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Microbial fuel cell operation on carbon monoxide: Cathode catalyst selection

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ABSTRACT

Electricity production from carbon monoxide (CO) in a microbial fuel cell (MFC) has recently been demonstrated. Efficient operation of this MFC requires a CO-tolerant and preferably inexpensive cathode. Pyrolysed CoTMPP, FeTMPP, and Co/FeTMPP gas diffusion cathodes were tested in MFCs operated on acetate or CO. When the MFC was fed with acetate the best cathode performance was obtained when using a Co/FeTMPP (3:1) cathode with a Me catalyst load of 0.5 mg cm^{-2} , although this performance was slightly lower than that obtained with a cathode containing $0.5 \text{ mg-Pt cm}^{-2}$. Tests using a MFC operated on CO showed a higher power output when using the Co/FeTMPP cathode when compared both with CoTMPP and Pt cathodes.

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1. Introduction

There are many efforts underway to use syngas in conventional fuel cells to generate electricity. Among these fuel cells, solid oxide fuel cells (SOFC) are thought to be the most promising [1,2]. SOFCs operate at high temperatures and can use syngas as fuel, but the anode is easily poisoned by fuel impurities, such as hydrogen sulfide [3]. A recent advancement in microbial fuel cell (MFC) development demonstrated an alternative method of syngas conversion to electricity where carboxydophilic microorganisms in a consortium with anodophilic microorganisms produce electricity from carbon monoxide or syngas [4–6].

In a mediator-less MFC anodophilic microorganisms transfer electrons from an electron donor to the anode and release protons [7]. The electrons are then transferred through

an external circuit to the cathode, commonly Pt-based, where the oxygen reduction reaction (ORR) takes place [8]. If an MFC uses carbon monoxide (CO), cathode poisoning would be anticipated [9]. To avoid the CO-poisoning problem, Kim et al. [4] divided the process into two reactor stages. In the first reactor the carboxydophilic microorganisms converted CO to volatile fatty acids and acetate, which were then used as a carbon source for electricity production in the second reactor (MFC).

In our recent work electricity production in a single chamber MFC has been demonstrated [6]. To avoid Pt poisoning at the cathode by CO, a cobalt tetramethoxyphenylporphyrin (CoTMPP) cathode with a cobalt load of 0.5 mg cm^{-2} was used in this study. However, optimization of the cathode composition was not attempted and CO-related inhibition of the cathode activity was not evaluated.

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Platinum as a cathode material has a high electrochemical activity and stability but its drawbacks include high costs, inhibition by CO, and migration and aggregation of nanoparticles [10]. CO chemisorbs onto the Pt due to the negative free energy of adsorption [9]. Even a small concentration of CO can result in the complete coverage of the Pt surface. Alternative catalysts are therefore needed for the optimal performance of a CO-fed MFC.

Besides Pt alloys (Pt–Ru, Pt–Ru–W, Pt–Mo) and chalcogenides systems, (RuSe, RuS and RhS) fuel cell research has focused on using metal porphyrines and phthalocyanines. Jasiniki et al. [11] was the first to report that transition metal porphyrines and phthalocyanines show an electrochemical activity towards the ORR and can be used as cathode catalysts in fuel cells. The tests of cathodes containing metal porphyrines and phthalocyanines in MFCs produced encouraging results demonstrating that MFCs with non-noble metal cathode catalysts such as CoTMPP can generate more power than that obtained with a Pt-containing cathode [12–17]. Also, MFC operation with Cu–MnO₂ and Co–MnO₂ cathodes has been demonstrated [18]. However, non-noble metal cathodes containing CoTMPP or Iron(III) tetramethoxyphenylporphyrin (FeTMPP) have not yet been optimized for electricity production from CO in an MFC. In the study presented below we compared the performance of different CoTMPP and FeTMPP cathodes in a MFC operated on carbon monoxide.

