**Fig. 4** — Electrode potential of AC cathode MFC (vs. Ag/AgCl): (A) cathode potential; (B) anode potential. Labels indicate the concentration of NaCl in mM.

![Graph B](image2.png)

![Graph C](image3.png)

![Graph D](image4.png)

**Fig. 5** — Linear sweep voltammetry of different cathodes: (A) Pt cathode, without current interrupt; (B) Pt cathode via current interrupt; (C) CoTMPP cathode with current interrupt; and (D) AC with current interrupt. Labels indicate the concentration of NaCl in mM.
There was an improvement in the AC cathode performance at higher salinities based on LSV data, which showed an increase of 40–120 mV when the NaCl concentration was increased to 250 mM (Fig. 5D). This consistent improvement for the AC cathode that was observed in LSV tests was also observed in MFC tests except at the very highest NaCl concentration where the anode biofilm performance was adversely affected. The main disadvantage of the AC cathode, however, is that the current densities overall were lower than those of the CoTMPP cathode at the same applied potentials.

In order to further examine the effect of salt concentration on \( R_{\text{int}} \) and catalytic activity, CVs were obtained for all cathodes in air or under an \( \text{N}_2 \) atmosphere (Fig. 6). CVs for the Pt cathode were nearly identical with \( \text{N}_2 \) at different salt concentrations (Supporting information, Fig. S5), and therefore showed no catalytic activity in the absence of oxygen and no effect of salt concentration under these conditions. There was a slight broadening of the curves with increased salt concentration with Pt or AC in air, or with AC in \( \text{N}_2 \), but only the cathode containing CoTMPP had pronounced peaks showing the improved effects of higher salt concentrations. This CV data therefore confirms the direct advantage of the CoTMPP catalytic activity with increased salt concentrations, compared to the other two catalysts.

### 4. Discussion

It was shown that the CoTMPP catalyst provided improved performance of the MFC at all salinities tested, although this change was not a linear function of salt concentration. Pt catalyst performance decreased for NaCl additions above 100 mM. This finding with Pt is consistent with previous reports that elevated NaCl concentrations decrease the oxygen reduction activity of Pt\(^{[14]}\) due to a decrease in the oxygen reduction rate in the presence of adsorbed Cl\(^{-}\)/C\(^{2-}\) ions \(^{[15]}\). Considering its lower cost and the enhanced performance at a higher salt concentration, CoTMPP is therefore a better choice that Pt for several reasons when using MFCs with more saline solutions. Using CoTMPP in MFCs not only eliminates the need for a precious metal like Pt but it also takes advantage of the positive effect of the higher salinity on catalyst performance. The cost of CoTMPP, while lower than that of Pt, is still considerably more than that of AC. Although MFCs with AC cathodes produced less power than those with CoTMPP cathodes, the advantages of substantially reduced cathode costs for the AC could make it a better choice than CoTMPP in practice.

It has been suggested that the activity of bacteria on the anode at high current densities could become a critical factor for MFC performance with saline wastewaters \(^{[13]}\). If the biofilm could be better acclimated for current generation to the higher salinities, then this might further improve power densities above those measured here. Further investigation is needed on the long-term impacts of higher salinities on both the anode biofilms and the CoTMPP and AC cathodes. Tests are underway using these materials and the higher-salinity wastewaters generated in Hong Kong.

### 5. Conclusions

The performance of three different types of cathodes was increased in higher salinity solutions. Most of the increased performance resulted from a reduction in ohmic resistance as...
the solution conductivity was increased by adding the NaCl. However, LSV scans using current interrupt to compensate for the drop in potential due to the decrease in the electrolyte resistance showed that the potential of the CoTMPP and AC cathodes increased independently of solution conductivity. CV tests in air also showed that there was a noticeable improvement in catalytic activity for the CoTMPP catalyst. This showed that there was a significant increase in the oxygen reduction activity at higher salt concentrations for the CoTMPP catalyst but not the Pt catalyst. This suggests that CoTMPP may be more suitable for solutions containing higher concentrations of chloride such as wastewaters containing seawater.

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Appendix. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.ijhydene.2011.03.052.

REFERENCES