

A microbial fuel cell using manganese oxide oxygen reduction catalysts

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Abstract Microbial fuel cells (MFCs) are a potential method for enhanced water and waste treatment, which offer the additional benefit of energy generation. Manganese oxide was prepared by a simple chemical oxidation using potassium permanganate. Carbon-supported manganese oxide nanoparticles were successfully characterised as cathode materials for MFCs. The manganese oxide particles when used in a two-chamber MFC, using inoculum from an anaerobically digested sewage sludge, were found to exhibit similar oxygen reduction performance to that in separate electrochemical tests. MFC tests were conducted in a simple two chamber cell using aqueous air-saturated catholytes separated from the anode chamber by a Nafion membrane. MFC peak power densities were ca. 161 mW m^{-2} for MnO_x/C compared to 193 mW m^{-2} for a benchmark Pt/C, in neutral solution at room temperature. The catalyst materials demonstrated good stability in the 7.0–10.0 pH range. Theoretical (IR free) peak power densities were 937 mW m^{-2} for MnO_x/C compared with 1037 mW m^{-2} for Pt/C in the same experimental conditions: showing the MFCs performances can easily be improved by using more favourable conditions (more conductive electrolyte, improved cathode catalyst etc.). Our studies indicated that the use of our low cost MnO_x/C catalysts is of potential interest for the future application of MFC systems.

Keywords Electrocatalysis · Oxygen reduction reaction · Microbial fuel cell · Manganese oxides · Mixed microbial inoculum · Waste water

1 Introduction

Electrogenic reactors based on microbial fuel cells (MFCs) represent a new approach for generating electricity from waste and biomass [1–3]. Recently, the technology has been improved due to the capability of certain micro-organisms to connect directly to graphite anodes and to transfer the electrons, they extracted from different fuels contained in marine sediments or domestic wastes [4–6]. This direct electron transfer from micro-organisms to the anode avoids the use of platinum, as catalyst of the anode reaction, thus reducing cell cost making it potentially more viable for further industrial development [7]. The more promising applications of MFCs will be to treat wastewater whilst obtaining a source of clean and renewable energy [8, 9].

The amount of research devoted to MFC has considerably increased over the last 5 years, particularly in biotechnology and microbiology fields. Some significant research has been carried out consequently on MFC anodes [10–14], although there have been fewer studies dealing with the cathode reaction and catalysts for the oxygen reduction reaction (ORR); which remains a major factor in the design of low cost MFCs. Indeed, poor kinetics of ORR at neutral pH and low temperatures has hindered the improvement of MFC performances [15–17]. Platinum is known to be the best catalyst for the ORR in acidic and alkaline media [18], and is the most commonly used catalyst in the MFC. However, Pt cost is prohibitive to economic MFCs and platinum-free electrocatalysts represent a necessary alternative. A limited number of catalysts have retained the focus of the scientific community. As well as a range of carbons and activated carbons, transition metal porphyrines and phthalocyanines are good candidates for materials in the cathode of MFC [19]. Electrochemical

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studies have been carried out in neutral pH solution with metal tetramethoxyphenylporphyrin (TMPP), CoTMPP and FeCoTMPP, and metal phthalocyanine (Pc), FePc, CoPc and FeCuPc, supported on Ketjenblack (KJB) carbon: the FePc/KJB catalysts exhibited remarkable activity towards the ORR [19].

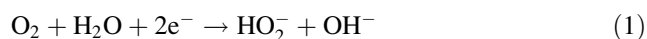
Only a few studies of manganese oxide cathodes for MFCs have been reported [20, 21]. Clauwaert et al. [20] used an electrochemical precipitation of manganese dioxide to treat a graphite felt cathode and compared the performance with a non-treated cathode. After start up; the cell performance was reported to be similar for both cathodes. This may have been a result of a large particle size which occurred in electrochemical produced manganese dioxide (EMD is a battery material) and/or the use of a graphite fibre substrate which tend not to produce well adhered electrodeposits.

Very recently, Zhang et al. [21], published (in 2009) on manganese dioxide as an alternative cathode catalyst to platinum in microbial fuel cells. They prepared three materials: α , β and γ forms of MnO_2 by a hydrothermal method. Tests were made with a pure culture (*K. pneumoniae strain 117*) and good volumetric power densities were reported using an air cathode.

The use of biocathodes, as alternatives to noble and non-noble metal cathode catalysts, which are more sustainable has been proposed more recently [20, 22]. Lefebvre et al. [22] published work on an alternative cathode catalysts, namely sputter-deposited cobalt (Co) and denitrifying bacteria (biocathode). The performance of the cathodes was compared to Pt-cathodes. Co competed well with Pt, but further research is still required for the biocathodes. Overall, although biocathodes in MFC have some promise, more significant research is required for their practical and economic development.

Although the electrochemical properties of manganese oxides were studied in strong alkaline solution, their catalytic activity in neutral solution is less well characterised. Mixed valency spinel $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$ oxides were first described in neutral and slightly acid solutions: their good activity being mainly explained by the role of the MnIV/MnIII redox couple on the competing 4 and 2-electron O_2 reduction pathways [23, 24].

The ORR mechanism in alkaline media on MnO_x is usually described by the partial 2-electron reduction of O_2 as follows:



Manganese oxides were found to facilitate the decomposition of hydrogen peroxides, according to the

HO_2^- disproportionation reaction (3) [25, 26]. Oxygen can then be reduced according to the reaction (1); the overall reaction is then the apparent 4-electron reduction of O_2 :



The 4-electron pathway (4) is in competition with the 2-electron reduction (1) yielding peroxide ions as intermediates. They are corrosive [27, 28] and can degrade the membrane and/or corrode the fuel cell cathode. Manganese oxides are able to prevent peroxide formation and facilitate their decomposition [25, 26] and are, in that case, candidate materials for the cathode. However, due to the complex chemistry of manganese oxides [29], the ORR mechanism on MnO_x surfaces still needs satisfactory characterisation in alkaline and neutral solution.

