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Effect of chemically modified Vulcan XC-72R on the performance of air-breathing cathode in a single-chamber microbial fuel cell

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A B S T R A C T

The catalytic activity of modified carbon powder (Vulcan XC-72R) for oxygen reduction reaction (ORR) in an air-breathing cathode of a microbial fuel cell (MFC) has been investigated. Chemical modification was carried out by using various chemicals, namely 5% nitric acid, 0.2 N phosphoric acid, 0.2 N potassium hydroxide and 10% hydrogen peroxide. Electrochemical study was performed for ORR of these modified carbon materials in the buffer solution pH range of 6–7.5 in the anodic compartment. Although, these treatments influenced the surface properties of the carbon material, as evident from the SEM-EDX analysis, treatment with H₂PO₄, KOH, and H₂O₂ did not show significant activity during the electrochemical test. The HNO₃ treated Vulcan demonstrated significant ORR activity and when used in the single-chamber MFC cathode, current densities (1115 mA/m², at 5.6 mV) greater than those for a Pt-supported un-treated carbon cathode were achieved. However, the power density for the latter was higher. Such chemically modified carbon material can be a cheaper alternative for expensive platinum catalyst used in MFC cathode construction.

1. Introduction

Treatment and disposal of wastewaters represent one of the major problems of the modern society due to insufficient and inadequate treatment. Present technologies used for wastewater treatment are energy intensive and they are not able to recover valuable products present in different wastewaters. This can be solved by using microbial fuel cell (MFC), due to capacity of specific bacteria to transform organic compounds in electricity and simultaneously achieving wastewater treatment (Rabaey and Verstraete, 2005). The major limitations faced by MFCs towards commercialization is very high cost of the catalysts used for cathode construction to harvest more power.

In order to minimize the operating cost, an air-breathing single-chamber MFCs are being developed by the researchers (Liu et al., 2004); such air-cathode MFC is an efficient and sustainable MFC configuration for recovering electrical energy from organic substances. In a graphite-granule anode and tubular air-cathode MFC, continuous electricity generation was reported at a maxi-

mum volumetric power of 50.2 W/m³ with a current density of 216 A/m³ from glucose (You et al., 2007). Increased use of single-chamber air-cathode MFC is being observed with simple or modified carbon (pretreated or with metals coating) acting as cathode electrode material (Liu et al., 2004; Wang and Han, 2009). The important characteristics for any catalyst used on the electrodes are: stability, mechanical properties, surface area and chemical composition (Rodriguez-Reinoso, 1998).

Electrode modifications were actively investigated to increase cathodic oxygen reduction. In fuel cells, Pt-coated carbon cathodes yielded higher performance than those with only graphite or carbon cathodes, by increasing their affinity for oxygen and decreasing the activation energy of the oxygen reduction reaction (ORR) occurring on the cathode surface (Freguia et al., 2007). However, its poor kinetics of ORR in neutral pH environment and low temperature, associated with its sulphide poisoning in wastewater applications, has limited its use in MFC cathode investigation (Karyakin et al., 2005; Shukla et al., 2004). Other cheaper catalysts, such as, CoTMP, Mn(IV), Fe(III), deposited on air-breathing cathode can also increase the power output (Roche and Scott, 2009; Yu et al., 2008). For example, Park and Zeikus reported a 100-times increase in current output of a MFC testing Mn(IV) supported on graphite as cathode instead of graphite alone (Park and Zeikus, 2003, 2002). More recently, Yu et al. demonstrated higher activity

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towards oxygen reduction than Pt in neutral media using iron phthalocyanine supported on Ketjenblack (FePc-KJB) (Yu et al., 2008).

Carbon powder or activated carbon powder could be cheaper alternative to noble metal catalyst (Auer et al., 1998; Harnisch et al., 2009). Carbon was considered to be an inert material in comparison with other catalysts; however, research conducted in the past proved that the carbon surface is not as inert as it was expected (Kukushkina and Shteinberg, 1987; Kukushkina et al., 1987). This superficial activity can be explained due the presence of different heteroatoms (O, H, S, N) bonded on the surface of carbon particles, because of which the active sites appear. Carbon catalytic activity can be increased by changing the quantities of heteroatoms bonded on the surface and by changing the material porosity.

