

Microbial fuel cell performance with non-Pt cathode catalysts

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Abstract

Various cathode catalysts prepared from metal porphyrines and phthalocyanines were examined for their oxygen reduction activity in neutral pH media. Electrochemical studies were carried out with metal tetramethoxyphenylporphyrin (TMPP), CoTMPP and FeCoTMPP, and metal phthalocyanine (Pc), FePc, CoPc and FeCuPc, supported on Ketjenblack (KJB) carbon. Iron phthalocyanine supported on KJB (FePc-KJB) carbon demonstrated higher activity towards oxygen reduction than Pt in neutral media. The effect of carbon substrate was investigated by evaluating FePc on Vulcan XC carbon (FePcVC) versus Ketjenblack carbon. FePc-KJB showed higher activity than FePcVC suggesting the catalyst activity could be improved by using carbon substrate with a higher surface area. With FePc-KJB as the MFC cathode catalyst, a power density of 634 mW m⁻² was achieved in 50 mM phosphate buffer medium at pH 7, which was higher than that obtained using the precious-metal Pt cathode (593 mW m⁻²). Under optimum operating conditions (i.e. using a high surface area carbon brush anode and 200 mM PBM as the supporting electrolyte with 1 g L⁻¹ acetate as the substrate), the power density was increased to 2011 mW m⁻². This high power output indicates that MFCs with low cost metal macrocycles catalysts is promising in further practical applications.

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1. Introduction

Increased economic growth and social development are leading to a large gap between energy demands and the availability of fossil fuels. Current methods to produce energy are not sustainable, and concerns about climate change and global warming require developing new methods of energy production using renewable and carbon-neutral sources. The development of electrogenic reactors based on microbial fuel cells (MFCs) represent a new approach for generating electricity from waste and biomass [1–3]. Although the concept of electricity production from bacteria was conceived nearly a century ago [4–6], only recently the technology has been sufficiently improved to make it useful as a method for energy generation. One near-term application of MFCs will be to produce electricity from wastewater, providing a new way to simultaneously treat wastewater while

obtaining a source of clean and renewable energy [7–9]. Further development will allow MFCs to be used for renewable energy production from other sources of biomass.

In an MFC, electrons are produced on the anode from the oxidation of organic matter using bacteria as the biocatalyst, while oxygen is reduced on the cathode with the electrons transferred from the anode, and protons in the water. Poor kinetics of oxygen reduction at neutral pH and low temperatures hinder the improvement of MFC performance [10–12]. Research has been carried out intensively on MFC anodes [13–19], but MFC cathode catalysts have not been as thoroughly studied. Pt is the most commonly used catalyst on the cathode, but its high cost prohibits its use for commercial MFC applications. Transition metal porphyrines and phthalocyanines are good candidates for catalysts in MFCs, and they have been extensively studied as alternatives to Pt in conventional fuel cells for decades [20–27]. Good oxygen reduction activities from the metal macrocycles are achieved in both acid and alkaline media [23,28,29], but their performance under circum-neutral pH conditions is not as well studied.

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Preliminary studies using transition metal macrocycles as the MFC cathode have produced encouraging results with two different materials: cobalt tetramethoxyphenylporphyrin (CoTMPP) and iron phthalocyanine (FePc) [30–32]. In studies reported by Zhao et al. [30,32], FePc and CoTMPP were used as the oxygen reduction catalyst for a biohydrogen fuel cell (BHFC) that used a microorganism (*Escherichia coli* K12) to produce hydrogen that reacted at a metal-catalysed anode, rather than using an exoelectrogen to directly produce electrons. They studied the effects of pH and concentration of the electrolyte, and found that the performance decreased with increasing pH and decreasing buffer concentration. The oxygen reduction activity was decreased by 80% when pH increased from 2.4 to 7.0 in 0.5 M Na₂HPO₄ in an electrochemical cell; while in the BHFC system the cathodic polarisation curves showed a distinct shift toward more negative values and the maximum power output decreased by 35%, from 2.3 mW to 1.5 mW, when the electrolyte concentration was reduced from 500 mM to 50 mM at neutral pH. Their optimum cathode performance was obtained in an acidic medium (pH 3.3) and by using a higher conductivity solution (0.5 M Na₂HPO₄) than is typically used in an MFC system (neutral pH and lower conductivity of the electrolyte). Thus, the performance of these catalysts under conditions of interest here are not known. Compared to the MFC system using mixed culture to produce electricity directly from wastewater with a simple air cathode, BHFC is a more complicated system, and not practical for further commercialisation. It is important to study the feasibility of using non-Pt catalysts in a direct MFC system.