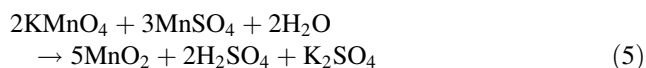
We recently studied the catalytic activity of carbon-supported manganese oxide nanoparticles in neutral [30], showing from rotating disk electrode (RDE) setups very good stability and ORR activity. As already explained for such catalysts in strong alkaline media [31], we proposed the first electrochemical step of the 4-electron ORR mechanism on MnO_x/C , to be the quasi equilibrium proton insertion in MnO_2 yielding MnOOH . The dispersed manganese oxide nanoparticles were found to favour the 4-electron pathway in neutral solution, following the very good activity of MnOOH for the HO_2^- disproportionation (3), yielding less corrosive peroxides [30]. The ability of manganese oxides to absorb or deliver a high quantity of charge in a very short time (flywheel effect) can be advantageously used in the air-cathode of fuel cells [32]. Long-term MFCs tests are needed to assess the MnO_x/C efficiency as material of the operating fuel cell cathode.

The present study investigated the performance of operating MFC using our manganese dioxide catalysts formed chemically on an activated carbon as cathode materials. We considered two samples: MnO_x/C and the high area (ca. $300 \text{ m}^2 \text{ g}^{-1}$) carbon substrate. A Pt/C (E-Tek) was used for comparison. We first performed long-term MFC tests using neutral pH solution as catholyte, and second investigated the influence of the catholyte pH on the MFC performances.

2 Experimental

2.1 Synthesis of MnO_x/C materials

The dispersion of manganese oxide nanoparticles over carbon substrate has already been described in previous papers [11, 33]. The method is based on the chemical oxidation of manganese sulphate by permanganate in the presence of carbon as follows [34]:



Briefly, 4.0 g of carbon black Monarch 1000 (Cabot) were mixed with 10 mmol of MnSO_4 (Aldrich) in 70 cm^3 aqueous solution and maintained at controlled temperature (80 °C) for 20 min under magnetic stirring to exhibit the impregnation of the carbon substrate by manganese sulphate. About 33 mmol of KMnO_4 (Merck) in 300 cm^3 aqueous solution at 80 °C were then gradually added to the agitated reaction medium. The mixture was agitated at 80 °C for 15 min, and then filtered and dried at 100 °C for approximately 10 h. Monarch 1000 from Cabot (called Monarch or C) has a specific area ca. 300 $\text{m}^2 \text{g}^{-1}$ [20]. Similar oxidations, using potassium permanganate, were performed on the carbon support alone (then called Monarch_{ox} or C_{ox}) for comparison. Chemical analysis revealed few impurities and a loading of Mn/[C + Mn + O] ca. 25 wt% for a water loading of ca. 9 wt%.

2.2 MFCs testing

2.2.1 MFC fuel

Synthetic wastewater containing acetate was used as the MFC fuel. It was prepared by dissolving sodium acetate (20 mM) and inorganic salts $\text{NH}_4\text{-N}(\text{NH}_4\text{Cl})$ (40 g dm^{-3}), MgCl_2 (10 g dm^{-3}), CuSO_4 (0.1 g dm^{-3}), CaCl_2 (5 g dm^{-3}), MnSO_4 (0.1 g dm^{-3}) and ZnCl_2 (0.1 g dm^{-3}) in 0.9 dm^3 of distilled water (pH ca. 7). The medium was autoclaved at 121 °C for 10 min; 80 cm^3 of a phosphate buffer (0.25 M, pH ca. 7.0) were then added to ensure the neutrality of the medium. 50 cm^3 of inoculums (see Sect. 2.2.2) were added to the fuel; anaerobic conditions and uniform microbial distribution being ensured by vigorous oxygen free N_2 purging for 10 min (55 mL min^{-1}). Finally, 0.1 mM of 2-hydroxy-1,4-naphthoquinone (HNQ) was mixed thoroughly as an external mediator. The fuel had a biomass concentration of 42.09 g dm^{-3} as volatile suspended solids (VSS) and 7.014 10^{11} cells dm^{-3} of bacteria.

2.2.2 Inoculum preparation

The inoculum was an anaerobically digested sewage sludge taken from an anaerobic digester at a local municipal sewage treatment works (Newcastle upon Tyne, UK). The same sludge was used throughout the study and stored at 4 °C, in order to arrest physicochemical changes in wastewater and minimize biological activities. It was first sieved ($d < 3$ mm) to remove any debris and large particles. Then the micro-flora were collected, by centrifugation, from sieved sludge and washed twice with sterile saline solution (0.9 wt% NaCl solution) to remove organic

compounds adhered to the microbial cells. The micro-flora sample was then re-suspended in 50 cm^3 of sterile distilled water for mixing with the MFC fuel (Sect. 2.2.1).

2.2.3 MFC configuration and operation

Experiments were conducted in a conventional 2-chamber fuel cell configuration (made with Borosil glass). The two chambers (120 cm^3 volume) of the cell were connected by a Nafion[®] 117 proton exchange membrane (PEM) (Sigma-Aldrich, Germany), 6 cm^2 in area. The top of the anode chamber was equipped with sample points for liquids and gases and for an electrical connection to the anode, which was suspended in the anode solution. The anode was carbon cloth (type A, E-Tek) 20 cm^2 in area.

