

Non-catalyzed cathodic oxygen reduction at graphite granules in microbial fuel cells

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Abstract

Oxygen is the most sustainable electron acceptor currently available for microbial fuel cell (MFC) cathodes. However, its high overpotential for reduction to water limits the current that can be produced. Several materials and catalysts have previously been investigated in order to facilitate oxygen reduction at the cathode surface. This study shows that significant stable currents can be delivered by using a non-catalyzed cathode made of granular graphite. Power outputs up to 21 W m^{-3} (cathode total volume) or 50 W m^{-3} (cathode liquid volume) were attained in a continuous MFC fed with acetate. These values are higher than those obtained in several other studies using catalyzed graphite in various forms. The presence of nanoscale pores on granular graphite provides a high surface area for oxygen reduction. The current generated with this cathode can sustain an anodic volume specific COD removal rate of $1.46 \text{ kg}_{\text{COD}} \text{ m}^{-3} \text{ d}^{-1}$, which is higher than that of a conventional aerobic process. This study demonstrates that microbial fuel cells can be operated efficiently using high surface graphite as cathode material. This implies that research on microbial fuel cell cathodes should not only focus on catalysts, but also on high surface area materials.

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1. Introduction

Microbial fuel cells (MFCs) are an emerging technology for the treatment of reduced organic carbon in aqueous waste [1]. In a MFC, bacteria use an anode as electron acceptor for the oxidation of organic carbon to carbon dioxide (CO_2), with production of protons and electrons. The protons and/or other cations in solution are transferred to a cathode through a cation exchange membrane (CEM), while the electrons are transferred via an electrical circuit, where a resistor or power user harvests the energy liberated by the reaction. At the cathode an electron acceptor is reduced using the electrons delivered by the anode. The most sustainable electron acceptor known to date for microbial fuel cells is oxygen, due to its availability in the environment

and its high redox potential. However, some limitations reduce the effectiveness of O_2 as electron acceptor. First, the low oxygen solubility in water limits the availability of the electron acceptor to the electrode. The oxygen mass transfer limitation in the liquid phase has been alleviated with the use of open air cathodes [2], but the concentration of oxygen can never exceed saturation (7.8 mg/L at 25°C), as the electrode must be covered by a liquid film in order to allow for cation/proton transfer. Secondly, the high activation energy of O_2 reduction to water at a graphite electrode leads to high cathodic activation overpotential, i.e. drop in cathodic potential from open circuit value ($E_{\text{C,OC}}$) to closed circuit value (E_{C}) due to losses associated with the reaction kinetics. By reducing the MFC voltage, overpotentials strongly hinder electron transfer. Zhao et al. [3] demonstrated that graphite foil performs very poorly in a linear sweep voltammogram compared to different catalyzed cathodes. Oh et al. [4] found that during the generation of polarization curves the voltage over a MFC dropped to zero much more rapidly when O_2 was reduced on a plain carbon cathode than when catalyzed cathodes were used. Several researchers have investigated graphite-bound catalysts or soluble redox mediators as possible solutions to increase the rates of cathodic oxygen reduction. The use of hexacyanoferrate

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(Fe(CN)₆³⁻) as a soluble redox mediator has been unsuccessful due to the low rates of reoxidation of the compound from ferrous to ferric state [5]. Instead, the use of platinum at MFC cathodes has confirmed the lessons learned from conventional fuel cell technology, by significantly enhancing oxygen reduction rates, even at catalyst loads as low as 0.1 mg/cm² [6]. However, platinum has some severe drawbacks. First, it is subject to sulfide poisoning in wastewater applications and the cost of catalyst replacement can be prohibitive; secondly, the production of platinum is highly energy-intensive (150–250 kg of ore must be processed to produce 1 g of platinum) and thus the environmental impacts may outweigh the benefits [7]. In the search for cheaper and more sustainable catalysts, transition metal porphyrins and phthalocyanines [3] have emerged, yielding overpotentials in the same range as achieved with platinum. Another strategy has been the use of solubilised ferric iron at low pH (<2.5) as a redox mediator, which could be reoxidised by a population of (for example) *Acidithiobacillus ferrooxidans* [8]. This method reduces the overpotentials because Fe³⁺, not oxygen is being reduced at the cathode. The results obtained in the aforementioned studies and others are summarized in Table 1.