2. Materials and methods

2.1. Cathode manufacturing

The cathodes were manufactured by dissolving CoTMPP and FeTMPP powders (Sigma–Aldrich Canada, Oakville, ON, Canada) in acetone by sonication using an ultrasonic probe. The solutions were sonicated for 30 min using a 0.5s/1s on/off cycle. This was followed by stirring at 20 °C, until completely dissolved. Carbon black Vulcan XC72R powder was added to the solution by 1 h sonication (also 0.5s/1s cycle) followed by stirring for 15 h at 20 °C (ratio of solvent to carbon black = 20 mL:1 g). The solution was subsequently evaporated at 80 °C on a hot plate. The solute was washed and dried at 80 °C, and ground at 25000 rpm for 2 min. The resulting CoTMPP/C powder was heat treated at 800 °C for 1 h in 100% N₂. FeTMPP/C and Co/FeTMPP/C powders were heat treated at 600 °C.

Ink fabrication and spraying was accomplished by dispersion of CoTMPP/C, FeTMPP/C and Co/FeTMPP/C powders in isopropyl alcohol:H₂O = 1:1 by ultrasonic probe treatment for 30 min at 20 °C (0.5s/1s on/off cycle). The cathodes were prepared by manual spraying of the catalyst ink on the gas diffusion electrodes with a microporous layer (GDL Sigracet DC25, SGL Group, Germany) on a hot plate at 80 °C, followed by drying at 90 °C for 20 min. The load of the metal precursor MeTMPP was 0.5 mg cm^{−2} for all catalysts. In addition, a carbon cloth gas diffusion Pt cathode with a load of 0.5 mg cm^{−2}, 30% Pt/Vulcan XC-72 carbon black (GDE LT 120EW, E-TEK Division, PEMEAS Fuel Cell Technologies, Somerset, NJ, USA) was also used to provide a basis for

comparison. A list of all cathodes manufactured and tested in this study is provided in Table 1.

2.2. Media composition and analytical measurements

The stock solution of nutrients was composed of (g/L):1.87 NH₄Cl, 14.81 KCl, 6.40 K₂HPO₄, 4.07 KH₂PO₄ and 0.415 yeast extract. When the MFC was operated with acetate, 34.59 g of NaC₂H₃O₂ (anhydrous) was added to the nutrients stock solution. The trace metal stock solution were prepared according to Tartakovsky et al. [19]. The chemicals used were all of analytical grade. The stock solutions were filter sterilized and maintained at 4 °C until used. The MFC influent solution was prepared by adding 35 mL of the nutrient solution and 1 mL of the trace metal solution to 1 L of de-ionized water. This solution had a conductivity of 12 mS cm^{−1}.

Acetate and other volatile fatty acids (VFAs) were analyzed in an Agilent 6890 gas chromatograph (Wilmington, DE) equipped with a flame ionization detector. The method details are provided in Tartakovsky et al. [19]. Gas inflow and outflow was measured by bubble counters connected to glass U-tubes and interfaced with a data acquisition system. The gas composition was measured using a gas chromatograph (6890 Series, Agilent Technologies, Wilmington, DE) equipped with a 11 m × 3.2 mm 60/80 mesh Chromosorb 102 column (Supelco, Bellefonte, PA, USA) and a thermal conductivity detector. The carrier gas was argon. The pH and conductivity of the effluent were measured periodically using a pH meter and a conductivity meter, respectively.

2.3. MFC design

The air-cathode MFC for CO tests was constructed with polycarbonate plates forming a 100 mL anodic chamber (10 cm × 5 cm × 2 cm). The anodic chamber contained a 5 mm thick graphite felt anode measuring 10 cm × 5 cm (Speer Canada, Kitchener, ON, Canada) and a sparger. A cathode was attached to a side of the anodic chamber and separated from the anode by a piece of J-cloth [20], such that the estimated distance between the electrodes was 0.5–0.7 mm. The MFC was equipped with lines for influent, effluent, liquid recirculation, gas exit and entry. Two 5 L gas bags (Control Concepts Inc., Calgary, Alberta, Canada) were attached to the line for gas entry and used for the continuous supply of CO and N₂ to the anodic chamber through the sparger. Also an external gas recirculation loop was used to increase gas transfer efficiency.

