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# Nitric acid activation of graphite granules to increase the performance of the non-catalyzed oxygen reduction reaction (ORR) for MFC applications

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## A B S T R A C T

Nitric acid and thermal activation of graphite granules were explored to increase the electrocatalytic performance of dissolved oxygen reduction at neutral pH for microbial fuel cell (MFC) applications. Electrochemical experiments showed an improvement of +400 mV in open circuit potential for graphite granules when they were activated. The improvement of ORR performance observed with activated granules was correlated to the increase of Brunauer–Emmett–Teller (BET) surface of the activated material and the emergence of nitrogen superficial groups revealed by X-ray photoelectron spectroscopy (XPS) analysis on its surface.

The use of activated graphite granules in the cathodic compartment of a dual-chamber MFC led to a high open circuit voltage of 1050 mV, which is among one of the highest reported so far. The stable performance of this cathode material (current density of  $96 \text{ A m}^{-3}$  at +200 mV/Ag–AgCl) over a period of 10 days demonstrated its applicability as a cathode material without any costly noble metal.

### Keywords:

Microbial fuel cell  
Oxygen reduction reaction  
Activated granules  
High voltage

## 1. Introduction

The cathodic overpotential of oxygen reduction reaction (ORR) at microbial fuel cell (MFC) cathodes based graphite is actually a limiting drawback for the wide development of the technology [1,2]. Basically, the cathode performance can be improved in two ways, either by using a catalyst to reduce the activation energy or by increasing the specific surface area of the graphite material. Many studies reported an increase of the ORR rates involving innovative and cheap catalysts [3,4], and several researchers have used in cathode construction non-catalyzed three-dimensional graphite such as cloth, felt, sponge, or granules [5,6]. The use of activated graphite material for cathode has not been enough explored so far.

Activated carbon and graphite are widely used materials in the industry as catalytic support in industrial reactions mainly because of its inertness, low cost, high surface area, and low deactivation [7]. Their main applications are in the water and wastewater treatment and as adsorbent of heavy metals and organic compounds. Activated carbon has oxygen and nitrogen groups on its surface, which gives many of its chemical properties [8]. Thermal or chem-

ical pretreatments are known to introduce these groups and change the texture of the material surface.

In this work, both chemical and thermal activation of graphite granules were explored to increase the electrocatalytic performance of dissolved oxygen reduction at neutral pH. The new surface properties were analysed coupling BET and XPS analysis. Additionally, activated graphite granules were tested as cathode material in a dual-chamber MFC involving an optimized bioanode prepared under constant potential as described by [9].

## 2. Experimental procedure

### 2.1. Activation of graphite granules

Graphite granules were dispersed in a 1000 ml flask of 5% nitric acid. The mixture was refluxed for 12 h at 120 °C. Treated granules were filtered and washed for 15 min with a continuous flow of deionized water, and then dried at 110 °C in an oven for 12 h.

### 2.2. Electrochemical analysis

ORR performance was investigated at room temperature (20 °C) performing cyclic voltammetries on 50 mL of graphite granules at a scan rate of 1.0 mV/s. Experiments were performed in a 100 mM

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phosphate buffer solution at pH 7.0 (PBS 7.0) continuously sparged with air using a three-electrode system implemented with a potentiostat/galvonostat (Gill AC, ACM instruments, UK). The auxiliary electrode was a platinum mesh (4 cm<sup>2</sup>) and all potentials were measured using Ag–AgCl reference electrode.

### 2.3. Material analysis

XPS analyses were performed using a Perkin Elmer PHI5700 (Physical Electronics, USA). Each sample was screened with Al K $\alpha$  ( $h\nu = 1486.6$  eV) as the X-ray source and the vacuum degree in analysing room was controlled as  $9.3 \times 10^{-8}$  Pa. BET surface area measurements were made using a ASAP 2020 M (Micromeritics Instrument Corporation, USA).

### 2.4. Dual-chamber MFC tests

MFC performances were evaluated in dual-chamber MFC constituted by two cylinder compartment of 50 mL (4 cm diameter), separated by a Entek<sup>®</sup> membrane (Entek International INC). Both anode and cathode compartments were filled with graphite gran-

ules packed into titanium mesh which was used to collect the current. Synthetic wastewater supplemented with 1 g/L acetate was used as fuel in anodic chamber whilst the catholyte was 100 mM PBS 7.0. The MFC was operated in batch conditions at room temperature (20 °C). Voltage and electrode potentials were recorded using a data acquisition system (Pico data logger, PicoTechnology, UK). Electrochemical polarization curves were performed by varying the external resistance over a range from 1 to 3 M  $\Omega$ .