This study proposes a different approach to reduce the oxygen reduction overpotential. This approach is based on surface area rather than catalysis. Based on electrochemistry principles, the overpotential of oxygen reduction is dependent on the current density, as shown in Eq. (1) (Butler–Volmer equation):

$$i = i_0 \left[\exp \frac{\beta F \eta_{\text{cathode}}}{RT} - \exp \frac{-(1 - \beta) F \eta_{\text{cathode}}}{RT} \right] \quad (1)$$

In the equation, η_{cathode} is the cathodic overpotential ($E_{C,OC} - E_C$, V), R the ideal gas constant (8.31 J/mol K), T the absolute temperature (K), β the symmetry factor (a constant

which determines the dependence of the activation energy on the electrode potential and for a cathodic process reflects that the activation energy increases with electrode potential), F the Faraday's constant (96,485 C/mol), i the current density (mA/m²) and i_0 is the exchange current density, a parameter that depends on the activation energy of the reduction at equilibrium conditions (in a way that higher activation energy corresponds to lower exchange current). If the overpotential is large enough (greater than 80–100 mV at 25 °C) the second term in parenthesis becomes negligible and the equation can be simplified in the form known as Tafel equation:

$$\ln \left(\frac{i}{i_0} \right) = \frac{\beta F \eta_{\text{cathode}}}{RT} \quad (2)$$

The equation shows that the activation overpotential increases with the current density. Instead of using a catalyst to reduce the activation energy for oxygen reduction (i.e. increasing the parameter i_0), our approach has been to reduce the current density through use of a non-catalyzed material with a high surface area. This would still cause a decrease of the overpotential, through a reduction of the current density rather than the activation energy. The material selected was coarse and highly porous industrial grade granular graphite. Some investigators have previously observed currents generated in sediments fuel cells by oxygen reduction on plain graphite in marine environments [9,10]. However, it was suggested that in those cases bacterial colonization of the cathode may have aided electron transfer through a biocatalytic process. In this study we eliminated every possible chemical and biological catalytic process to test the ability of plain graphite granules to carry out cathodic oxygen reduction.

Table 1
Summary of performance parameters of different oxygen cathode microbial fuel cells

Reference	[4]	[4]	[3]	[8]	[18]	This work
Cathode material	Carbon paper	Carbon paper	Carbon cloth	Graphite felt	Carbon cloth	Graphite granules
Catalyst	None	Platinum (0.5 mg/cm ²)	COMTPP	Fe ³⁺ /Fe ²⁺	Platinum (0.5 mg/cm ²)	None
Aeration mode	Air sparged	Air sparged	Air sparged	Air sparged	Passive air cathode	Air sparged
Reactor operation	Batch	Batch	Batch	Batch	Continuous	Continuous
Cathode nominal surface area (m ²)	1.13 × 10 ⁻³	1.13 × 10 ⁻³	3.0 × 10 ⁻³	2.9 × 10 ⁻²	7.0 × 10 ⁻⁴	1.26
Cathode total volume (m ³)	2.5 × 10 ⁻⁴	2.5 × 10 ⁻⁴	2.5 × 10 ⁻⁴	6.2 × 10 ⁻⁴	1.3 × 10 ⁻⁶	3.5 × 10 ⁻⁴
Reactor total volume (m ³)	5.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴	1.2 × 10 ⁻³	1.4 × 10 ⁻⁵	7.0 × 10 ⁻⁴
Current to cathode surface area at MPP ^a (mA m ⁻²) ^b	133	373	1900	1300	6200	17
Current to cathode total volume at MPP ^a (A m ⁻³) ^c	0.6	1.7	24	61	3340	63
Power to cathode total volume at MPP ^a (W m ⁻³) ^c	0.08	0.8	14	25	1240	21
Power to reactor total volume at MPP ^a (W m ⁻³)	0.04	0.4	7	13	115	11
COD removal	n/a	80%	n/a	n/a	n/a	91%
Max. coulombic efficiency	n/a	63–78%	n/a	80–95%	30–60%	65%
Max. energy efficiency	n/a	<15%	n/a	18–29%	15%	13%

Some values are calculated from other data reported by the investigators; n/a: Value not reported by the authors and could not be calculated from other data.

