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Application of iron-based cathode catalysts in a microbial fuel cell

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ABSTRACT

Catalysts for the oxygen reduction reaction (ORR) in a microbial fuel cell (MFC) were prepared by the impregnation on carbon black of Fe^{II} acetate (FeAc), Cl-Fe^{III} tetramethoxyphenyl porphyrin (ClFeTMPP), and Fe^{II} phthalocyanine (FePc). These materials were subsequently pyrolyzed at a high temperature. The ORR activity of all Fe-based catalysts was measured at pH 7 with a rotating disk electrode (RDE) and their performance for electricity production was then verified in a continuous flow MFC. Catalysts prepared with FeAc and pyrolyzed in NH₃ showed poor activity in RDE tests as well as a poor performance in a MFC. The ORR activity and fuel cell performance for catalysts prepared with ClFeTMPP and FePc and pyrolyzed in Ar were significantly higher and comparable for both precursors. The iron loading was optimized for FePc-based catalysts. With a constant catalyst load of 2 mg cm⁻² in a MFC, the highest power output (550–590 mW/m²) was observed when the Fe content was 0.5–0.8 wt%, corresponding to only 0.01–0.16 mg Fe/cm². A similar power output was observed using a Pt-based carbon cloth cathode containing 0.5 mg Pt/cm². Long-term stability of the Fe-based cathode (0.5 wt% Fe) was confirmed over 20 days of MFC testing.

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1. Introduction

Microbial fuel cells (MFCs) have been shown to produce electricity from a wide range of organic materials, including wastewater with a complex and varying composition of organic matter. This opens up a broad range of potential MFC applications where energy is produced from wastewater, which otherwise has to be treated, resulting in a significant consumption of electricity.

MFC development has significantly progressed due to intensive research [1,2]. Nevertheless, further improvements in MFC design and materials, including improved cathode long-term stability and replacement of expensive Pt-based cathodes, are required. MFCs are typically operated at pH values close to 7, while either strongly alkaline or strongly acidic electrolytes are used in conventional low temperature fuel cells. The sluggish kinetics of the oxygen reduction reaction (ORR) at a neutral pH and low temperatures at which MFCs are operated results in high energetic losses at the cathode, even at small currents.

In pure electrolytic solutions, Pt is the best known oxygen reducing catalyst. However MFCs are often intended for wastewater treatment. Therefore, inhibition of Pt activity by a variety of chemicals present in wastewater might be anticipated. Following Jasinski's discovery of the catalytic properties of Co phthalocya-

nine for the oxygen reduction reaction [3], Co/N/C and Fe/N/C ORR electrocatalysts have been studied worldwide and their application as non-noble metal catalyst (NNMC) for cathodes in MFCs has recently been demonstrated [4–10]. Such catalysts can be prepared, for example, by loading Co- or Fe-N₄ macrocycles (porphyrins, phthalocyanines, tetraazannulenes) on a carbon support and pyrolyzing these materials at a high temperature in an inert atmosphere [9,11–13]. With such macrocycles, the metal (Co or Fe) and the nitrogen, both needed to obtain good electrocatalysts, are impregnated together on the carbon support since they are part of the same Co- or Fe-N₄ macrocycle. It is also possible to obtain NNMC electrocatalysts for the ORR by providing the metal and the nitrogen precursors as two different molecules [14–16]. For example, the pyrolysis of iron acetate (as the metal precursor) in an NH₃ atmosphere (as the nitrogen precursor) has often been used [15,17–19]. With such precursors, a high temperature heat-treatment is absolutely necessary to transform them into active catalysts for ORR.

The influence of the catalyst loading on MFC power output has already been investigated [7–9]. It was shown that the increase of the catalyst load is an effective approach to improve the cathode performance in a MFC. In this study we continue to investigate the performance of Fe-based cathodes in a neutral pH solution by, first, comparing several Fe and/or N precursors and then increasing the Fe content in the catalyst while maintaining a constant cathode catalyst loading of 2 mg cm⁻² in MFC tests. This method provides a constant thickness of the catalyst layer

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while varying the volumetric density of the catalytic sites on the cathode.