An exhaustive literature dealing with activated carbon production is available (Aksoylu et al., 2000, 2001; Chen et al., 2008; de la Fuente et al., 2006; Guha et al., 2007; Wang et al., 1999). Recently, the effect of carbon supports treatment with oxidative acids in the electrocatalytic oxidation of H_2 (de la Fuente et al., 2006) and CO (de la Fuente et al., 2006; Li et al., 2006) has been investigated. After treating Vulcan XC-72R carbon powder with HNO_3 an enhancement of the amount of oxygen groups was reported (de la Fuente et al., 2006). The objective pursued in this work was to prepare different chemically modified Vulcan XC-72R (Cabot Corporation) activated carbon and probe the surface nature variations by employing scanning electron microscopic technique. Furthermore, the catalytic activity of such modified carbons has been investigated towards oxygen reduction reaction in air-breathing cathode MFC.

2. Methods

2.1. Materials used

The Vulcan XC-72R carbon powder was supplied by Cabot Corporation. Sulphuric acid, nitric acid 65%, phosphoric acid, potassium hydroxide, hydrogen peroxide, isopropyl alcohol (IPA) and acetone were procured from Sigma. Entek membrane (Entek International INC), Nafion[®] 117 solution (5 wt.%, Aldrich), PTFE solution (60 wt.%, Aldrich), carbon felt (E-TEK USA), commercial Pt catalyst (20 wt.% Pt/C, E-TEK, USA) and Ag/AgCl reference electrode (BASi) were used in the study. Millipore water with 18 M Ω cm resistivity was used to prepare solutions.

2.2. Preparation of modified Vulcan XC-72R carbon powder

The chemical modification of Vulcan XC-72R carbon powder was carried out by employing various chemicals namely 5% nitric acid, 0.2 N phosphoric acid, 0.2 N potassium hydroxide and 10% hydrogen peroxide. Carbon powder (1 g) was dispersed in a round bottom flask with 1000 ml of the selected chemicals diluted in the de-ionized water. The mixture was refluxed for 16 h at 120 °C (Guha et al., 2007), except for hydrogen peroxide treatment where it was refluxed for the same duration at 105 °C (Chen et al., 2008). Treated carbons were filtered and washed for 15 min with de-ionized water, and then dried at 110 °C in an oven for 12 h. This procedure removed the ash which is present in significant quantities in the activated carbons.

2.3. Carbon powder analysis

SEM and EDX analyses were carried out by using a JEOL microscope (model JEM-2010). The average of 10 measurements at the surface of each sample is reported for EDX analysis.

2.4. Anodes and air-breathing cathodes preparation

All anodes were constructed using carbon felt with a projected surface area of 12.5 cm². Carbon felt was used in order to provide a higher surface area for microbial development. The anodic current was collected with a Ti wire. Air-breathing cathode was prepared by bonding the cathode catalyst layer on top of the polymer electrolyte membrane and covering this catalyst layer with Ti mesh based current collector. The catalyst layer was made from ink obtained by mixing carbon nano-powder with PTFE, Nafion 117, isopropyl alcohol (IPA) and acetone. This ink was sprayed on top of the polymer electrolyte membrane in order to produce the air-breathing cathodes. Nafion 117 solution was used as a binder in the catalyst layer, since its ability to act as a binder in fuel cells is proved (Duteanu et al., 2007a,b). PTFE was used in air-breathing cathode construction in order to control hydrophobicity. The amount of carbon powder loading on the membrane was 0.5 mg cm⁻² for all cathodes used in this work. For the control experiment Pt catalyst (Pt-supported on C with 20 wt.% Pt) of 0.5 mg cm⁻² was used along with the carbon power loading of 0.5 mg cm⁻².

2.5. Study of oxygen reduction reaction by cyclic voltammetry

The ORR performance was investigated at room temperature (20 °C) by performing cyclic voltammetries on air-breathing cathodes at a scan rate of 1.0 mV/s. Each cathode involved in this work had a projected surface area of 12.56 cm² and was tested in a single-chamber cylindrical MFC having volume of 50 mL with one side exposed to air and the other side exposed to electrolyte using a three-electrode system implemented with a potentiostat/galvanostat (Gill AC potentiostat/galvanostat, ACM instruments, UK). The auxiliary electrode was a platinum mesh (4 cm²) and all potentials were expressed with reference to the Ag/AgCl reference (+0.208 V versus normal hydrogen reference, NHE). The electrolyte was 50 mM phosphate buffer solution (PBS) having pH of 7.0.