^a Maximum power point.

^b Nominal (or projected) surface area.

^c The cathodic volume includes the electrode volume and the liquid volume.

2. Materials and methods

2.1. Microbial fuel cell

A double-chambered microbial fuel cell was built as previously described [11]. Both compartments had a total volume of 350 mL and were filled with granular graphite. The cathode granular graphite (El Carb 100, Graphite Sales Inc., USA) had a diameter <1 mm, a void fraction of 42% (giving a net liquid volume of 147 mL) and a bulk density of 951 kg m⁻³. The anode contained larger graphite granules (same manufacturer, 2–6 mm diameter, void fraction 48%, giving a net liquid volume of 168 mL). The compartments were separated by an Ultrex cation exchange membrane (CMI-7000, Membranes International, USA). The anodic compartment was inoculated with a microbial consortium previously enriched in MFCs [11], and continuously fed with a modified M9 medium as previously described [11]. Acetate was added to the growth medium as electron donor to a concentration of 642 mg/L as sodium acetate, which was fed to the anodic reactor at a flow rate 540 mL/d, giving rise to an organic loading rate of 1.61 kg_{COD} m⁻³ d⁻¹. The anolyte was recirculated at 100 mL/min to achieve well-mixed conditions. The catholyte consisted of the same modified M9 medium, also recirculated at 100 mL/min, but without addition of an electron donor. A 2 L bottle was used as a buffer tank to reduce the rate of pH increase at the cathode. During generation of polarization curves, the pH was instead controlled to a set point with a pH probe and controller as previously described [11]. To provide oxygen for the cathodic reaction, the cathodic chamber was continuously sparged with air using an aquarium pump. The external resistance of the circuit was maintained at 10 Ω except during the generation of polarization curves.

2.2. Cathode characterization

The granules were washed for 24 h in 32% HCl to remove metals from the surface. To achieve thorough removal of metals leaching from the inner pores of the granules, the washing process was repeated four times. The purpose of this treatment was to eliminate any potentially catalytic foreign compounds from the graphite material. By killing all microorganisms, this treatment also eliminated any potential biocatalyst that could affect the cathode performance. To ensure that no biofilm would affect the results, the experiments were started immediately after adding the sterile granules to the reactor. The fact that the cathode performance did not change over time indicated that no biocatalysis developed during the operation of this reactor. The surface concentrations of metals before and after wash were determined by the following procedure. The granules were finely ground and 10 g of the <425 μm fraction was digested using an Anton Paar Multiwave microwave system in PTFE digestion vessels in aqua regia (3:1 HCl/HNO₃) at 150 °C and 3000 kPa. The digest solutions contained the metals extracted by the acid. Metal concentrations were determined with a Thermo-Electron X-7 series inductively coupled plasma-mass spectrometer (ICP-MS). The surface area of the granules was determined by the mercury porosimetry method described by Favas and Jackson [12]. The

method is able to quantify the surface area of pores as small as 6 nm.

2.3. Electrochemical monitoring, calculations and analysis

During continuous operation the cell voltage was recorded using an Agilent 34970A data acquisition unit. The current was calculated from the external resistance using Ohm's law. COD removal, Coulombic efficiency and energy efficiency were calculated as previously described [13]. Polarization curves were generated during the continuous feeding regime using a potentiostat (VMP3 multichannel potentiostat, Princeton Applied Research, USA). The MFC was first run at open circuit for 2 h to achieve a steady open circuit voltage and subsequently the MFC voltage was varied with the potentiostat at the scan rate of 0.1 mV/s. Liquid samples from the microbial fuel cell anode side were analysed for volatile fatty acids (VFAs) as previously described [11].