2. Experimental

2.1. Media composition and analytical measurements

The stock solution of nutrients for MFC operation was composed of (g L^{-1}): 18.6 NH_4Cl , 148.09 KCl , 64.04 K_2HPO_4 , 40.69 KH_2PO_4 , 0.830 yeast extract, and 55.34 $\text{NaC}_2\text{H}_3\text{O}_2$ (anhydrous Na acetate). The stock solution of microelements contained (g L^{-1}): $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2), H_3BO_3 (0.05), ZnCl_2 (0.05), CuCl_2 (0.03), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.5), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.05), AlCl_3 (0.05), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05), NiCl_2 (0.05), EDTA (0.5) and $1 \mu\text{L/L}$ of 36% HCl . The dilution water used during MFC operation contained 1 mL of the microelement stock solution per liter of distilled water. The combined solution (dilution water, microelements, and nutrients) had a conductivity of $12\text{--}14 \text{ mS cm}^{-1}$ and a pH of 6.9–7.1. The buffer solution used in rotating disk electrode (RDE) experiments contained 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 resulting in a pH of 7. The chemicals used were all of analytical grade. The stock solutions were filtered, sterilized and maintained at 4°C until used.

Carbon source (as Na acetate) concentration in the MFC effluent was analyzed in an Agilent 6890 gas chromatograph (Wilmington, DE) equipped with a flame ionization detector. The method details are provided in Tartakovsky et al. [20]. The pH and conductivity of the effluent were measured periodically using a pH meter and a conductivity meter, respectively.

2.2. Synthesis of Fe-based catalysts

Iron precursors used in this study were Fe^{II} acetate (FeAc), $\text{Cl-Fe}^{\text{III}}$ tetramethoxyphenyl porphyrin (ClFeTMPP), and Fe^{II} phthalocyanine (FePc). FeAc (Sigma–Aldrich) was first impregnated on carbon Vulcan XC-72R (Cabot) with a loading of 0.2 wt% Fe and then pyrolyzed under NH_3 flow at 950°C for 25 min. ClFeTMPP (Tri-PorTech GmbH) was impregnated on carbon Vulcan XC-72R (Cabot) in order to obtain a loading of 0.2 wt% Fe. This impregnation was followed by a pyrolysis under either (i) NH_3 flow at 950°C for 20 min or (ii) Ar flow for 30 min at 800°C . Catalysts prepared similarly but with an Fe content of 0.4 wt% Fe on the Ketjen Black (Akzo Nobel Chemicals Inc., Chicago, IL, USA) were also synthesized.

FePc -based catalysts were prepared by mixing FePc with Ketjen Black to obtain a loading from 0.2 to 1.0 wt% Fe. This was followed by pyrolysis under Ar flow for 1 h at 700°C . The impregnation and pyrolysis conditions are described in more details elsewhere [17]. A list of all cathodes prepared and tested in this study is provided in Table 1.

2.3. Ink and electrode preparation for Fe-based catalysts

The catalyst ink formulation used in RDE and MFC tests was the same: 10 mg of catalyst, $270 \mu\text{L}$ of ethanol, $217 \mu\text{L}$ of 5 wt% Nafion

solution in alcohol and $135 \mu\text{L}$ of water. For the ink preparation in RDE tests, a K-salt of Nafion was prepared by adding 1 mL of a 3 M KCl solution into 10 mL of the 5 wt% Nafion solution resulting in the cation exchange (K^+ instead of H^+). The cathodes for RDE were prepared by dropping a $7 \mu\text{L}$ aliquot of the ink on a glassy carbon electrode, resulting in a catalyst loading of $800 \mu\text{g cm}^{-2}$.

For MFC cathode fabrication, the catalyst loading (carbon + Fe) was 2 mg cm^{-2} . The first layer was obtained by spreading the ink on the 66 cm^2 carbon paper electrode, using a mask and a brush. Several successive layers were then deposited on top of each other to reach the loading of 2 mg cm^{-2} . It was ascertained that the previous layers were dry before adding another layer.