Table 1 – Cathode catalyst composition. All cathodes were prepared with a metal catalyst load of 0.5 mg cm^{−2}.

No	Catalyst composition
C-1	30% Pt on C
C-2	10% of CoTMPP on C
C-3	20% of CoTMPP on C
C-4	50% of CoTMPP on C
C-5	50% of FeTMPP on C
C-6	10% of CoTMPP : FeTMPP (1:1) on C
C-7	50% of CoTMPP : FeTMPP (1:1) on C
C-8	50% of CoTMPP : FeTMPP (3:1) on C

The air-cathode MFC for acetate tests had a similar design except that the gas sparger and gas recirculation lines were not installed and one polycarbonate plate was removed resulting in a 50 mL anodic chamber. Fig. 1 shows schematic diagrams of the two MFC setups.

2.4. MFC operation and characterization

The MFCs were inoculated with 10 mL of anaerobic sludge (Lassonde Inc, Rougemont, QC, Canada) with an average VSS content of 50 mg L⁻¹. The MFCs were operated at a temperature of 30–31 °C and continuously fed with a solution of nutrients and microelements prepared as described above. When the MFC was operated with acetate, a liquid flow rate of 150 mL d⁻¹ was maintained corresponding to a hydraulic retention time of 8 h. For all CO tests an influent liquid flow rate of 75 mL d⁻¹ was maintained (HRT = 16 h). To avoid the inhibition of microbial activity at high concentrations of dissolved CO, the MFC was fed with a CO/N₂ mixture. Gas flow rates were maintained at 477 and 204 mL d⁻¹ for CO and N₂, respectively. Voltage was measured on-line at 20 min intervals using a data acquisition system (Labjack U12, Labjack Corp., Lakewood, CO, USA).

Throughout the tests with acetate, the MFC power output was maximized using a Perturbation and Observation MPPT algorithm [21,22]. When the MFC was operated with CO the external resistance was maintained 30–60 Ω above MFC internal resistance estimated in polarization tests.

The polarization tests were periodically carried out as follows. First, open circuit voltage (OCV) was measured by disconnecting the external resistance for 30 min. Then the external resistance was re-connected and progressively decreased starting at OCV, then to 5000 Ω, 1000 Ω, 500 Ω, 250 Ω, 100 Ω, 50 Ω, and ending at 20 Ω, every 10 min with voltage and electrode potential measurements at the end of each period. Electrode potentials were measured using a standard Ag/AgCl electrode (0.222 V vs NHE), then all results were expressed vs a normal hydrogen electrode (NHE). These measurements were used to plot polarization (voltage vs. current density) and power (output power vs. current density) plots. The linear part

of the polarization curve produced was used to estimate the total internal resistance [23].

3. Results and discussion

3.1. Cathode comparison using acetate

Several cathodes with different catalysts were manufactured, tested under the same operating conditions, and compared. The initial tests were performed with acetate as a sole carbon source. The MFC was started using a Pt-based gas diffusion cathode (C-1 in Table 1). Once a stable power output was observed, cathode performance was evaluated by conducting a polarization test and the results of this test were used as a basis for comparison with all non-Pt cathodes. When the MFC was operated at an optimal external resistance ($R_{ext} \sim R_{int}$) using the Perturbation and Observation MPPT algorithm [22] a power output of 33.2 ± 2.2 mW L⁻¹ was obtained. This value was comparable with the maximal power output obtained in the polarization test (34.6 mW L⁻¹ or 0.35 W m⁻², Fig. 2a) thus confirming the accuracy of the on-line optimization procedure. Other cathode characteristics estimated in the polarization test are listed in Table 2.

Following MFC operation with the Pt cathode, the cathodes containing 10%, 20% and 50% CoTMPP, all with a Co load of 0.5 mg cm⁻² (C-2, C-3, and C-4 in Table 1), were sequentially installed and tested. The tests were performed in the same MFC with the same anode to minimize the variations in power output resulting from the differences in the microbial population. After each cathode was installed, the MFC performance was observed to stabilize within the first 3–12 h. Nevertheless, each cathode was tested for a period of 5–7 days to ensure a stable performance. As in the first test, the external resistance was controlled on-line to maximize power output. At the end of each test a polarization test was carried out to estimate MFC OCV, cathode open circuit potential (OCP), and MFC internal resistance (R_{int}).