The anode was pre-treated and sterilised before use by boiling in distilled water for 1 h and then washed and boiled for 30 min. The electrical contact with the electrodes was ensured by titanium wires. Both anode and cathodes were positioned at a distance of 6 cm from either side of the proton membrane. Prior to each test, the anode fuel (100 cm^3 for each MFC) was purged by pure nitrogen bubbling for 15 min (12 $\text{cm}^3 \text{min}^{-1}$), in order to obtain an anaerobic environment in the reactor. Experiments were conducted at room temperature ca. 20 °C. A homogeneous distribution of substrate in the anodic compartment was maintained by mixing with a magnetic stirrer bar. The cathode chamber contained 100 cm^3 of potassium phosphate buffer (0.25 M, pH ca. 7.0). The catholyte was neither aerated nor mixed but had an open surface exposed to air.

The cathode was made from the MnO_x/C material. The backing layer consisted of carbon cloth (E-Tek, USA) to which a diffusion layer was applied. This diffusion layer consisted of ultrasonically mixed carbon Ketjenblack EC 300 (Akzo Nobel), acetone and 10 wt% Nafion suspension (Aldrich). The catalyst layer was then deposited by spraying from an ink containing the MnO_x/C material, Nafion solution (Aldrich) and acetone. The MnO_x/C loading was estimated to be ca. 0.82 $\text{mg}_{\text{Mn}} \text{cm}^{-2}$. Each MFC studying was duplicated to determine reproducibility of data. Similar experiments were conducted using different MnO_x/C loadings or pH 10.0 catholyte to assess the effect of pH on the MFC performances (see Sect. 3.2).

For comparison, similar MFCs were prepared using the 20 wt% Pt/Vulcan XC72 from E-Tek (ca. 0.82 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$) and Monarch_{ox} (ca. 0.82 $\text{mg}_{\text{C}} \text{cm}^{-2}$) catalysts as cathode materials.

2.2.4 Electrochemical measurements

The change in cell voltage under different external load was recorded hourly using a data acquisition system (ADC 16, Pico Technology Ltd, UK) connected to a personal

computer via a BS 232 Pico high resolution analogue cable. Polarisation curves were carried out using a variable resistor box (10^6 – $10\ \Omega$). Cathode and anode potentials were measured during polarisation using a Ag/AgCl (sat) reference electrode connected via a luggin capillary probe (in contact with the electrode-electrolyte interface) filled with phosphate buffer.

3 Results and discussion

3.1 pH 7 Catholyte

MnO_x/C was shown by RDE studies to exhibit promising ORR activities and to be stable in neutral and slightly basic media [16]. From our experiments, we proposed the quasi equilibrium proton insertion process in MnO_2 yielding MnOOH to be the first electrochemical step of the 4-electron ORR mechanism in the 7–10 pH solution. The ORR kinetic greatly increased with increasing temperatures in the 5–40 °C temperature range. The formation of hydrogen peroxides, consecutive of the 2-electron ORR mechanism may, however, be favoured over the 4-electron reduction of O_2 at higher temperatures.

MFC tests were conducted using MnO_x/C as cathode material, similar testing was performed using C_{ox} alone (see part 2.1), as cathode material and with the benchmark 20 wt% Pt/Vulcan XC72 (E-Tek). All experiments were performed at room temperature.

Figure 1 shows the experimental anodic and cathodic polarisation curves for our different materials as measured in actual MFCs. Both electrode potentials vary linearly with current density, following the linear Butler–Volmer approximation in the low current densities range. We considered k_a and k_c (Ωm^2), as kinetic polarisation constants, i.e. the slopes of the linear anode and cathode polarisation curves and were determined (see Table 1) in the current densities range (Fig. 1). By considering k_c and extrapolating at +0.5 V vs. SHE, we estimated current densities of $0.5\ \text{A m}^{-2}_{\text{geom}}$ for MnO_x/C and $4.1\ \text{A m}^{-2}_{\text{geom}}$ for Pt/C (E-Tek). From the Tafel plots (RDE experiments) [16] we estimated at +0.5 V vs. SHE current densities of $0.01\ \text{A m}^{-2}_{\text{geom}}$ for MnO_x/C and $2.1\ \text{A m}^{-2}_{\text{geom}}$ in neutral pH solution, showing better results for the operating MFC than expected.

In the case of the benchmark Pt/C, from 0.00 to $1.05\ \text{A m}^{-2}$, the anode potential increased more than the cathode potential decreased (+0.110 V compare to $-0.040\ \text{V}$):

Fig. 1 Experimental polarisation curves of the MFC electrodes, 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room} , pH 7.0 or 10.0

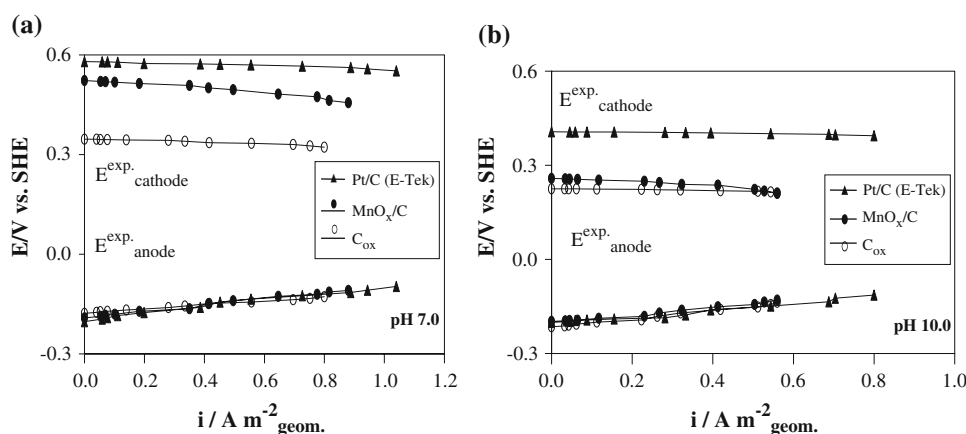


Table 1 Parameters of the MFC, 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room} , pH 7.0 or 10.0