2.4. Pt electrode preparation for RDE measurements

An electrode made with 46 wt% Pt nanoparticles dispersed on Vulcan (Tanaka Kikinzoku Group, Tokyo, Japan), henceforth labeled as Pt/C, was used as a Pt benchmark. The ink formulation was 5 mg of catalyst (mass Pt + C), $40 \mu\text{L}$ of a 5 wt% Nafion solution in alcohol, $222 \mu\text{L}$ of ethanol and $10 \mu\text{L}$ of distilled water. The ink was ultrasonicated for 30 min and then shaken for 15 min, this cycle was repeated twice. Then a $7 \mu\text{L}$ aliquot of ink was dropped on a glassy carbon electrode (0.196 cm^2) and air-dried at room temperature, resulting in a loading of $657 \mu\text{g}$ of Pt + C/ cm^2 .

2.5. Rotating disk electrode measurements

RDE measurements were performed either in a phosphate buffer solution (pH 7) or in a MFC media solution obtained by combining 1 L of the dilution water solution with 5 mL of the nutrient stock solution.

Measurements were performed at room temperature under atmospheric pressure. The counter electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE). At 25°C , the potential of a SCE is $+0.24 \text{ V}$ vs. a standard hydrogen electrode (SHE) and 0.66 V vs. a reversible hydrogen electrode (RHE) at pH 7. Cyclic voltammograms (CVs) with a scan rate of 10 mV s^{-1} were recorded in N_2 - or O_2 -saturated solution. The Faradaic ORR current was obtained by subtracting the current measured in the N_2 -saturated electrolyte from the current measured in the O_2 -saturated electrolyte.

2.6. MFC design and operation

All cathodes were tested in an air–cathode MFC with the 50 mL anodic chamber constructed with nylon plates. The anodic chamber contained a 5 mm thick graphite felt anode measuring $10 \text{ cm} \times 5 \text{ cm}$ (SGL Group, Germany). A cathode was attached to a wall of the anodic chamber and separated from the anode by a piece of J-cloth [21], such that the distance between the electrodes was 0.5–0.7 mm. The MFC was equipped with lines for influent, effluent and liquid recirculation. More details on MFC construction can be found elsewhere [22].

The MFC was inoculated with 10 mL of anaerobic sludge (Las-sonde Inc, Rougemont, QC, Canada), which had a concentration of $40\text{--}50 \text{ mg L}^{-1}$ of volatile suspended solids. The MFC was operated at a temperature of $30\text{--}31^\circ\text{C}$ and continuously fed with a solution of nutrients and trace elements prepared as described above. A flow rate of $160\text{--}170 \text{ mL day}^{-1}$ was maintained corresponding to a hydraulic retention time of 7–8 h in the anodic chamber. MFC operation was started with a carbon cloth cathode with $0.5 \text{ mg Pt cm}^{-2}$ (E-tek, BASF Fuel Cell Inc, Somerset, NJ, USA).

Throughout the MFC tests, the power output was maximized using a perturbation and observation maximum power point tracking (MPPT) algorithm, which constantly adjusted the value of the external resistance (R_{ext}) connected to the MFC so that it was

Table 1
List of cathodes tested.

No.	Description	Heat-treatment	Tests
1	$\text{FeAc/Vulcan XC-72R}$ (0.2 wt% Fe)	NH_3 950°C	RDE/MFC
2	$\text{ClFeTMPP/Vulcan XC-72R}$ (0.2 wt% Fe)	NH_3 950°C	RDE/MFC
3	$\text{ClFeTMPP/Vulcan XC-72R}$ (0.2 wt% Fe)	Ar 800°C	RDE/MFC
4	$\text{ClFeTMPP/Vulcan XC-72R}$ (0.4 wt% Fe)	Ar 800°C	RDE/MFC
5	$\text{ClFeTMPP/Ketjen Black}$ (0.4 wt% Fe)	Ar 800°C	RDE/MFC
6	FePc/Ketjen Black (0.2 wt% Fe)	Ar 700°C	RDE/MFC
7	FePc/Ketjen Black (0.5 wt% Fe)	Ar 700°C	RDE/MFC
8	FePc/Ketjen Black (0.8 wt% Fe)	Ar 700°C	RDE/MFC
9	FePc/Ketjen Black (1.0 wt% Fe)	Ar 700°C	RDE
10	46 wt% Pt/C (from Tanaka Kikinzoku)	–	RDE
11	30 wt% Pt/C (from E-tek)	–	MFC