Table 2 and Fig. 2 provide a comparison of electrochemical characteristics of each CoTMPP cathode. It can be seen that for the same CoTMPP load the power output was maintained or

Fig. 1 – Diagrams of MFCs used for cathode testing on (a) acetate and (b) CO. Electrode assembly design is shown in the insert. Notations: P1–P5–peristaltic pumps, BC1–BC3–gas bubble counters.

Fig. 2 – MFC polarization (a) and power (b) curves obtained during MFC operation with Pt and CoTMPP cathodes on acetate.

even decreased with an increase in CoTMPP percentage or an increase in the Co to C ratio. Nevertheless, the overall performance of the CoTMPP electrodes was only slightly below that obtained for the Pt-based cathode.

The pyrolysed FeTMPP cathode (C-5) was subsequently tested. Immediately after installing this cathode a relatively high MFC power output was observed (40 mW L⁻¹), but this power output declined within the first hour of MFC operation and then stabilized at 9.0 ± 0.2 mW L⁻¹. This low power

output was maintained throughout the test. Although FeTMPP catalysts have demonstrated a high catalytic activity in fuel cells [24], operating conditions in hydrogen and direct methanol fuel cells differ from those of an MFC. More specifically, MFC used in this study was lacking a proton exchange membrane thus resulting in a direct contact between the catalyst, microorganisms, and media components. Organic molecules present in the influent stream and produced by the microorganisms might interact with cathodic catalysts decreasing catalytic activity. Furthermore, the presence of microorganisms in the anodic compartment requires the pH to be maintained at around 7. It can be hypothesized that these factors led to the lower activity of the FeTMPP cathode.

In an attempt to improve cathode stability while maintaining its activity, cathodes containing pyrolysed Co/FeTMPP catalysts at different Co/Fe ratios were prepared and tested. This composition was selected since pyrolysed CoTMPP/C has a higher durability than pyrolysed FeTMPP/C, but at a lower ORR activity. Based on the available literature data, heat treatment of these cathodes was carried out at 600 °C, as opposed to 800 °C used for CoTMPP cathode manufacturing. The temperature was decreased to avoid FeTMPP oxidation [24]. The resulting pyrolysed Co/FeTMPP cathodes contained either 1:1 or 3:1 Co/Fe catalyst at a total MeTMPP load of 0.5 mg cm⁻² (Table 1). When these cathodes were tested in the MFC, while keeping the same anode as in the previous tests, the best performance in terms of power output was observed when the cathode contained 3:1 Co/FeTMPP ratio was used ($P_{\max} = 33.8$ mW L⁻¹), while the cathode with 1:1 Co/FeTMPP showed an inferior performance (Table 2 and Fig. 2). This result is different from that obtained by Chu and Jiang [24] where for a direct methanol fuel cell the best performance was demonstrated by 1:1 pyrolysed Co/FeTMPP. Based on available literature results for cathode testing in hydrogen fuel cells, it can be hypothesized that the presence of Co and Fe atoms allowed to improve stability of Fe and prevent its washout while improving catalytic activity of the electrode. Importantly, a comparison of the pyrolyzed Co/FeTMPP cathode with the Pt-based cathode show similar polarization curves and long-term performance (Table 2 and Fig. 2).

Table 2 – Performance estimation of pyrolysed CoTMPP and Co/FeTMPP cathodes in an MFC operated on acetate and CO.