Further development and commercialisation of MFC make it essential that we have a better understanding of the performance of non-Pt cathode catalysts. Alternatives to Pt for oxygen reduction under conditions of neutral pH media have not been well explored. We therefore conducted electrochemical half-cell studies, and the performance of MFCs with various non-Pt catalysts for oxygen reduction. It is shown that MFC power output was improved with non-Pt cathodes compared to that achieved with a commercially available Pt catalyst, further indicating the utility of low cost metal macrocycles as MFC cathode catalysts.

2. Experimental

2.1. Catalyst preparation

In this study both commercial cathode catalysts and in-house manufactured catalysts were examined. The commercial catalysts (used as-received) were iron phthalocyanine (FePc, TCI America), cobalt phthalocyanine (CoPc, Aldrich), copper phthalocyanine (CuPc, Alfar Aesar), manganese(II) phthalocyanine (MnPc, Alfar Aesar), and cobalt tetraamethoxyphenylporphyrin (CoTMPP, Aldrich). A carbon supported Pt cathode catalyst (Etek, 20 wt.%) was used for comparison with other non-precious metal cathodes. Carbon supported phthalocyanine catalysts were prepared using the method described by Ladouceur et al. [33]. Metal phthalocyanine salts were dissolved in concentrated H₂SO₄ (98%) before adding carbon nanopar-

ticles (Ketjenblack EC 300, Akzo Nobel and Vulcan XC72, Cabot) while stirring. The resulting mixture was poured into cold water and stirred overnight. The carbon adsorbed with the metal salt, was filtered and washed thoroughly, and then dried in an oven at 110 °C for more than 12 h. This was followed by pyrolysis (800 °C in argon for 2 h) and cooling (with argon).

Carbon supported metal TMPPs were made with the procedure used by Gojkovic et al. [34]. The catalyst was prepared by dissolving metal TMPPs in acetone, then mixing with Ketjenblack carbon with constant stirring for 20 h. The solid was filtered and heat-treated (800 °C under with argon gas for 2 h), and then cooled (with argon).

2.2. Electrode preparation

Electrodes for electrochemical studies were prepared using 20% wet-proofed Toray 90 carbon paper (Etek). Catalyst ink containing 10 wt.% Nafion (5% Nafion solution from Aldrich) the binder was painted to the carbon paper to the desired loading. Using a Nafion binder has been shown to enhance fuel cell performance [31].

MFC anodes were carbon cloth (type A, Etek) treated with a high-temperature ammonia gas process previously shown to increase power generation in MFCs [19]. Cathodes were gas diffusion-type electrodes (30 wt.% wet-proofed type B carbon cloth; Etek) coated with four PTFE diffusion layers on the side exposed to air [35]. The catalyst layer was prepared from catalyst ink with 10 wt.% Nafion painted on the side of the carbon cloth exposed to solution. MFCs were also examined with Pt (30% Nafion) at catalyst loadings of 1 mg cm⁻² for non-Pt catalysts and 0.5 mg cm⁻² for a Pt catalyst to compare differences arising from the two preparation methods.