close to the MFC internal resistance [22,23]. Polarization tests were periodically carried out as follows. First, after disconnecting the external resistance for 30 min the open circuit voltage (OCV) was measured. Then the external resistance was re-connected and progressively decreased every 10 min with voltage and electrode potential measurements at the end of each period. Electrode potentials were measured using an Ag/AgCl electrode (+0.222 V vs. SHE at 25 °C) placed in the anodic compartment. The results were expressed vs. a SHE. These measurements were used to plot the voltage vs. current density and the power vs. current density graphs. The linear part of the polarization curves produced was used to estimate the total internal resistance of the MFC [24].

3. Results and discussion

3.1. RDE measurements

The evaluation of the cathode activity in a MFC is a tedious task. Long starting times are required before a stable MFC performance is reached due to the uncontrollable variations in microbial activity and density, which are typical for microbiological systems. Thus, this study was started with RDE tests to compare the catalytic activity of Fe- and Pt-based cathodes. The RDE technique was also used to study the effect of pH and MFC media ingredients on the cathode activity. When a stationary electrode (0 rpm) is scanned at a given scan rate (here 10 mV s⁻¹), the potential at which the current for the O₂ reduction reaches a maximum (called peak potential and labeled E_{pr}) is characteristic of the catalytic activity for the ORR. The activity was also measured with the electrode rotating at 1500 rpm. A shift of the reduction wave towards positive potentials corresponded to an increase of the activity.

Initially, all catalyst inks were prepared with a H-Nafion ionomer. Attempts to measure E_{pr} values for all prepared Fe-based catalysts in RDE tests resulted in a high variability of the obtained E_{pr} values with deviations exceeding 0.1 V. As the use of the rotating electrode at 1500 rpm did not solve this problem, it was hypothe-

sized that it might be caused by localized low pH regions, attributed to H⁺ present initially in the Nafion ionomer used to prepare the RDE cathodes. As a remedy to this problem, H⁺ ions were replaced by K⁺ ions during the ink preparation, as described in Section 2. This procedure significantly increased the reproducibility with typical standard deviation of the measurements below 5 mV. All electrodes used in the following RDE tests were prepared using the K-Nafion ionomer instead of the commercial H-Nafion solution.

First, the activity of FePc/C and Pt/C catalysts was compared in cyclic voltammetry. Fig. 1A shows the cyclic voltammograms (CVs) obtained for the FePc/C catalyst (#7 in Table 1) in the pH 7 buffer solution. The solid line corresponds to the capacitive current measured in the N₂-saturated solution. When the solution is saturated with O₂, the ORR can be characterized by the peak potential, E_{pr} , if the electrode is idle (0 rpm, dashed line). The dotted line presents the current density measured at a rotation of 1500 rpm in a O₂-saturated solution. These results can be compared with the CVs obtained for the Pt/C catalyst in a pH 7 buffer solution (Fig. 1C). In this case, the peak for the O₂ reduction using the idle electrode (dashed line) is not well defined. Thus, it is better to use the O₂ reduction wave obtained at 1500 rpm to evaluate the activity of this Pt/C catalyst. The ORR activity of these cathodes was also measured in the MFC media solution, as shown in Fig. 1B and D. It can be seen, that the Pt/C catalyst is more active in the pH 7 buffer solution (dotted line in Fig. 1C) than in the MFC media solution (dotted line, Fig. 1D). This is probably due to the presence of metals and acetate in the MFC media solution that strongly adsorb on Pt. Pt is, indeed, well known to be very sensitive to even trace amounts of metals [25]. This is confirmed by the measurement of the capacitive current in both solutions. In the N₂-saturated pH 7 solution (solid line, Fig. 1C) the CV shows the peaks related to the H adsorption and desorption between -0.25 and -0.50 V vs. SCE. In the MFC solution (solid line, Fig. 1D), the intensity of these H peaks decreases. This is certainly due to the adsorption of metals and other impurities on the Pt/C catalyst. Their adsorption also inhibits the ORR on the Pt/C catalyst.