No	carbon source	OCV ^a (mV)	cathode ^a OCP (mV)	$P_{\max}^a$ (mW L ⁻¹)	R_{int}^a (Ω)	P_{out}^b (mW L ⁻¹)
C-1	acetate	589	140	1.73	44	33.2 ± 2.2
C-2	acetate	591	117.9	~1.4	33	31.7 ± 1.5
C-3	acetate	545	76.2	1.23	51	22.9 ± 0.4
C-4	acetate	526	90.2	1.11	61	19.9 ± 0.8
C-5	acetate	553	87.5	0.46	118	9.0 ± 0.2
C-6	acetate	476	44	1.18	47	20.9 ± 0.4
C-7	acetate	533	65	0.95	65	9.3 ± 0.1
C-8	acetate	640	198	1.69	61	26.4 ± 1.2
C-1	CO	690	216	0.73	135	12.0 ± 0.2
C-2	CO	561	150	0.73	93.2	12.8 ± 0.2
C-8	CO	729	260.3	1.06	82.5	16.0 ± 0.2

a based on polarization tests.

b based on MFC operation at $R_{\text{ext}} \sim R_{\text{int}}$ (acetate tests) and $R_{\text{ext}} = 160$ Ω (CO tests).

In addition to voltage measurements, anode and cathode potentials were acquired during the polarization tests. Since all tests were performed using the same anode, the anode potentials were similar in all tests, as shown in Fig. 3. In agreement with on-line measurements of MFC power output, cathode potentials measured for C-8 (Co/FeTMPP) were similar or slightly above the values obtained for C-1 (Pt), while the cathode potential of C-2 was lower at all current densities. When the linear parts of the polarization curves were used to estimate the total resistance (ohmic and solution resistance) of each electrode, the anode resistance values were in the range of 19–21 Ω , while the total cathode resistance for all cathodes was estimated at 26–28 Ω .

3.2. Cathode comparison using CO

Based on the results of cathode tests with acetate, two cathodes were selected for CO tests: 10% CoTMPP (C-2) and 3:1 Co/FeTMPP (C-8). The Pt cathode (C-1) was also selected and used as a basis for comparison. To evaluate cathode stability in the presence of CO, each cathode test was performed for at least two weeks.

The 10% CoTMPP cathode was used during MFC startup, which resulted in a longer testing period for this cathode. Throughout the test, which lasted 25 days, cathode potential remained at 130–150 mV, while anode potential changed from 100 mV to –250 mV (vs Ag/AgCl) due to anode colonization by anodophilic microorganisms. Polarization curve analysis at end of the CoTMPP test showed an MFC internal resistance of 93 Ω and a maximal power output of 14.6 mW L^{–1}.

When the Co/FeTMPP cathode was installed, a recovery period of one week was required before MFC power output returned to its previous value. Furthermore, the recovery was observed only after re-inoculating the MFC. This was different from instant recovery in MFC performance observed after cathode replacements in the acetate-fed MFC. Also, cathode replacement when operating the MFC with acetate did not require MFC re-inoculation. During the recovery period CO consumption was very low and there was no acetate in the effluent (results not shown). Anaerobic carboxydrotrophic microorganisms are known to be highly sensitive to oxygen

Fig. 3 – Cathode and anode potentials (plotted vs NHE) measured during MFC operation with acetate using Ag/AgCl reference electrode. All tests were performed using same anode.

[25] and the long recovery period can be attributed to the exposure of these strictly anaerobic microorganisms to oxygen during cathode replacement.

Once power production resumed, the power output observed when using the Co/FeTMPP cathode slightly exceeded that obtained for the CoTMPP cathode (Table 2). This was consistent with the results of the polarization tests in Fig. 4 and the periodic measurements of cathode OCP during the test (Fig. 5), which showed a higher potential of the Co/FeTMPP cathode. An active oxygen reduction reaction (ORR) catalyst allows for a quicker break of the O–O bond at the ORR catalytic site. The rate of the ORR is determined by the energy of adsorption of molecular oxygen on the surface of the active catalyst. The presence of CO in the MFC results in CO competition with oxygen for the adsorption on catalytic sites. The non-noble pyrolysed MeTMPP catalysts are known for their high CO-tolerance [24]. Also it is known that ORR pathways can be different and these pathways affect electrode stability. Chu and Jiang [24] show that CoTMPP-based cathodes have a higher stability but the ORR proceeds through the formation of hydrogen peroxide and involves 2-electrons. This reaction is combined with FeTMPP, which shows less durability but has a 4-electron pathway of ORR leading to water formation [26–30]. It can be hypothesized that the presence of the two different metals in Co/Fe cathodes decreases the energy required to break the O–O bond and accelerates the ORR. The possible reasons for a high ORR and CO-tolerance of pyrolysed Co/FeTMPP/C include the close location of the two

Fig. 4 – MFC polarization (a) and power (b) curves obtained during MFC operation with Pt and CoTMPP cathodes on carbon monoxide.