## 3. Results and discussion

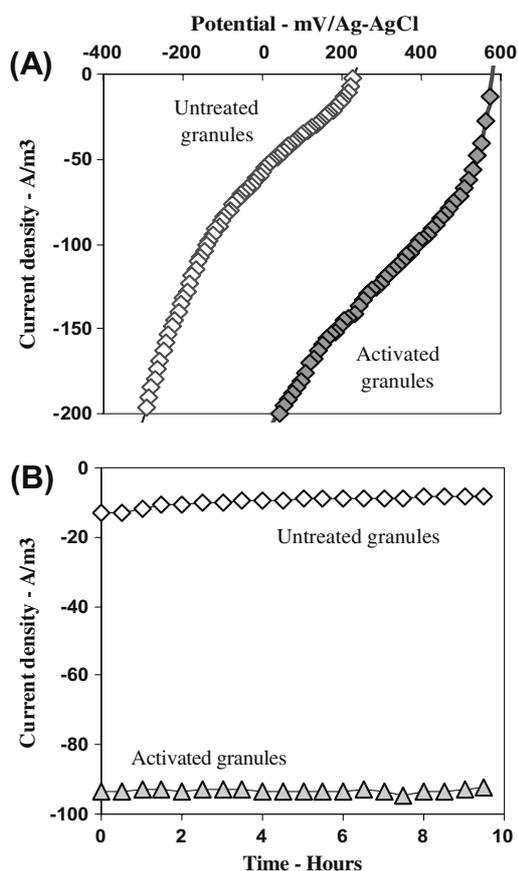
### 3.1. Effect of HNO<sub>3</sub> activation on ORR performance

The electrocatalytic performance for dissolved oxygen reduction on graphite granules was first investigated by using cyclic voltammetry measurements. A huge improvement of ORR was observed with activated granules in comparison to untreated one, as shown in Fig. 1A. The open circuit potential (OCP) of the graphite granules increased to +600 mV/Ag–AgCl, instead of +200 mV/Ag–AgCl, when they are activated by HNO<sub>3</sub>/temperature treatment. The stability of performance was evaluated from the current density resulting from the ORR on activated granules for 10 days at a constant potential of +200 mV/Ag–AgCl. The electrochemical oxygen reduction on activated granules was stable during the 10 days experiment and furnished an average current density of 96 A m<sup>-3</sup> of granules whilst the control experiment led with untreated granules could sustain only 16 A m<sup>-3</sup> (Fig. 1B).

Data reported in the literature showed that the increase of the catalytic performance of graphite material can be related to the increase of real surface area or due to the presence of superficial functional groups such as nitrogen groups [10] or oxygenated groups [8]. To determine how the acidic treatment affected the material surface, the granules structure, the porosity and the superficial groups composition were characterized from BET and XPS analysis. Nitric acid activation increased the specific surface area of graphite granules 2.5-times (i.e. 4.4 m<sup>2</sup>/g after treatment). XPS analysis data obtained for both untreated and activated graphite granules are presented in Table 1. As expected, carbon represented the most abundant element of the surface in both samples. Si was present in both samples showing that the acidic treatment did not remove this element from granules. Nitric acid activation led to a slight increase of both C and N contents. The oxygen quantity decreased in activated granules, due to the replacement with nitrogen during the chemical treatment. Relatively higher amount of nitrogen present in activated sample can be related to the presence of pyridinic groups on the surface or other CN<sub>x</sub> groups like amorphous carbon [10]. Thus, the improvement of ORR performance might be explained by the modification of BET surface area coupled to the emergence of nitrogen superficial groups on the activated granules surface.

### 3.2. MFC performances with graphite granules as cathode material

To assess the possibility of using activated granules in cathodic compartment of MFCs, two experiments were carried out in a dual-chamber MFC. The cathodic compartment received first 50 mL of untreated granules and in the second test 50 mL of activated granules. In both tests, the anodic compartment was filled with 50 mL



**Fig. 1.** Current–potential curves (A) and performance stability at +200 mV/Ag–AgCl (B) of the non-catalyzed oxygen reduction recorded on 50 mL of untreated and activated graphite granules immersed in 50 mM PBS pH 7.0; 20 °C; potential scan rate 1 mV/s.

**Table 1**  
Relative atomic concentration (%) on graphite granules surface.

Sample	C1s content (%)	O1s content (%)	S2p content (%)	Si2p content (%)	N1s content (%)
Untreated graphite granules	66.60	25.62	0.29	4.71	0
Activated graphite granules	69.58	21.60	0.32	5.58	2.37

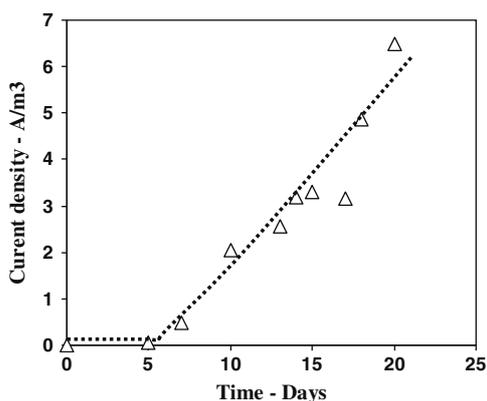


Fig. 2. Current density recorded on a microbial graphite granule electrode polarized at  $-200$  mV/Ag–AgCl inoculated with activated sludge.