Fig. 1. Cyclic voltammograms (at 10 mV s⁻¹) obtained for FePc/C catalyst #7, in (A) the pH 7 buffer solution and (B) the MFC solution saturated with N₂ or O₂; and for Pt/C catalyst #10 in (C) the pH 7 buffer solution and (D) the MFC solution saturated with N₂ or O₂. The catalyst ink was prepared with K-Nafion ionomer.

In the case of FePc/C catalysts, the ORR activity measured in the MFC media solution (Fig. 1B) is also lower than the one obtained in the pH 7 buffer solution, as illustrated in Fig. 1A. The E_{pr} is shifted by approximately 0.03 V. The limiting current density obtained at 1500 rpm in the O_2 -saturated MFC solution (dotted line in Fig. 1B) is also slightly smaller than the one in the pH 7 solution, while the capacitive current (solid line) remains the same in both solutions. For an apparent 4e ORR at 1500 rpm, a limiting current density of about 6 mA cm^{-2} is expected (based on the diffusion flux of O_2 from the electrolyte to the electrode through the quiescent film of electrolyte found near the electrode surface (Sawyer et al. [26], p. 230). We observed approximately 5 mA cm^{-2} . It is possible that the ORR does not proceed through a complete 4e pathway on Fe-based catalysts. A more detailed investigation involving H_2O_2 measurements might be useful to elucidate the exact pathway.

The E_{pr} values obtained for RDE tests with a pH 7 (filled symbols) or MFC (empty symbols) solution, for all catalysts are shown in Fig. 2. In particular, the catalyst made with FeAc as the Fe precursor and heat-treated at 950°C in NH_3 flow (squares in Fig. 2; catalyst #1 in Table 1) is less active towards the ORR at a neutral pH than all other catalysts made with the same nominal Fe loading of 0.2 wt% (catalysts 2, 3 and 6). When ClFeTMPP was used as the Fe precursor instead of FeAc, while retaining the heat-treatment in NH_3 , the activity was improved (circles; catalyst #2 in Table 1). The ORR activity was further improved with ClFeTMPP by doing a heat-treatment in Ar at 800°C instead of NH_3 at 950°C (triangles; catalyst #3). Doubling the iron content in a catalyst made with ClFeTMPP and pyrolyzed at 800°C in Ar (triangles at 0.4 wt% Fe on x-axis; catalyst #4) gave an activity similar to that of sample #3. From this series of experiments, the pyrolysis of ClFeTMPP at 800°C in Ar was considered as the optimal procedure for ORR in neutral media.

The use of a carbon support with a higher surface area than Vulcan XC-72R, such as Ketjen Black, was then tested with ClFeTMPP as the Fe precursor (filled triangle at 0.4 wt% Fe labeled Ketjen Black in Fig. 2; catalyst #5). A higher surface area is expected to improve the dispersion of the Fe precursor during the impregnation step. This should lead to an increased ORR activity, which is indeed observed in Fig. 2 when the activities of catalysts #4 and #5 are compared. Ketjen Black was therefore used as the carbon support for further optimizations.

The molecular structure of FePc is similar to that of ClFeTMPP. They are both FeN_4 macrocycles. However, the cost of FePc is about 2.5 times lower than that of ClFeTMPP (on a 10 g basis). For this

reason, it was decided to optimize the Fe content using catalysts made with FePc and Ketjen Black pyrolyzed in Ar.

Furthermore, it was also found, by comparing catalysts #7 and #5 in Fig. 2, that using 0.5 wt% Fe as FePc and a pyrolysis temperature of 700°C in Ar produced a catalyst (#7) with an activity similar to that of catalyst #5. The latter was made with 0.4 wt% Fe as ClFeTMPP but after a pyrolysis treatment in Ar at 800°C instead of 700°C . As FePc is less expensive than ClFeTMPP, the increased load of FePc vs. that of ClFeTMPP required to obtain a similar ORR activity is compensated in terms of cost of catalyst production by lowering the pyrolysis temperature from 800 to 700°C .