2.3. Electrochemistry study

Electrochemical tests were carried out using a three-electrode H-cell previously described [31]. The working electrode with a projected surface area of 0.64 cm² exposed to air, with a Pt foil counter electrode (2 cm²) and a Ag/AgCl (3 M NaCl, EE009, Cypress System) reference electrode. All electrode potentials given here are with reference to the Ag/AgCl electrode (0.208 V versus normal hydrogen electrode, NHE), unless stated otherwise. The electrolyte was 50 mM phosphate buffered nutrient medium (PBM, pH 7.0) [31], which was also used for MFC tests. Electrochemistry and MFC tests were carried out in a temperature-controlled room (30 °C).

2.4. MFC set-up and operation

MFC tests were conducted using a single chamber cube reactor with electrode geometric (projected) areas of 7 cm². The electrode spacing was 4 cm, with a total reactor volume of 26 mL as previously described [31]. MFCs were inoculated with bacteria from another previous-acclimated reactor to reduce start up times. The medium contained 50 mM PBM (pH 7.0) and vitamins and minerals, and glucose (1 g L⁻¹) as substrate [15]. An external resistance of 1 kΩ was used except as noted. After

reproducible power generation was demonstrated over several fed-batch cycles, electrochemical polarisation and other tests were performed. Electrochemical polarisation was conducted by varying the external resistance from 50 Ω to 1000 Ω , and fed solutions were replaced when the cell voltage dropped below 50 mV, forming one operating cycle. In MFC tests under optimized conditions, acetate (1 g L⁻¹) in 200 mM PBM was used as the substrate. An ammonia-treated graphite brush was used as the anode. The brush anode was made of graphite fibres (PANEX33 160 K, ZOLTEK) and a titanium wire core.

Power densities (mW m⁻²) were calculated based on

$$P = \frac{V^2}{RA}$$

where V (mV) is the cell voltage, R (Ω) the external resistance loaded to the cell, and A (m²) is the area of the cathode.

The coulombic efficiencies (CE) for the MFCs were calculated using

$$CE = \frac{C_{EX}}{C_{Theo}} \times 100\%$$

where C_{EX} is the total charge obtained from integrating current measured each time interval over time $C_{EX} = \sum_{i=1}^T (V_i t_i) / R$. The theoretical charge C_{Th} was calculated from glucose oxidation based on Faraday's law, $C_{Th} = 24FMv$, where F is the Faraday's constant, 24 the number of electrons theoretically produced from each mole of glucose oxidation, M the concentration, and v is liquid volume.

3. Results and discussion

3.1. Electrochemical study of oxygen reduction in neutral media

The open circuit potentials (OCPs) of the air cathode catalysts on Ketjenblack (KJB) carbon were similar and in the range of 0.320 V, with a slightly lower value measured for carbon lacking a catalyst (Table 1). However, OCP values were \sim 30 mV lower for the catalysts on with the electrodes using Vulcan XC carbon than on KJB. This indicates that the carbon substrate can affect the catalyst activity. The higher OCP with KJB could be caused by increased amounts of oxygen adsorbed on the catalyst/carbon surface as a result of higher surface area. The specific surface

Table 1
OCP of air cathode in 50 mM PBM at 30 °C

Catalyst	OCP (V) vs. Ag/AgCl
Pt (in-house)	0.342
CoTMPP	0.325
Pt (commercial)	0.324
FePc	0.319
FeCoTMPP	0.317
CoPc	0.317
KJB	0.313
FeCuPc	0.312
FePcVC	0.289
MnPc VC	0.285