2.4. Cathodic electron and proton balances

The putative cathodic process is given by reaction (3):



The electron and proton balances at the cathode were closed by measuring all the identified sources and sinks of electrons and protons, in order to prove that Eq. (3) completely describes the cathodic process. The current was monitored as described above. The oxygen uptake rate (OUR) and proton consumption rate (PCR) were measured with a titration and off-gas analysis (TOGA) sensor, first developed by Pratt et al. [14] and previously applied to close balances at MFC anodes [11]. The cathodic compartment was sparged with an oxygen containing gas at a known composition (50% O₂, 46.5% Ar, 3.0% N₂ and 0.5% CO₂). The off-gas concentration was subsequently measured with a mass spectrometer (Omnistar, Balzers AG, Liechtenstein), revealing the rate of oxygen consumption. The rate of H⁺ consumption was determined by measuring the amount of acid required to maintain the pH at a constant set point of 6.50 ± 0.01. Proton diffusion across the CEM was neglected based on the findings of a previous study [11].

3. Results

3.1. Electrode characterisation

The total surface area of the granules (including all pores larger than 6 nm) was determined by mercury porosimetry to be 6.0 × 10⁶ m²/m³. This is the true surface area that should be used for the calculation of current densities in the Tafel equation. This area is three orders of magnitude higher than the nominal surface area (calculated assuming the granules to be spheres of 1 mm diameter) of 3600 m²/m³. As a basis of comparison, the total surface area of graphite felt (Morgan Carbon Australia) was measured with the same method. Its value was 2.8 × 10⁶ m²/m³, smaller than the value for the granules, demonstrating that the

granules likely owe their activity for oxygen reduction to their large specific surface area.

The metals content of the graphite surface was substantially reduced following the acid wash process. The Fe surface concentration went from 675 mg/m² (nominal electrode surface, see definition above) to 46 mg/m², Mn from 8.0 to 1.7 mg/m², Ni from 12.4 to 4.2 mg/m², and Al from 123 to 35 mg/m². Other metals were present in much lower quantities. The surface concentrations of these metals were assumed to be too low to support significant catalytic activity. Previous studies [6] reported that platinum, the most active catalyst for oxygen reduction, need to be present with a surface concentration of at least 1000 mg/m² in order to be sufficiently active.

3.2. Proof of the nature of the cathodic process

Electron and proton balances were closed with errors of 4.7 and 11.5% respectively, demonstrating that Eq. (3) is a satisfactory description of the cathodic process and that no side processes occur at the cathode. Also, this result shows that no parasitic diffusion of electron donor/acceptor across the CEM is happening. Lack of diffusion of oxygen across the Ultrex CEM was also independently proven with diffusion tests in an abiotic fuel cell. Oxygen was shown to diffuse with a low mass transfer coefficient of $3.30 \pm 0.04 \times 10^{-5}$ cm/s (0.147 mgO₂/h for the reactor used in this study). Acetate diffusion through Ultrex was shown to be negligible in a previous study [15].

3.3. Polarization curves and power curves

Polarization curves were generated at pH 3.0 ± 0.01 , 6.5 ± 0.01 and 9.0 ± 0.01 . The Nernstian effect of the pH (Eq. (4)) is reflected by the fact that the voltage dropped even at open circuit with increasing pH:

$$E_C = E_C^0 + \frac{RT}{4F} \ln(P_{O_2}) - \frac{2.3RT}{F} \text{pH} \quad (4)$$

In the equation, P_{O_2} is the partial pressure of oxygen in atm and E_C^0 is the cathodic potential at standard conditions ($T = 25^\circ\text{C}$, pH 0, $P_{O_2} = 1$ atm).