Catalysts	E°/V	$i_{0.00\text{V}}/\text{A m}^{-2}$	r_i/Ω	$k_c/\Omega\ \text{m}^{-2}$	$k_a/\Omega\ \text{m}^{-2}$	$p_{\text{peak}}^{\text{exp}}/\text{mW m}^{-2}$	$i_{\text{peak}}^{\text{exp}}/\text{A m}^{-2}$
pH 7.0							
MnO_x/C	0.714	0.88	320	0.042	0.094	161	0.44
C_{ox}	0.527	0.80	270	0.022	0.067	106	0.40
Pt/C	0.781	1.04	320	0.019	0.098	193	0.51
pH 10.0							
MnO_x/C	0.449	0.57	310	0.053	0.121	67	0.29
C_{ox}	0.429	0.56	310	0.014	0.133	65	0.29
Pt/C	0.597	0.80	360	0.011	0.107	104	0.39

indicating at least initially that the anode was the limiting electrode. This is not particularly surprising from the good RDE behaviour of the cathodes, and since the microbiological processes at the anode are difficult to control and can be kinetically limiting; especially at low temperatures. In the case of the MnO_x/C catalysts, the changes in cathode potentials were similar to those for the anode (+0.070 V and -0.080 V for the anode and the cathode, respectively, Fig. 1). In the case of C_{ox} , the changes in cathode potentials were approximately of -0.030 V. Notably, in all MFC tests, the variation in anode potentials were consistent and reproducible. Thus, the manganese oxides do not appear to have diffused across the membrane and, as a consequence, do not pollute the anode side (Mn being toxic for microorganisms).

The variations in the anodic and cathodic potentials clearly affect the MFC cell voltages (Fig. 2, Table 1) and power densities (see Fig. 3, Table 1). Indeed, the activation potential was less apparent for Pt/C, since the open circuit voltages (OCVs) were +0.781, +0.714 and +0.527 V for Pt/C (E-Tek), MnO_x/C and C_{ox} , respectively, (Fig. 2, Table 1). Moreover, the highest peak power densities were obtained with MFCs with the benchmark Pt/C (E-Tek) as cathode material. However, our manganese catalysts exhibit good performances since the peak power densities were similar in neutral pH solution (ca. 190 mW m^{-2} for

Pt/C compare to ca. 160 mW m^{-2} for MnO_x/C , see Table 1 and Fig. 3). These observations are in agreement with the previous RDE experiments [30], the performances of MnO_x/C being even better than expected. Note that, although the dispersion of manganese oxide nanoparticles over the support improved the catalyst performance, C_{ox} exhibited a good ORR activity with p_{peak} close to 110 mW m^{-2} (Fig. 3, Table 1). It has been previously reported and explained [30] that oxidation of the carbon by permanganate increases the functionalisation of the carbon surface and opens up the microporosity, yielding better interactions with the O_2 molecule during the ORR, and also improves degradation of peroxides.

Note that the difference between the experimental cathode and anode potentials (Fig. 1) was greater than the experimental cell overvoltage (Fig. 2); due to the combined internal {catholyte + membrane + anodic fuel} resistance (r_i). For example, for MnO_x/C as cathode material, at 0.42 A m^{-2} , $E_{\text{cathode}}^{\text{exp}} = +0.501\text{V}$ vs. SHE, $E_{\text{anode}}^{\text{exp}} = -0.149\text{V}$ vs. SHE, compared to $E_{\text{cell}}^{\text{exp}} = +0.388\text{V}$ ($\neq E_{\text{cathode}}^{\text{exp}} - E_{\text{anode}}^{\text{exp}} = +0.650\text{V}$). Figure 4 shows the estimated internal resistances, r_i measured from the difference in the combined electrode potentials and the cell voltage in the current densities range for the Pt/C (E-Tek), MnO_x/C and C_{ox} catalysts. The high value of the internal resistance was mainly due to the low ionic conductivity of

Fig. 2 MFC experimental polarisation curves, 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room} , pH 7.0 or 10.0