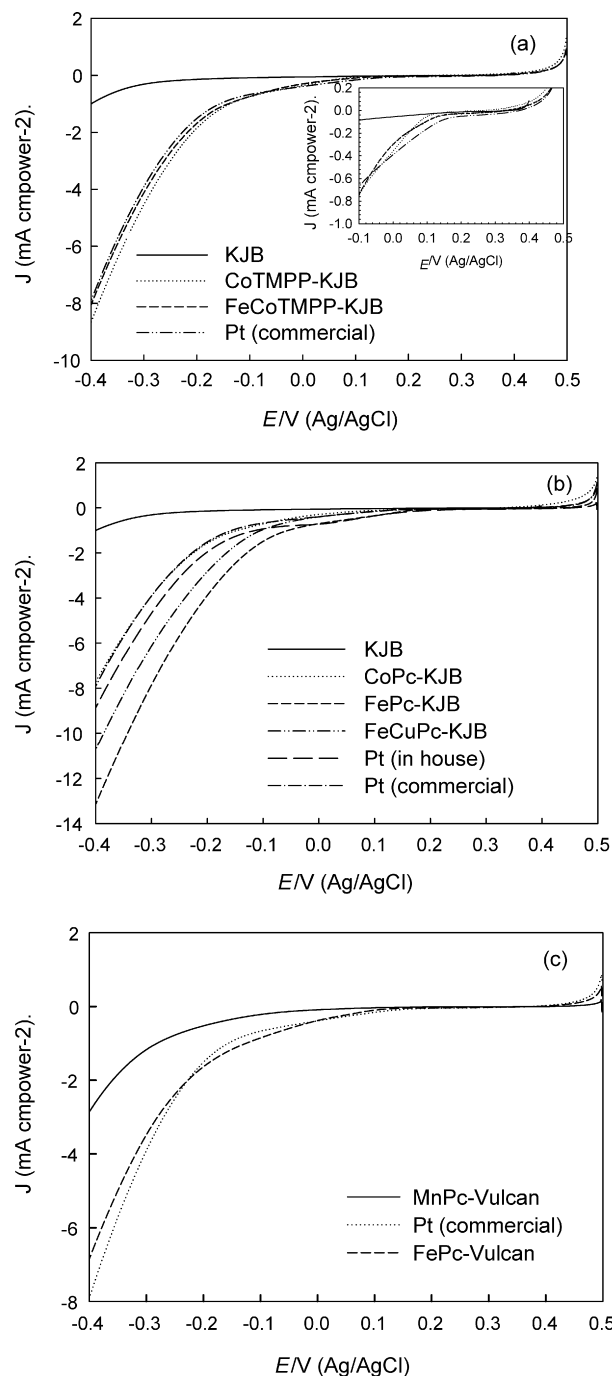


Fig. 1. Linear sweep of O₂ reduction: (a) Pt, CoTMPP and FeCoTMPP on KJB; (b) Pt and metal phthalocyanine on KJB; (c) metal phthalocyanine on Vulcan carbon (passive electrode without air sparging, catalyst loading 1 mg cm⁻², 50 mM phosphate buffer with nutrients, pH 7.0, $T = 30$ °C, scan rate 1 mV s⁻¹, and $A = 0.64$ cm²).

area of KJB was about 800 m² g⁻¹, while it was approximately 250 m² g⁻¹ for Vulcan XC.

The oxygen reduction activity of metal porphyrine and phthalocyanine catalysts was compared to a commercial Pt-carbon catalyst using linear sweep voltammetry (LSV) (Fig. 1). CoTMPP and FeCoTMPP supported on carbon nanoparticles (KJB) produced currents similar to that obtained using Pt over the range of -0.4 V to 0.5 V (Fig. 1a). When the potential was

more positive than -50 mV, the Pt electrode showed a slightly higher current response than the metal TMPPs. However, when the potential was more negative to -50 mV, a higher reduction current was obtained with the TMPP catalysts. With a plain carbon electrode treated with only the carbon particles (KJB), the oxygen reduction activity was substantially lower than with the catalysts.

Metal phthalocyanines in general demonstrated higher oxygen reduction activities in neutral media than electrodes using Pt (Fig. 1b). Only the CoPc catalyst produced an oxygen reduction current similar to that of Pt. The highest reduction current obtained using FePc on KJB is likely the result of higher catalyst utility and less diffusion resistance. A higher reduction current was obtained with the in-house Pt electrode than with the commercial Pt electrode, or the CoPc and FeCuPc electrodes, when the potential was greater than -0.1 V. However, over the whole potential range, FePc on KJB demonstrated the highest activity, even compared to the in-house Pt cathode.