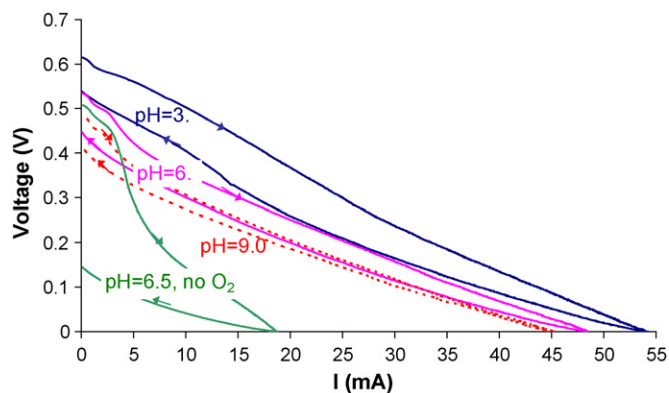


Fig. 1. Polarization curves at different conditions for MFC with non-catalyzed high surface area (6×10^6 m²/m³) granular graphite oxygen cathode.

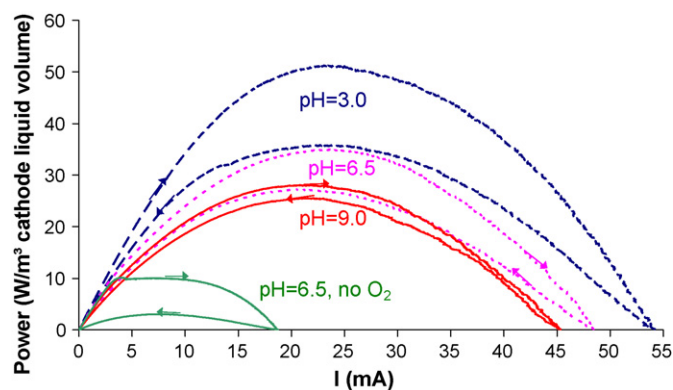


Fig. 2. Power curves at different conditions for MFC with non-catalyzed high surface area (6×10^6 m²/m³) granular graphite oxygen cathode.

Fig. 1 shows the forward (from open circuit to short circuit) and backward (from short circuit to open circuit) polarization curves. The difference between the forward and backward curves is due to the hysteresis effect when oxidizing/reducing compounds at a certain scan rate. A fourth curve was generated at pH 6.5 without aeration and after depletion of all the dissolved oxygen through nitrogen stripping. In this case the open circuit voltage before starting the polarization experiment was of similar value to the aerated case, possibly due to previous oxygen adsorption onto the pores of the graphite or to the presence of small residual quantities of metal ions (primarily iron), which can act as alternative electron acceptors. After a rapid depletion of these oxidized species the voltage rapidly dropped and the current decreased to negligible levels, thus confirming that oxygen is indeed the terminal electron acceptor at this cathode. Fig. 2 shows the forward and backward power curves for the four test conditions.

The polarization curves generated with the same reactor and hexacyanoferrate as cathodic electron acceptor (data not shown) reached currents greater than 100 mA, indicating that the abiotic cathode was the limiting step to current generation in this study.

3.4. Oxygen reduction kinetics

During generation of the aforementioned polarization curves the values of the cathodic potential versus a standard Ag/AgCl reference electrode were continuously recorded. This allowed for the calculation of cathodic overpotentials as a difference between the open circuit and the closed circuit potentials. Tafel plots ($\ln(i)$ versus η) could thereby be generated as shown in Fig. 3. After an initial steep current increase, the Tafel lines become linear. Based on the Tafel equation, the slope is $\beta F/RT$ and the y-axis intercept is the logarithm of the exchange current ($\ln i_0$). The resulting symmetry factor β was found to be pH-dependent, with values of 0.17, 0.32 and 0.38 at pH 3, 6.5 and 9, respectively. A β value less than 0.5 is normally considered an indicator that a high activation energy is required to bring the electron acceptor to the chemical state at which it is able to exchange electrons with the electrode [16]. Typically, cathodic oxygen reduction gives β values less than 0.5.