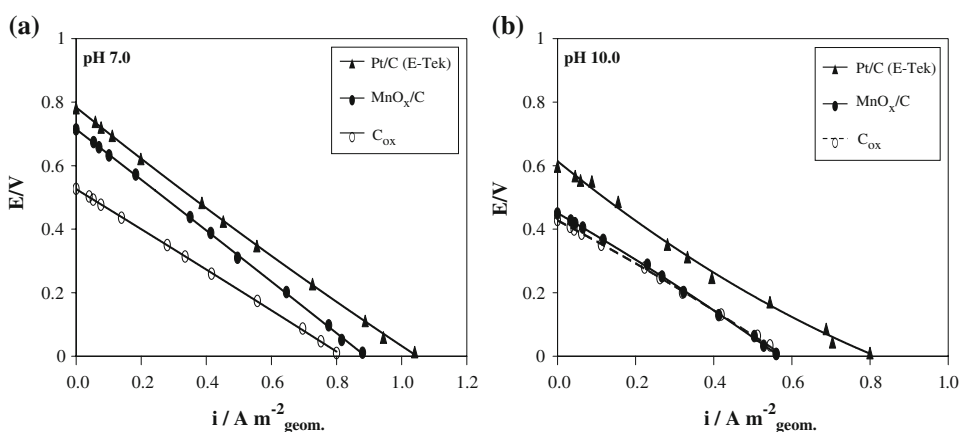
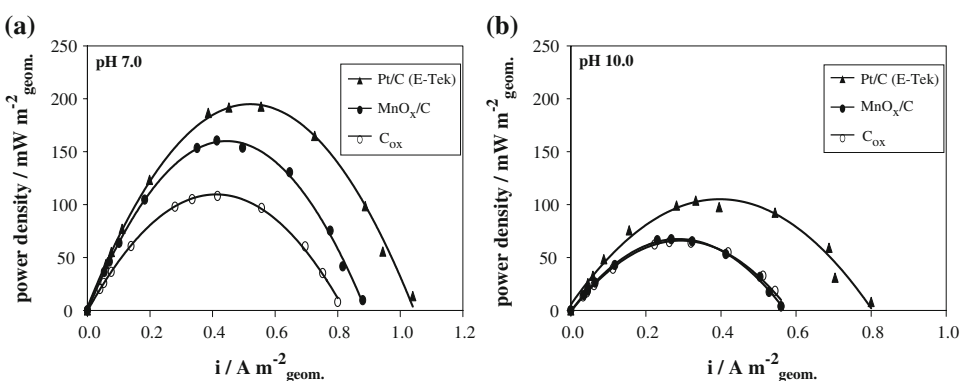


Fig. 3 MFC power densities curves, 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room} , pH 7.0 or 10.0



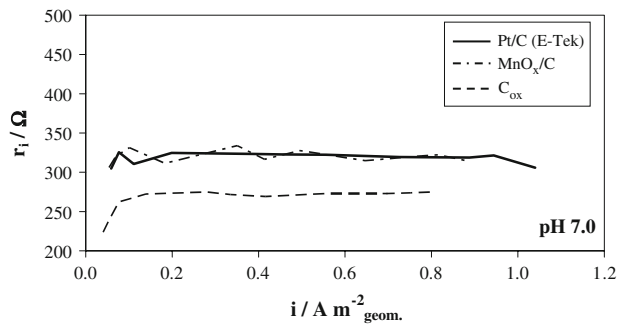


Fig. 4 Internal resistance r_i (i), 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room} , pH 7.0

the electrolytes and the relatively large inter-electrode gap (l). The MFC performance can thus be improved by reducing the inter-electrode gap, by changing the cathode electrolyte and by perhaps using a gas diffusion air cathode.

From a theoretical perspective, it is interesting to examine what may be the best power performance the cell could give. As both electrode potential and cell voltage variations vary linearly with current density, it is possible to estimate the impact of internal resistance on cell performance as follows:

The cell voltage E (V) is given by

$$E = E^\circ - i\rho l - \eta_a - \eta_c \quad (6)$$

where E° (V) is the open circuit voltage, η_a and η_c (V) are anode and cathode overpotentials, l ($6.0 \cdot 10^{-2}$ m) is the effective interelectrode distance and ρ (Ω m) is the combined internal resistivity.

The cell power density, p ($\text{Wm}_{\text{geom.}}^{-2}$) is thus given by

$$p = iE = i[E^\circ - i\rho l - \eta_a - \eta_c] = iE^\circ - i^2(\rho l + k_a + k_c) \quad (7)$$

where k_a and k_c (Ω m²) are kinetic polarisation constants of the anode and cathode. The peak power density p_{peak} ($\text{Wm}_{\text{geom.}}^{-2}$) obtained under the conditions is found, when $dp/di|_{\text{peak}} = 0$, i.e.

$$dp/di|_{\text{peak}} = E^\circ - 2i_{\text{peak}}(\rho l + k_a + k_c) = 0 \quad (8)$$

then,

$$p_{\text{peak}} = E^{\circ 2}/[4(\rho l + k_a + k_c)]. \quad (9)$$

The inter-electrode distance of the operating MFCs is 6×10^{-2} m. From the experimental power densities, knowing the kinetic polarisation constants (Table 1), and considering the Eq. 9, we calculated the resistivity ρ for all the MFCs tests. We can first note that ρ is from 9.4 to 11.2 Ω m for all the studied catalysts, showing that the combined internal resistivity is not affected by the nature of the catalyst. For an MFC with a practical inter-electrode gap of 1.0 cm, the power density would equate to 520 mW m^{-2} at 1.46 $\text{A m}_{\text{geom.}}^{-2}$ for MnO_x/C (Table 2). It clearly shows the detrimental effect of the inter-electrode distance on the MFC efficiency. To that extent, the peak power densities based on IR free voltage (no internal resistance but kinetic losses at cathode and anode) would be 937, 780 and 1300 mW m^{-2} in neutral solution for MnO_x/C , C_{ox} and Pt/C (E-Tek), respectively, (Table 2).