Lower oxygen reduction currents were obtained for FePc on Vulcan carbon (FePcVC), again indicating that the carbon substrate affects catalytic activity (Fig. 1c). This effect of the carbon support is also reflected in the OCPs of the electrodes (Table 1). OCPs of the catalysts on KJB were all higher than that of the catalysts on Vulcan. Among the catalysts tested, MnPc showed much lower oxygen reduction currents than FePc on the same substrate, suggesting lower catalytic activity. FePcVC showed comparable activity to the commercial Pt electrode. Pt showed slightly higher activity than FePcVC for the potential positive to 0 V, and for the potential range of -0.25 V to 0 V, which is the high current region for MFC tests. FePcVC showed higher activity than Etek Pt electrode.

3.2. Morphology of catalysts

The morphology and compositions of the catalysts analysed by SEM showed that application of FePc on KJB produced a highly irregular surface with an open structure (Fig. 2). The

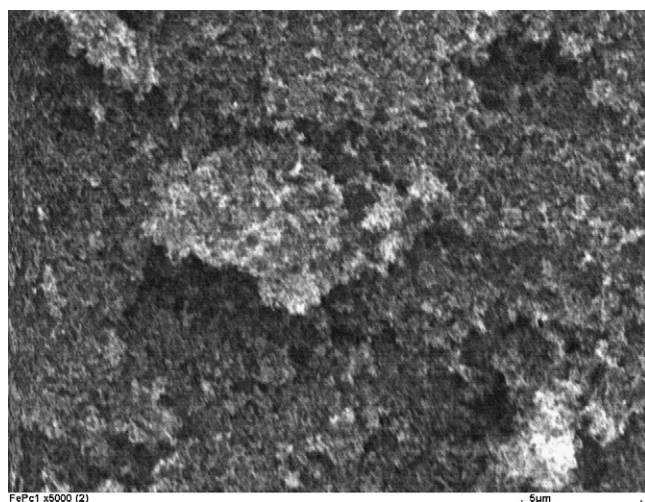


Fig. 2. SEM image of FePc catalyst on KJB. Note that the particles have a fluffy, amorphous shape showing a highly porous surface.

image revealed that the carbon supported catalyst has an accumulation of small fluffy particles and that it has a porous and open structure. Analysis was also conducted on catalysts supported on Vulcan carbon. A porous and open structure was also observed from Vulcan carbon. There were no significant differences in the morphology observed from the catalyst on KJB or Vulcan carbon. The composition of the catalysts determined by EDAX, and the weight percentage of the FePc on carbon was ~ 37 wt.%. The catalyst loading on electrodes for MFC tests were calculated based on 37 wt.% FePc/C.

3.3. MFC performances

The above electrochemistry studies demonstrated that CoTMPP and FePc on KJB produced better performance than other TMPP and Pc catalysts, and thus MFC tests were conducted only using these two catalysts (with Pt as a control). Power density curves with acclimated reactors demonstrated that the highest power density of 634 mW m^{-2} was produced using the FePc catalyst, while cathodes with CoTMPP and Pt produced lower power densities of 483 mW m^{-2} and 474 mW m^{-2} , respectively. The polarisation curves show that the activation potential loss for FePc was lower than for CoTMPP and Pt, suggesting that this was the main reason for the superior catalytic activity of FePc.

Power densities produced using an in-house Pt cathode was compared produced with the other cathodes. The maximum power density with the in-house Pt electrode was 593 mW m^{-2} , and thus it performed better than the commercial Pt catalyst but not as well as the FePc catalyst. At OCV and at current densities $< 0.16 \text{ mA cm}^{-2}$, however, the in-house Pt cathode gave the highest performance, while at higher current densities ($> 0.16 \text{ mA cm}^{-2}$) the FePc showed the best performance. Thus, the performance of these cathodes in the MFC was consistent with that predicted by the electrochemical studies.