Catalysts 6–9 were prepared similarly, except for the Fe content ranging from 0.2 to 1 wt% Fe. For this series, there is a significant increase in activity with an increase in Fe content. This demonstrates that by increasing the density of catalytic sites on the NNMCs, the ORR activity is improved. The optimum Fe-based catalysts (in terms of activity and cost) were therefore prepared with FePc as the Fe (and N) precursor impregnated at a loading ≥ 0.5 wt% Fe on Ketjen Black and pyrolyzed at 700°C in Ar. These Fe-based catalysts were expected to be less inhibited than Pt/C by the adsorption of trace metals and acetate present in the MFC media solution [8].

Fig. 3 shows the Faradaic current density obtained at 1500 rpm in the O_2 -saturated solutions for FePc/C catalysts and the Pt/C cat-

Fig. 2. Peak potential for the O_2 reduction, E_{pr} , vs. the Fe content for all the INRS catalysts, obtained in the pH 7 buffer solution and the MFC solution.

Fig. 3. ORR faradic current density obtained at 1500 rpm and 10 mV s^{-1} for (A) the FePc/C catalysts and the Pt/C catalyst in the pH 7 buffer solution and (B) the MFC solution saturated in O_2 .

alyst. Fig. 3A shows that the Pt/C catalyst has a better ORR activity than the FePc/C catalysts in the pH 7 buffer solution. But when the measurements are done in the O₂-saturated MFC media solution (Fig. 3B) catalysts #8 (green dash-dotted line) and #9 (red dashed line) display an ORR activity very similar to that of Pt/C. With a further increase in the Fe content, the catalytic activity slightly improved (for interpretation of the references to color in this text, the reader is referred to the web version of the article). Overall, it was concluded that for operating a cathode in a MFC media solution at a neutral pH, a Fe concentration between 0.5 and 0.8% might be considered near optimal. This is in agreement with the results presented in Yu et al. [8].

3.2. MFC tests

Following the RDE tests, the activity of selected cathodes was tested in a MFC. As described in Section 2 the MFC was operated with each cathode until observing a stable power output for at least 2–3 days. All cathodes were tested using the same anode. This approach minimized variations in MFC power output related to the differences in microbial populations of the anode. MFC operation was started with a carbon cloth Pt/C cathode. Once a stable power output was observed, the Pt/C cathode was replaced with NNM/C cathodes made from FeAc, ClFeTMPP and FePc iron precursors (cathodes #1, 2–3 and 6, respectively). For this comparison, all cathodes were prepared using the same Fe content (0.2 wt% Fe) and same catalyst loading but under different pyrolysis conditions as outlined in Table 1. Polarization tests were carried out at the end of each cathode test.

Fig. 4 compares cathode polarization curves of the three cathodes along with the polarization curve of the Pt/C cathode. The catalyst with the highest ORR activity was that made with ClFeTMPP and pyrolyzed at 800 °C in Ar (catalyst #3). The catalyst prepared with FeAc and pyrolyzed at 950 °C in NH₃ demonstrated the lowest ORR activity (catalyst #1). These results agree with the E_{pr} values obtained in the RDE experiments shown in Fig. 2. Also, the results were consistent with the average power outputs observed during MFC operation with these cathodes (Table 2).

As discussed above, the FePc precursor is less expensive than ClFeTMPP. For this reason, FePc-based cathodes were chosen to validate results of the RDE tests in a MFC. Several FePc cathodes with different Fe percentages were produced on Ketjen Black as described in Table 1. A comparison of FePc cathodes with an increasing percentage of Fe is presented in Fig. 5. Once again, the results of MFC and RDE tests were in a full agreement. Cathode performance was increased by increasing the Fe content from

Fig. 4. Cathode polarization curves obtained in the MFC for the catalysts made with three different Fe precursors loaded on the carbon support with the same nominal Fe content (0.2 wt%), and for the Pt/C catalyst.

Fig. 5. Cathode polarization curves obtained in an MFC for the FePc/C catalysts prepared with different Fe contents (wt% Fe), and the Pt/C catalysts.

Table 2

Performance of NNM/C and Pt/C cathodes in RDE and MFC tests.