The MFC design used in this study was not intended to optimize power generation, as single chamber MFCs with air cathodes can produce higher power for the same experimental conditions. The use of MnO_x/C as cathode material was, however, found promising regarding other work published in the literature. Zhang et al. [21] prepared three manganese dioxide catalysts using a hydrothermal process and found that $\beta\text{-MnO}_2$ was the best cathode. The power performance of the MFC using a graphite-packed bed anode and a pure culture (*K. pneumoniae strain 117*) was 466 mW m^{-3} based on the volume of a cube cell (425 cm^3). This performance is equivalent to a power density of 172 mW cm^{-2} based on the cross sectional area of the cathode (11.5 cm^2). They also increased the volumetric power density of the MFC by a factor of 7 (3773 mW cm^3) using a tube cell, although the cathode was increased by an order of magnitude. Essentially, the performance of both cells was similar based on the cathode

Table 2 Theoretical peak power densities and corresponding current densities for an interelectrode distance of 1 cm, IR free peak power and current densities, 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room} , pH 7.0 or 10.0

Catalysts	ρ/Ω m	$p_{\text{peakth, 1 cm/A m}^{-2}}$	$i_{\text{peakth, 1cm/A m}^{-2}}$	$p_{\text{peakth, IR free/m W m}^{-2}}$	$i_{\text{peakth, IR free/A m}^{-2}}$
pH 7.0					
MnO_x/C	10.9	520	1.46	937	2.63
C_{ox}	9.4	379	1.44	780	2.96
Pt/C	11.2	666	1.71	1303	3.44
pH 10.0					
MnO_x/C	9.6	187	0.83	290	1.29
C_{ox}	9.4	191	0.89	313	1.46
Pt/C	12.3	370	1.24	755	2.53

area used. The performance of the MFC of Zhang et al. [21] was similar to that achieved in this work, although we used a mixed microbial culture, not a pure culture. In addition, Zhang et al. used a graphite-packed bed anode to increase biofilm surface area and reduce internal resistance, where we used a simple plain carbon cloth anode and a MFC with a greater internal resistance. Zhang et al. also used a gas diffusion cathode which would be expected to perform better than a aqueous electrolyte system where low concentrations of oxygen would cause mass transport and kinetic limitations. Thus, the performance of our MFC was at least as good as that achieved previously and, based on a low internal resistance, indicates that our simple low cost synthesis of manganese dioxide catalysts produced good performance in an MFC.

Yu et al. [19] performed single chamber MFCs tests with 50 mM phosphate buffer medium pH 7.0 and 1 g L⁻¹ of glucose in the chamber. They reported, at 30 °C, peak power densities of 634 mW m⁻² for FePc/KJB as cathode electrocatalyst compared with 474 mW m⁻² for a benchmark 20 wt% Pt/Vulcan XC72, showing better MFC performances with such platinum free materials, in agreement with their previous RDE experiments [19]. Carbon-supported FePc seem as efficient as the carbon-supported MnO_x as Pt-free materials for the cathode of MFC. A question over the use of such materials is that the cyanine radical is known to be potentially toxic for human health. Phthalocyanines are not expensive, although more expensive than manganese oxides. They are used in industry and not referred as toxic, the toxicity being more possibly due to the incorporated metal (copper for example). Another question still arises due to the issue of their stability: it is widely known that they are unstable in acidic solution, while being stable in alkaline medium [21]. Their stability in near neutral medium has yet to be demonstrated, especially if used in conjunction with proton conducting membranes. Note that the comparisons in terms of fuel cell performances are difficult to make from one study to another since experimental conditions (nature of the

electrolyte, temperature, interelectrode gap, electrode geometric area, etc.) greatly modify the MFC efficiency.

The catalysts were found to be stable in neutral pH solution during all the experiments, especially in the low current densities range experienced. For example, Fig. 5 shows the variation of current density with the time, at pH 7.0, of the MFCs with an external resistance of 1 kΩ for the three different catalysts (see the corresponding stable values in Fig. 2). The MFCs with Pt/C took a longer time to reach a stable current than with MnO_x/C (Fig. 5); the tests were duplicated and reproducible. The decline in current near the end of the test was due simply to depletion of fuel in the anode chamber.

Figure 6 shows the effect of Mn catalyst loading on the current generated during the MFC tests. The MFC performance improved, with over a 100% increase in current density, on increasing the Mn loading from 0.8 to 4.0 mg_{Mn} cm⁻². We believe that further improvements in MFC efficiency can be achieved, for a given loading of manganese, by improving the dispersion of the manganese oxide nanoparticles over the carbon (average diameter, particle size distribution).

Overall, the carbon-supported manganese oxides nanoparticles are very promising as cathode materials in neutral

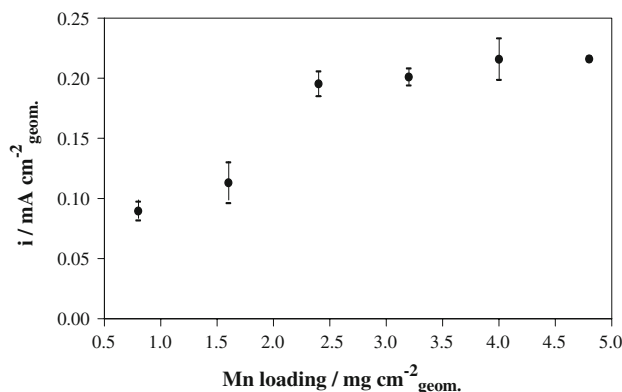
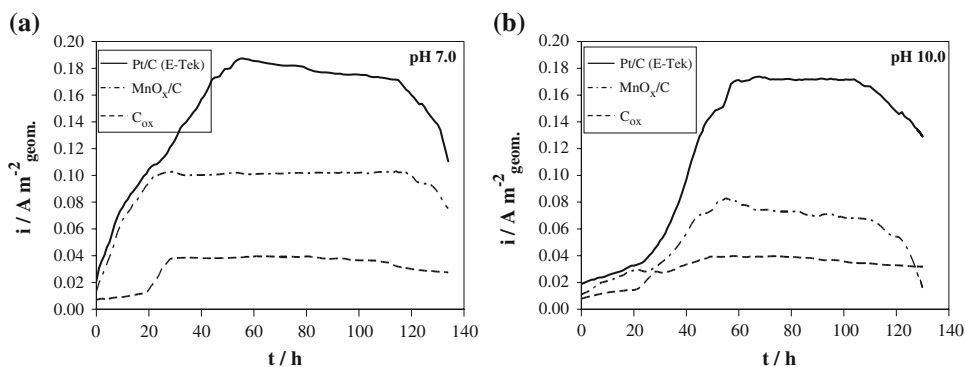