The maximum power density of FePc on Vulcan was 530 mW m^{-2} (Fig. 3b) Although this value was lower than that obtained for FePc on KJB, the performance using the Vulcan support was still better than that obtained with the commercial Pt cathode, and similar to that of the in-house Pt cathode. This again demonstrated that the catalyst activity was affected by the carbon substrate material.

Despite the difference in maximum power densities produced by these different catalysts, the CEs were all *ca.* 20% (Table 2). This implies that the CE was either mainly determined by the

Table 2
Maximum power densities produced in MFCs (50 mM PBM, pH 7.0 and 1 g L^{-1} glucose) and coulombic efficiencies

Catalysts/electrode	P (mW m^{-2})	CE (%)
FePc-KJB	634	20.45
Pt (home made, ink)	593	20.25
FePcVC	530	28.29
Pt (home made, paste)	526	20.82
CoTMPP	483	19.73
Pt (commercial)	474	19.60
MnPc	353	20.13

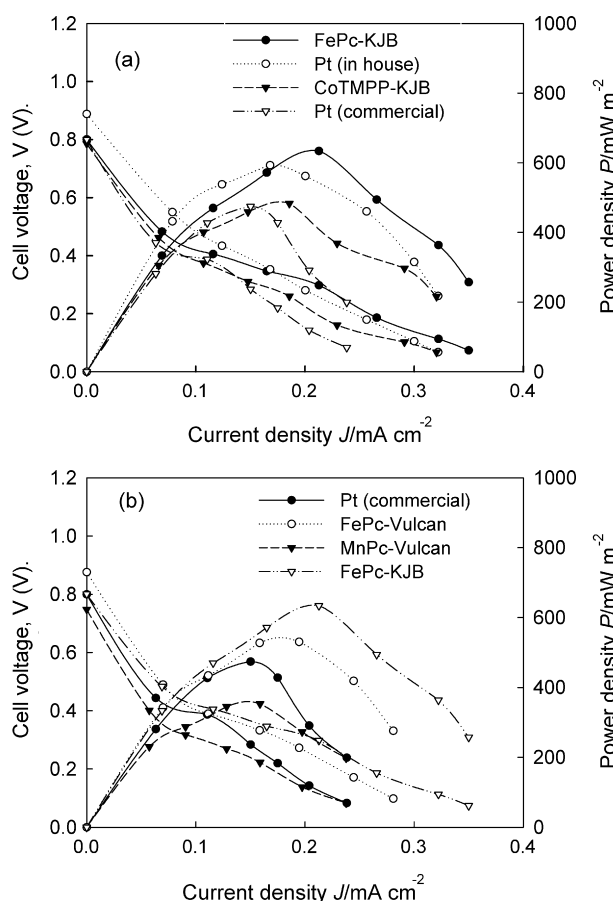


Fig. 3. MFC polarisation and power density curves with various cathode catalysts (50 mM phosphate buffer and $T = 30^\circ\text{C}$).

performance of the anode (i.e. by the ability of bacteria to oxidize the substrate), or that the differences in the cathode materials for the conditions examined here were not sufficiently different in terms of oxygen diffusion or other characteristics.

In previous MFC studies, a maximum power density of 400 mW m^{-2} was achieved with CoTMPP as the cathode catalyst for flat electrode cube reactor operated (50 mM PBM) [31]. In this study, the power density was increased by 60% to 634 mW m^{-2} using FePc-KJB as the cathode catalysts.

Compared to the performance from a biohydrogen fuel cell (BHFC), reported by Zhao et al. [30,32], which used FePc and CoTMPP, prepared by different preparation methods, higher power output was also achieved by this study. In the BHFC study, with usual MFC operating conditions (neutral pH and low electrolyte concentration), the maximum power output was only 7.5 mW L^{-1} , and the highest power output was obtained as 13.9 mW L^{-1} and 14.3 mW L^{-1} for FePc supported on Vulcan and unsupported porous CoTMPP, respectively, operated in acidic media and higher electrolyte concentration. As shown in Table 3, most fuel cells with non-Pt cathodes showed higher power output than the commercially available Etek Pt cathode, apart from the BHFC operated in neutral pH. The highest power outputs were from FePc-KJB (17.8 mW L^{-1}) and in-house Pt cathodes 16.6 mW L^{-1} . It is important to note that the operating conditions were quite different for the BHFC and MFC systems.