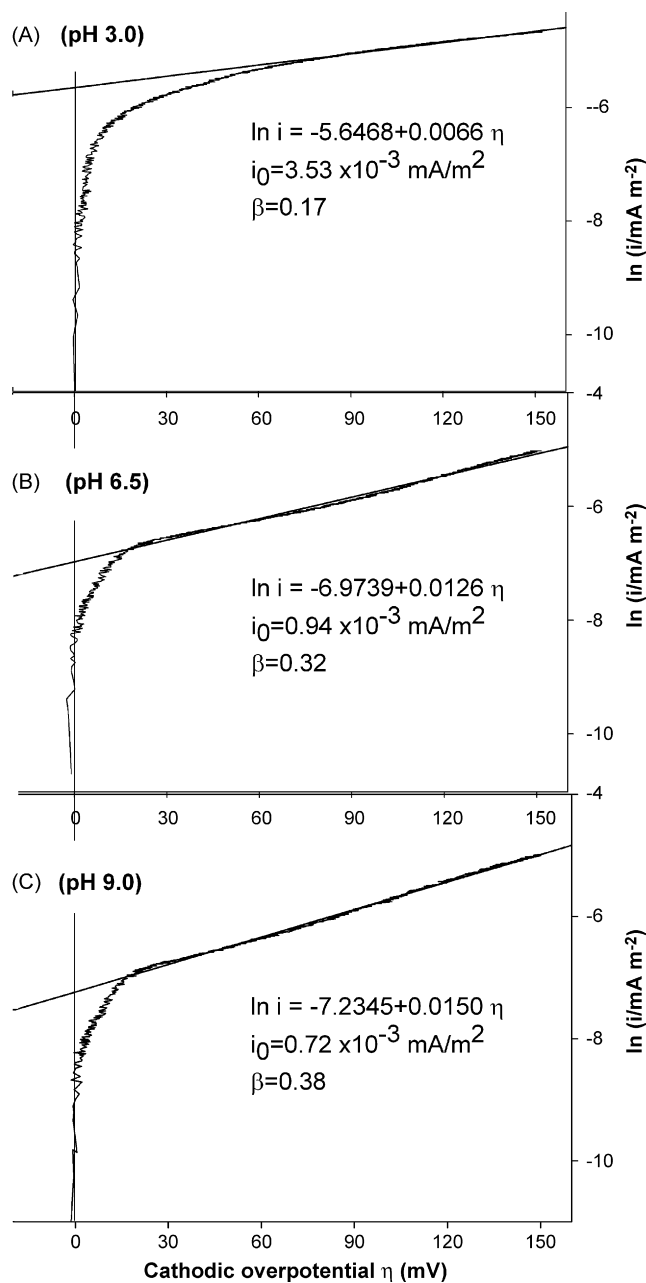


Fig. 3. Tafel plots for the estimation of i_0 and β for the reduction of oxygen on non-catalyzed graphite granules at pH 3.0 (A), pH 6.5 (B) and pH 9.0 (C).

As previously reported [17], oxygen is reduced on a platinum electrode with β values of 0.25 at pH 0 and 0.30 at pH 14 (both values at 25 °C). The exchange current was also dependent on the pH, its values being 3.53×10^{-3} , 0.94×10^{-3} and $0.72 \times 10^{-3} \text{ mA/m}^2$ at pH 3, 6.5 and 9, respectively (currents normalized to the true surface area). As expected, these values are very small compared to the exchange currents observed for oxygen discharge on catalyzed cathodes. For example, Hamnett [17] reported a value of 10 mA/m^2 for the reduction of O_2 on platinum. The i_0 values suggest that at low pH the activation energy for O_2 reduction is smaller than at high pH in open circuit conditions.

3.5. Continuous operation

The reactor ran in continuous mode for several weeks. At pH 6.5, the current production was $21.8 \pm 0.3 \text{ mA}$ at an external resistance of 10Ω . Overall acetate removal was $1.46 \text{ kgCOD m}^{-3} \text{ d}^{-1}$, of which $0.95 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ were converted to current, yielding a Coulombic efficiency of 65% and an energy efficiency of 11%. These volume specific removal rates are slightly higher than those of a typical activated sludge process. The energy calculation did not include the energy required for cathode aeration and recirculation of the medium: only electrochemical losses were included.