Fig. 6 Mn loading influence on the MFC performances, external resistance 1 kΩ, MnO_x/C as cathode materials, T_{room}, pH 7.0

Fig. 5 MFC i(t) curves, external resistance 1 kΩ, 20 wt% Pt/Vulcan XC72 (E-Tek), MnO_x/C or C_{ox} catalysts as cathode materials, T_{room}, pH 7.0 or 10.0



pH solution since they exhibit high ORR activities and very good stability in operating MFCs at very attractive cost. The MFC power performance reported here could be easily improved using more favourable conditions (more conductive electrolyte, cathodic catalyst improvement, etc.). In particular, using wastewater of low conductivity is important to design cells with low inter-electrode gaps to minimise Ohmic voltage losses.

3.2 pH influence

Figure 1 shows that the anodic potentials do not change with increasing pH of the cathode solution for all the studied catalysts. There was no noticeable effect of pollution by manganese species of the anodic side in the 7.0–10.0 pH range, i.e. no manganese diffusion across the membrane from the cathodic to the anodic sides. The value of the cathode potential $E_{\text{cathode}}^{\text{EXP}}$, however, decreased with higher pH for the three catalysts (around -0.4 V for MnO_x/C compare around -0.2 V for Pt/C). Note that by considering the Nernst equation of the ORR reaction, the difference in equilibrium potentials at pH 7.0 and 10.0 under standard conditions is -0.177 V, and partly explains the difference in cathode potentials at the two values of pH for Pt/C. In agreement with the RDE experiments [16], MnO_x/C exhibited higher ORR activity with decreasing OH^- concentration, platinum being unaffected in the 7.0–10.0 pH range. For C_{ox} , the cathode potential decreased with increasing pH to a lesser extent (around -0.1 V, Fig. 1) than the carbon-supported MnO_x or Pt catalysts. As noted previously [16], a non negligible quantity of hydrogen peroxides is formed per mole of oxygen reduced on the carbon surface; the 2-electron pathway is slightly improved by increasing OH^- concentration in the 7.0–10.0 pH range. Manganites (MnOOH) are formed by the proton insertion, first step of the ORR mechanism on MnO_x/C . Although their ability to degrade hydrogen peroxides can be improved by increasing OH^- concentration, less manganites are formed at pH 10.0. As a consequence, the manganese oxide nanoparticles dispersed on carbon are less interesting for use in pH 10.0 medium. Also note that the Pt/C efficiency also decreased with the increasing OH^- concentration in the considered pH range.

The detrimental influence of high pH on cathode potentials is also reproduced in the MFC cell voltage and power performance (Figs. 2, 3; Table 1). The OCVs were lower at pH 10.0 and there was a significant decrease of the depth of discharge, i.e. lower achievable current densities. The power densities curves (Fig. 3) show that the MFC performances were close, at pH 7.0–10.0, in the low current densities range ($i < 0.2 \text{ A m}_{\text{geom.}}^{-2}$) for the benchmark Pt/C catalyst. However, at greater cell polarisation, the power density performance of the MFC at pH 10.0 is much

lower than that at pH 7.0: experimental peak power densities are reduced from 161 to 67 mW m^{-2} for MnO_x/C catalysts. Notably with C_{ox} , the power density increase is much lower.

During MFC tests under a constant external resistance, MnO_x/C produced greater variations in current density than with other catalysts. For example, for the benchmark Pt/C (E-Tek), Fig. 3 shows that MFC performance was similar in the 7.0–10.0 pH range in the low current densities range (ca. $0.18 \text{ A m}_{\text{geom.}}^{-2}$ at pH 7.0 compare ca. $0.17 \text{ A m}_{\text{geom.}}^{-2}$ at pH 10.0). The MFC performance was however significantly different for MnO_x/C as cathode material (ca. $0.10 \text{ A m}_{\text{geom.}}^{-2}$ at pH 7.0 compare $0.07 \text{ A m}_{\text{geom.}}^{-2}$ at pH 10). Moreover, they were less stable ($-0.01 \text{ A m}_{\text{geom.}}^{-2}$ between 60 and 100 h for MnO_x/C compared with -0.00 for Pt/C). This small instability could be due to a slight dissolution of manganite in the pH 10 catholyte and then a loss of cathodic active catalyst with the time. However shorter term (1–2 days) RDE experiments did not reveal this possible material loss. Also note that the current took a longer time to stabilise with higher OH^- concentrations for MnO_x/C (ca. 60 h at pH 10.0 compared with ca. 25 h at pH 7.0), probably reflecting the slower ORR kinetics.