Table 3

Comparison of MFC and BHFC performance in terms of OCV and maximum power

Fuel cell	Catalysts	OCV (V)	P (mW L^{-1})
BHFC ^a	FePc	1.07	13.9
	CoTMPP	1.10	14.3
BHFC ^b	FePc	0.850	7.5
	Pt (in-house, ink)	0.889	16.6
MFC ^c	Pt (commercial)	0.800	13.3
	FePc-KJB	0.801	17.7
	FePcVC	0.876	14.8
	CoTMPP-KJB	0.786	13.5

^a BHFC operated in 0.5 M Na_2HPO_4 , cathode pH of 3.3 at 37°C , with a catalyst loading of 2 mg cm^{-2} .

^b BHFC in 50 mM PBM, cathode pH of 7.0 at 37°C , with a catalyst loading of 1 mg cm^{-2} .

^c MFC operated in 50 mM PBM, cathode pH of 7.0 at 30°C , with the non-Pt catalyst loadings of 1 mg cm^{-2} and Pt loading of 0.5 mg cm^{-2} .

In the BHFC, hydrogen produced by microorganisms was the electron carrier, and thus the anode potential was set as a result of hydrogen oxidation. In an MFC the anode potential is set by the bacteria as they release electrons directly to the anode. Thus, there is a higher OCV reported for the BHFC than for the MFC. Also in this BHFC study, to obtain the best performance, the operating pH was 3.3, the electrolyte concentration was 0.5 M (Na_2HPO_4), the operating temperature was higher (37°C), and the catalyst loading was 2 mg cm^{-2} . In the current MFC study, the pH was 7.0, which reduces proton availability at the cathode; the electrolyte concentration was lower (50 mM), which reduces power output [30]; the operating temperature was 30°C , which decreases bacterial kinetics; and the highest catalyst loading was only 1 mg cm^{-2} . This suggests that the power output reported here could be improved using more favourable conditions, as further examined below.

3.4. Influence of electrode preparation method

MFC performance with various non-Pt catalysts can be due to the carbon substrate and the catalyst synthesis process, but it is also a result of the electrode preparation method. In this study, cathode catalyst layers were prepared by ink spraying or paste painting. Ink spraying produces a thin and evenly distributed catalyst layer with a highly porous structure compared to that produced by paste painting methods used in previous studies [15,31]. As shown in Fig. 4, the MFC with the cathode prepared using the ink method showed better performance in the high current region than the paste method, suggesting less potential loss due to mass transfer. This indicates that the improved catalyst utilisation, due to modification of the catalyst morphology, was likely increased due to a reduced diffusion resistance and improved oxygen mass transfer [36]. In the low current region, the two polarisation curves essentially overlap, indicating the two different preparation methods did not affect the MFC performance in a region where catalyst activity and reaction kinetics dominate performance, and not mass transfer.

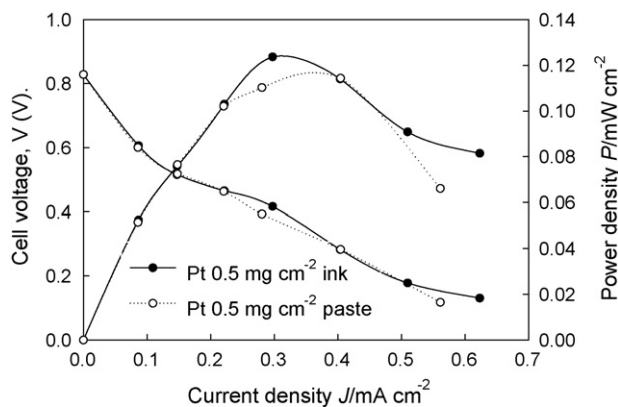


Fig. 4. MFC polarisation and power density curves with Pt cathodes prepared by ink and paste method (Pt loading 0.5 mg cm^{-2} , 200 mM PBM , 1 g L^{-1} glucose, $\text{pH } 7$, and 30°C).