4. Discussion

In previous research, the problem of the overpotential of oxygen reduction at microbial fuel cell cathodes has been addressed through specific selection of catalysts and electrode materials. Only few data were generated for non-catalyzed cathodes, as they were thought not to have the ability to sustain the current demanded by microbial fuel cell anodes. Only two studies done on MFC oxygen cathodes have reported data on plain carbon electrodes [3,4]. In both cases they performed poorly compared to catalyzed materials. To our knowledge, no research has been carried out to date to test non-catalyzed graphite with high available surface areas as a cathode. Table 1 summarizes the results of some major previous research on oxygen cathodes, including studies on plain graphite [4], platinum on graphite [4], cobalt tetramethoxyphenylporphyrin (COMTPP) on graphite [3], Fe^{3+} as a mediator at low pH [8], and platinum on carbon in open air configuration [18]. The current and power data (at the maximum power point) are presented normalised both to the cathode surface area and to the total cathode volume (electrode volume plus liquid volume). While surface specific parameters are indicators of the performance of the electrode material, current and power per unit volume are parameters that can quantify the cathode performance as a whole and can be used to compare the performance of very different reactor configurations. The non-catalyzed graphite granules studied here have a performance in terms of current and power per unit volume that is comparable to that of most other catalyzed aqueous cathodes. Air cathodes in two dimensions [18] have larger current and power densities due to the compactness of the cathode. However, the total reactor volume is often controlled by the anode side, so the power output per unit of total reactor volume is of similar magnitude regardless of the cathode configuration, as shown in Table 1. The current per unit area is much smaller for the non-catalyzed granules than for the other materials. This confirms that the high surface area is responsible for keeping the overpotential low and hence enables the cathodic effects observed in this process. The COD removal, Coulombic efficiency and energy efficiency are in the same range as other oxygen cathode MFCs. The energy efficiency for direct oxygen reduction on the cathode appears to be consistently limited to around 15% for all the reported studies as a consequence of the large overpotential of this reaction, even with chemically catalyzed cathodes. Ter Heijne et al. [8] obtained larger energy efficien-

cies (up to 29%) by avoiding the direct reduction of O₂ at the cathode.

This study showed that a stable microbial fuel cell process can be obtained with a catalyst-free material as a cathode, which requires little maintenance and is capable of sustaining a volume specific COD removal rate similar to that of an activated sludge process. The cost of the material is approximately US\$ 1.75 kg⁻¹, which would be equivalent to US\$79 per Watt based on the maximum power output reported in Table 1. In comparison, using the best power output achieved with Pt-catalyzed cathodes (Cheng and Logan [18], see Table 1) and a cost of platinum of US\$ 45 g⁻¹ as of April 2007 [19], the cost of the platinum alone for a Pt-catalyzed cathode would be US\$ 98 W⁻¹, which does not include the cost of the carbon and PTFE used as cathode materials, nor the cost of depositing platinum on the electrode surface. The non-catalyzed granules are thereby competitive with the platinum-catalyzed cathodes even on a cost basis, despite the need of larger quantities of material.

The limitation of this process is that the cathodic pH continuously increases based on reaction (3) because of the lack of selectivity for protons of the currently available ion exchange membranes. However, this problem is common to all oxygen cathodes of microbial fuel cells that use a cation exchange membrane.

5. Conclusions

Despite common belief that oxygen reduction on plain graphite cannot sustain the current densities delivered by microbial fuel cell anodes, in this study we proved that granular graphite is able to support cathodic oxygen reduction thanks to its very large specific surface area. Granular graphite is competitive with low-surface catalyzed cathodes in terms of cost and power production, as it can be summarized as follows:

- Granular graphite is able to sustain volumetric power densities of up to 11 W m⁻³ total reactor volume (50 W m⁻³ cathode liquid volume), which is in the same order of magnitude as most catalyzed materials previously tested.
- The cost of electrode material per Watt produced is US\$ 79 compared to US\$ 98 of a platinum-coated cathode.
- The energy losses at the cathode are similar to those of catalyzed materials, with energy efficiencies around 13%.

The use of plain granular graphite as a cathode material is very promising for wastewater treatment applications, where the use of expensive catalysts is not justified and the environment conditions expose any metals to sulfide poisoning.

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