In agreement with the previous RDE experiments, operating MFCs, with MnO_x/C catalysts as cathode materials, exhibited good performances in the 7.0–10.0 pH range. This is of interest since wastewater could easily have a basic pH. However, although MFC performance was very stable in neutral pH medium, they could be unstable in more basic solution. Fuel cell testing using domestic wastewater is needed to assess the MFC ageing in real conditions. In particular, the carbon-supported manganese oxide nanoparticles morphology and chemistry could change with time in an operating fuel cell, especially in basic media. Moreover, hydrogen peroxides formed from the ORR, could corrode the cathode and degrade the membrane, decreasing MFC efficiency. It is important to study the ageing of all the components of the MFC during long-term operation. In addition, rotating ring disk electrode (RRDE) experiments would provide greater understanding of the ORR mechanism on MnO_x/C in the 7.0–10.0 pH and is part of on-going work.

4 Conclusion

Manganese oxide nanoparticles were chemically deposited over a carbon black having a great specific area, and successfully tested as electrocatalysts for 2 chambers microbial fuel cell cathodes. We showed that the dispersion of such particles over carbon has a beneficial effect on the MFCs performances since our MnO_x/C catalyst exhibits ORR activities close to those of a benchmark Pt/C (E-Tek)

especially because of the very attractive (low) price, with a good stability in the 7.0–10.0 pH range. In neutral pH solution and room temperature, the MFCs peak power densities were 161 mW m^{-2} and 193 mW m^{-2} for MnO_x/C and Pt/C , respectively, as cathode materials. The MFC performances could be easily improved using more favourable conditions (more conductive electrolyte, cathodic catalyst improvement etc.): theoretical IR free peak power densities being found to be 937 mW m^{-2} for MnO_x/C , compare $1,037 \text{ mW m}^{-2}$ for Pt/C . These results indicate that carbon-supported manganese oxides nanoparticles can easily replace platinum as cathode materials, showing promising interest for the successful commercialisation of MFCs systems.

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References

- Logan B (2005) *Water Environ Res* 77:211
- Logan B (2004) *Environ Sci Technol* A38:160A
- Rabaey K, Clauwaert P, Aelterman P, Verstraete W (2005) *Environ Sci Technol* 39:8077
- Tender LM, Reimers CE, Stecher HA, Holmes DE, Bond DR, Lowy DA, Pilobello K, Fertig SJ, Lovley DR (2002) *Nat Biotechnol* 20:821
- Kim HJ, Park HS, Hyun MS, Chang IS, Kim M, Kim BH (2002) *Enz Microbial Technol* 30:145
- Jang JK, Pham TH, Chang LS, Kang KH, Moon H, Cho KS, Kim BH (2003) *Process Biochem* 39:1007
- Delong EF, Chandler P (2002) *Nat Biotechnol* 20:788
- Liu H, Ramnarayanan R, Logan B (2004) *Environ Sci Technol* 38:2281
- Logan B (2005) *Water Sci Technol* 52:31
- Debabov VG (2008) *Microbiology* 77:123–131
- Rinaldi A, Mecheri B, Garavaglia V et al (2008) *Energy Environ Sci* 1:417–429
- Cheng S, Liu H, Logan B (2006) *Environ Sci Technol* 40:2426
- Davis F, Higson SPJ (2007) *Biosens Bioelectron* 22:1224–1235
- Logan B, Regan JM (2006) *Trends Microbiol* 14:512–518
- Gil GC, Chang IS, Kim BH, Kim M, Jang JK, Park HS, Kim HJ (2003) *Biosens Bioelectron* 18:327
- Jang JK, Pham TH, Chang IS, Kang KH, Moon H, Cho KS, Kim BH (2004) *Process Biochem* 39:1007
- Pham TH, Jang JK, Chang IS, Kim BH (2004) *J Microbiol Biotechnol* 14:324
- Kinoshita K (1992) *Electrochemical oxygen technology*, Wiley, New York
- Hao Yu E, Cheng S, Scott K, Logan B (2007) *J Power Sources* 171:275
- Clauwaert P, Van der Ha D, Boon N, Verbeken K, Verhaege M, Rabaey K, Verstraete W (2007) *Environ Sci Technol* 41:7564
- Zhang L, Liu C, Zhuang L, Li W, Zhou S, Zhang J (2009) *Biosens Bioelectron* 24:2825–2829
- Lefebvre O, Al-Mamun A, Ooi WK, Tang Z, Chua DHC, Ng HY (2008) *Water Sci Technol* 57(12):2031–2037
- Nguyen Cong H, Chartier P, Brenet J (1977) *J Appl Electrochem* 7:383–395
- Heller-Ling N, Poillierat G, Koenig JF, Gautier JL, Chartier P (1994) *Electrochim Acta* 39:1669
- Klápště B, Vondrák J, Velická J (2002) *Electrochim Acta* 47:2365
- Mao L, Zhang D, Sotomura T, Nakatsu K, Koshiba N, Ohsaka T (2003) *Electrochim Acta* 48:1015
- Chatenet M, Geniès-Bultel L, Arousseau M, Durand R, Andolfatto F (2002) *J Appl Electrochem* 32:1131
- Chatenet M, Arousseau M, Durand R, Andolfatto F (2003) *J Electrochem Soc* 150:D47
- Brock SL, Duan N, Tian ZR, Giraldo O, Zhou H, Suib SL (1998) *Chem Mater* 10:2619
- Roche I, Scott K (2009) *J Appl Electrochem* 39:197–204
- Roche I, Chainet E, Chatenet M, Vondrák J (2007) *J Phys Chem C* 111:1434–1443
- Vondrák J, Klápště B, Velická J, Sedlaříková M, Novák V, Reiter J (2005) *J New Mater Electrochem Syst* 8:1
- Bezdička P, Grygar T, Klápště B, Vondrák J (1999) *J Electrochim Acta* 45:913
- Roche I (2007) PhD INPG