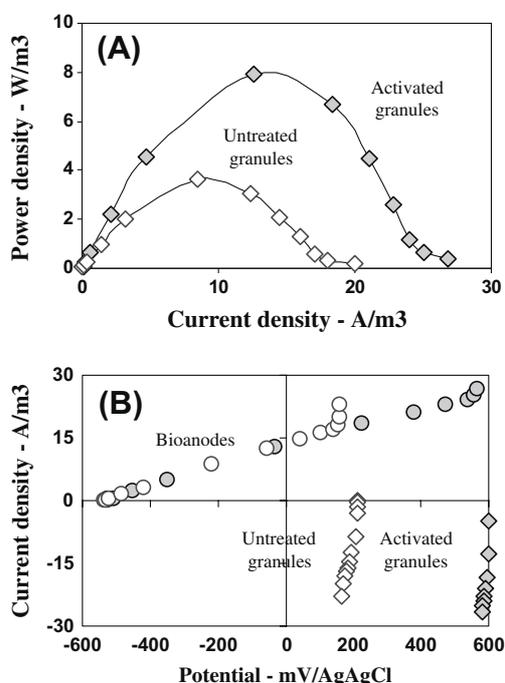


Fig. 3. Curves of polarization (A) and electrodes behaviour (B) obtained from a dual-chamber MFC using untreated and activated graphite granules as cathode materials for oxygen reduction reaction.

of microbial anode based graphite granule prepared as described by [9]. The 50 mL of untreated graphite granules were colonized under constant potential polarization at  $-200$  mV/Ag–AgCl in synthetic wastewater supplemented with 1 g/L of acetate and inoculated with 20% of activated sludge. After 3 weeks, this microbial anode showed an open circuit potential (OCP) of  $-540$  V/Ag–AgCl and could sustain  $7.0$  A  $m^{-3}$  at  $-200$  mV/Ag–AgCl (Fig. 2). Indeed, the start-up time of a MFC is strongly dictated by the potential at the surface of the anode. This potential is influenced by different parameters including the coupling between the performance of the cathode and the applied external resistance [11–13], which drive the anode potential in oxidation potential area (positive potential) or reduction potential area (negative potential). Here, the preparation of bioanode under controlled potential avoid the effect

of the start-up time and allow to compare directly the steady-state performance of the cells.

The MFC filled with 50 mL of untreated granules as cathodic material provided a maximum power density near  $3.9$  W  $m^{-3}$  and a maximum current density of  $19.8$  A  $m^{-3}$  (with respect to the cathode volume) as shown in Fig. 3A. These values were seriously limited by bioanode overpotential (Fig. 3B), i.e. increase of anodic potential from the OCP ( $-540$  mV/Ag–AgCl) to short-circuit value ( $+178$  mV/Ag–AgCl) due to losses associated with the microbial reaction kinetics. Consequently, the performance was lower than the  $21$  W  $m^{-3}$  and  $63$  A  $m^{-3}$  as already reported in the literature with graphite granules as cathode [5]. However, when the untreated granules were replaced by chemically activated granules, the voltage of the cell increased from 660 to 1050 mV that means a gain of approximately 400 mV due to the treatment of granules. An average voltage jump of 150 mV with  $MnO_2$  and 250 mV with Pt catalysts is often considered by the researchers [14,15]. In addition, the maximum power density reached  $8.1$  W  $m^{-3}$ , i.e. 2-times the maximum power obtained with the dual-chamber MFC initially filled with untreated granules and with the same conditions (pH, PBS concentration, temperature, Entek® membrane...) (Fig. 3A). The maximum current density output of the cell was also improved with a gain of  $8.0$  A  $m^{-3}$  since the current density approached  $28$  A  $m^{-3}$ . The analysis of the cathode behaviour during polarization, presented in Fig. 3B, revealed a very low cathode overpotential of 40 mV sustaining  $28$  A  $m^{-3}$ . This observation is interesting confirming the performance for dissolved oxygen reduction observed by using voltammetry measurements (Fig. 1A). A control test was conducted by depleting dissolved oxygen with a flow of nitrogen gas. As expected, a sharp drop of the cell voltage was consequently noted thus confirming that oxygen is indeed the oxidant at the cathode. The MFC was finally operated applying a  $560$   $\Omega$  external resistance and the cathode potential then remained stable during operation for a two weeks experiment.

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