Electrode number	RDE test		MFC polarization test				MFC operation
	E_{pr} vs. SCE ^b (mV)		R_{int} (Ω)	R_{anode} (Ω)	R_{cathode} (Ω)	Highest P_{out} (mW m ⁻²)	Average P_{out} (mW m ⁻²)
	Buffer	Medium					
1	−31	−81	40.3	15	24.2	300	377 ± 6
2	68	17	149	9.6	116.9	134	343 ± 12
3	77	42	50	7.2	43.3	380	330 ± 14
4	70	42	28.2	4.9	22.8	620	538 ± 6
5	107	87	23.4	6.7	16.2	660	604 ± 13
6	55	17	32.2	6.2	25.3	280	344 ± 6
7	103.5	71	31.9	4.3	27.2	720	552 ± 9
7 ^a	103.5	71	30.1	4.6	25.9	580	540 ± 68
8	111	86	28.8	8	21.4	676	588 ± 6
9	121.5	93	NM	NM	NM	NM	NM
10	NM	NM	NM	NM	NM	NM	NM
11	NM	NM	19.3	6.5	12.3	820	643 ± 20

^a After a 20-day test; NM: not measured.

^b At 25 °C, the potential of a SCE electrode is +0.24 V vs. a standard hydrogen electrode (SHE) and 0.66 V vs. a reversible hydrogen electrode (RHE) at pH 7.

Fig. 6. (A) Power density obtained on NNMC and Pt/C catalysts during 5 days or (B) 20 days of cathode #7 testing. In all tests MFC external resistance was optimized by a MPPT algorithm to maximize power output.

0.2 to 0.5 wt%. A further increase in Fe percentage to 0.8 wt% Fe did not improve MFC power output. The average power output with cathode #8 (0.8 wt% Fe) was comparable with that of cathode #7 (0.5 wt% Fe) with the differences within the range of standard deviation (Table 2). Also, the MFC power output with these cathodes was comparable to that obtained with the Pt-based cathode.

If RDE tests can be used for a fast comparison of catalytic activities, the long-term performance can only be demonstrated by a prolonged MFC operation. Fig. 6A presents the MFC power output measured during 5-day tests required for the comparison of the catalysts prepared with the three Fe precursors and the Pt cathode. The loss in activity was observed within the first 2 h after the startup of each test and this decrease was more pronounced for the Pt cathode. This is certainly due to the higher sensitivity of the Pt towards nutrients, trace metals or acetate present in the MFC medium, as shown in the RDE tests. All FePc-based catalysts showed good stability with cathode #8 (made with FePc 0.8 wt% Fe) appearing to be more stable than the others. In addition to these relatively short tests, the long-term stability of cathode #7 (0.5 wt% Fe) was tested in a 20-day test as shown in Fig. 6B. By the end of the test period MFC power output decreased but remained comparable to an output of a Pt-equipped MFC (400–500 mW m^{-2}) operated for a comparable

amount of time. Visual inspection of the anodic compartment at the end of the test suggested that an increased resistance between the carbon felt and a current collector (titanium wire inserted in the felt) can explain the observed decrease in power output. Indeed, when the MFC was reassembled the power output was restored to values obtained during the first days of the test.

4. Conclusions

This study demonstrates the performance of iron-based cathode catalysts in a MFC. The RDE tests performed at pH 7 suggested the existence of H^+ rich spots in the Nafion ionomer present in the catalyst layer deposited on the glassy carbon support, which led to a high variability of the measurements. Replacement of H^+ with K^+ greatly improved the reproducibility of the measurements and enabled a comparison between different Fe precursors and the optimization of the precursor loading on Ketjen Black, which was found to be the best carbon support. Overall, the use of the FeAc precursor pyrolyzed in NH_3 led to a low ORR activity, while both ClFeTMPP and FePc precursors pyrolyzed in Ar showed a higher activity. The best performance was observed for Fe/C catalysts prepared with FePc impregnated at a loading of ≥ 0.5 wt% Fe on Ketjen Black and pyrolyzed at 700 °C in Ar.

The results of the RDE tests were validated in a continuous flow MFC fed with acetate. The correlation between RDE and MFC results is excellent. RDE measurements are therefore very valuable to rapidly screen potential catalysts for MFCs. The power output of a MFC equipped with Fe-based cathodes was comparable to a power output observed with a Pt-based cathode, while a significant reduction in the cathode cost was achieved. Furthermore, continuous MFC operation in a 20-day test demonstrated a stable performance of a Fe-based cathode.

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