3.5. MFC performance under optimized conditions

In order to more fully evaluate the effectiveness of the catalysts, we examined the performance of the catalyst in reactors optimized for power generation. Recent research has shown that increasing the ionic strength solution using a phosphate buffer, using a graphite brush electrode, decreasing the electrode spacing, and using acetate instead of glucose will maximize power generation in the cube-shaped MFCs examined here [15,19,35,37]. A graphite brush electrode has a much larger surface area than flat electrode, providing essentially unlimited surfaces for bacteria. Treatment of the graphite electrode using an ammonia gas process reduces the start up time of the reactor and increases power generation. MFC tests were therefore conducted using the cube reactor with an ammonia-treated graphite brush and a 200 mM PBM , and acetate (1 g L^{-1}) as the substrate. Electrode spacing could not be reduced due to the size of the brush electrode (Fig. 5).

MFC performance was substantially increased by using new reactor conditions, and a carbon supported FePc cathode. The peak power density produced was 2011 mW m^{-2} , which is much higher than that achieved using the other test conditions examined here. This power density is significantly higher than that produced in tests of 1129 mW m^{-2} using a flat anode and a FePc

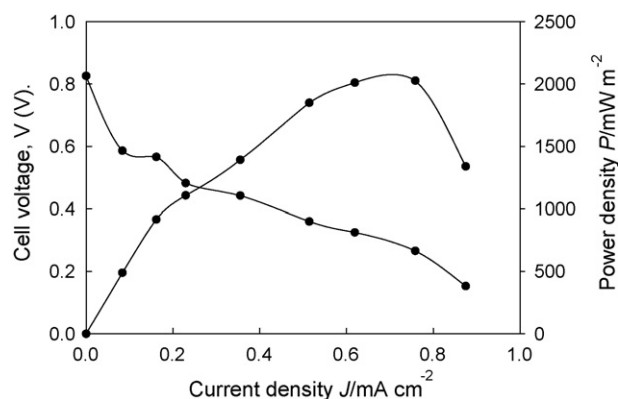


Fig. 5. MFC polarisation and power density curves with FePc catalyst cathode and a graphite brush (30°C , 200 mM PBM , $\text{pH } 7.0$, and 1 g L^{-1} acetate).

cathode catalyst with glucose as the substrate. This superior performance of low cost metal phthalocyanine compounds in this and previous studies show that these catalysts can effectively be used in MFC systems. This finding is important for the economical scale up and commercialisation of MFC technologies.

4. Conclusions

Transition metal porphyrines and phthalocyanines were used as the oxygen reduction catalysts in MFCs. Electrochemical studies and fuel cell polarisation tests performed with various non-Pt metal macrocycle catalysts showed that FePc supported on KJB carbon produced the highest oxygen reduction activity compared to Pt and other non-Pt catalysts. Most electrodes prepared using non-Pt catalysts demonstrated higher activity than a commercially available Pt electrode. In MFC tests comparing all catalysts (50 mM PBM , $\text{pH } 7$), the highest power density of 634 mW m^{-2} (17.7 mW L^{-1}) was achieved using the FePc-KJB cathode. With more optimal conditions (200 mM PBM , acetate substrate, and a graphite brush electrode), this power density was increased to 2011 mW m^{-2} (56.3 mW L^{-1}) using FePc as the cathode catalyst. These studies indicate that Pt can be replaced by inexpensive metal macrocycle catalysts, such as FePc, while at the same time increasing power output. These findings are critical to the successful scale up and commercialisation of MFC systems.

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