Fig. 5 – MFC OCV and electrode OCP (plotted vs NHE) measured during CoTMPP CoTMPP/FeTMPP, and Pt cathode tests in the MFC operated with the same anode and fed with CO.

catalytic sites, the presence of the N4 groups with a central metal ion [24] and the face-to-face structure [30].

In addition to CoTMPP and Co/FeTMPP cathodes, which were expected to perform well in the presence of CO, a Pt-containing gas diffusion cathode (C-1) was also tested. A fast decrease of the electrode catalytic activity was expected due to CO presence in the anodic chamber and the absence of a proton exchange membrane. Nevertheless, cathode potential measurements showed a potential of 190–210 mV and this value did not change much throughout the test, which lasted 14 days. As in the previous test, a one week lag-phase was observed after cathode installation, after which the anode potential reached the value observed in the previous test. A polarization test done at the end of the experiment showed that the Pt cathode retained its activity. This can be explained by CO consumption in the biofilm developed at the cathode surface and on the fabric separating the electrodes. Also, in hydrogen fuel cells addition of oxygen was suggested to avoid Pt poisoning at the anode [9].

Overall, the activity of the Pt cathode was lower than that of the Co/FeTMPP cathode but a stable performance was observed during the 14 days of the experiment. Nevertheless, considering the high cost of Pt catalysts and a possible decrease in catalytic activity over a longer period of time the use of pyrolyzed Co/FeTMPP cathodes in MFCs operated with CO is justified.

3.3. Perspectives

Solid organic waste represents a significant source of renewable energy and its biological conversion into an energy carrier such as methane is complicated by slow hydrolysis and the presence of non-degradable organic matter. However, solid organic waste can be transformed into syngas using a conventional thermochemical process [31]. Syngas can be burnt or converted into electricity in a solid oxide fuel cell (SOFC) with a high conversion efficiency [1].

Syngas transformation into electricity in an MFC by microorganisms (carboxydophilic and anodophilic microorganisms) with a low sensitivity to syngas impurities and at a high conversion efficiency presents an alternative approach. Carboxydophilic bacteria can use CO as their only carbon source [25,32,33]. Metabolic activity of the carboxydophilic bacteria was observed to result in the formation of several metabolic products, including acetate [33,34]. Our previous study demonstrated that these metabolic products can be utilized by anodophilic microorganisms for electricity production in a mediator-less MFC and that the anodophilic microorganisms are not inhibited by the presence of up to 70% of CO in the gas phase [6]. This process offers a number of advantages in comparison with SOFCs since noble catalysts are not required at the anode and hydrogen sulfide sensitivity is not an issue as has been previously observed with SOFC [1]. The MFC-based process can also be used to combine electricity production with hydrogen extraction from syngas or in a combination with syngas biotransformation to valuable fermentation products, such as butanol [33].

4. Conclusion

This study demonstrates electricity generation in an MFC operated with CO and provides a comparison of CoTMPP and Co/FeTMPP cathodes. It is shown that the best performance is achieved when using a Co/FeTMPP cathode with a Co:Fe ratio of 3 : 1. The observed performance of this cathode was close to that of a Pt-based cathode, with the same catalyst load of 0.5 mg cm⁻², when operating the MFC on CO. This finding suggests that a novel process can be developed in which syngas is converted efficiently into electricity in a single chamber MFC. In addition, an excellent performance of the Co/FeTMPP cathode suggests that it could be used in other MFC operations, such as wastewater treatment, where low catalyst cost and high tolerance to toxic compounds is of importance.

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