2.6. MFC tests and operation

MFC performances were evaluated in single-chamber cylindrical MFC constructed using Plexiglas material having internal diameter of 4 cm and a length of 4 cm. Both anode and cathode had a projected surface area of 12.5 cm². The anode was set parallel to the cathode separated by a distance of 2 cm from the membrane in the anodic chamber and connected by titanium wires.

PBS (50 mM) supplemented with 1 g/L of sodium acetate was used as a feed. These MFCs were inoculated with a 20% anaerobic sludge solution previously acclimated to acetate. An external resistance of 100 Ω was applied between both the cathode and the anode of each cell. Resulting voltage was recorded, at an interval of 5 min, using a data acquisition system (Pico data logger, PicoTechnology, UK) connected to the computer. Electrochemical polarization curves were performed periodically by varying the external resistance over a range from 1 to 3 M Ω . The chemical oxygen demand (COD) was measured in duplicate using standard methods (APHA and WPCF, 1998). The Coulombic efficiency was calculated as reported by Logan et al. (2006).

3. Results and discussion

3.1. Analysing carbon properties

The sulphur (S) content and the surface morphology of the different carbon materials used in this work were analysed by SEM-EDX analysis. Table 1 shows the C and S content of the

Table 1

Elemental content for un-treated and, respectively, treated carbon powder.

Sample	C%	S%
Un-treated Vulcan XC-72R	99.70 ± 0.0047	0.30 ± 0.0047
5% HNO ₃ treatment	99.82 ± 0.0082	0.18 ± 0.0082
0.2N H ₃ PO ₄ treatment	99.71 ± 0.020	0.29 ± 0.020
0.2N KOH treatment	99.67 ± 0.024	0.33 ± 0.024
10% H ₂ O ₂ treatment	99.77 ± 0.0124	0.23 ± 0.0124

samples obtained by EDX. The atomic sulphur content of the un-treated Vulcan XC-72R was 0.3%. Analysing the data presented in Table 1, it is obvious that the 5% nitric acid treatment decreased the sulphur content to 0.18%, and this is the least sulphur content produced among all other treatments. This observation clearly indicates that the strong mineral acid treatment (5% nitric acid) leads to the removal of sulphur impurity from the carbon support, correlated with a large increase of oxygen content (Tricás et al., 2005) and simultaneously increase the number of carboxylic acidic groups on the carbon surface (Aksoylu et al., 2001). This increase in superficial oxygen content was correlated with further increase in catalytic activity for ORR (Borrós et al., 2005).

The other treatments, like 0.2 N phosphoric acid and 10% hydrogen peroxide, also removed the sulphur content from the carbon support, but to a lesser extent. On the other hand the 0.2 N KOH treatment resulted in a sulphur content of 0.33%, which was in excess amount than the original value of 0.3%. It may due to the fact that the KOH treatment normally leads to an increase in N atomic content with enormous removal of O atomic content so that eventually the S atomic content will be raised in that sample. Further work is in progress to quantify the ratio of different atomic content on the surface by employing XPS technique.

The SEM morphology of different carbon powders used in this work showed that the different chemical treatments yield to a different kind of carbon surfaces with different porosity. Especially the strong mineral acid treatment (5% nitric acid) leads to a more porous and dispersed surface rather than the un-treated carbon powder (Aksoylu et al., 2000, 2001). The other treatments like 0.2 N phosphoric acid and 10% hydrogen peroxide also influences the surface but to a lower extent.

3.2. Electrochemical study of oxygen reduction reaction

The ORR performance furnished by different air-breathing cathodes was compared using cyclic voltammetry. This test was performed on the air-breathing electrode using a platinum mesh as a counter electrode and Ag/AgCl reference electrode placed in anodic chamber. Linear sweep voltammetry curves recorded at a low scan rate of 1 mV/s are presented in Figs. 1 and 2. All these curves were obtained using 50 mM PBS of pH 7.0 excepting the curves obtained when pH influence was studied.

Best performance was demonstrated by Pt/C air-breathing cathode – around 4 A/m² at –0.300 V versus Ag/AgCl. In the small current region – under 0.2 A/m² – all air-breathing cathodes constructed using only carbon catalyst showed similar behaviour, e.g., at –0.100 V versus Ag/AgCl they furnished a maximum current around 0.2 A/m². When the current is increased, the HNO₃ treated Vulcan XC-72R carbon air-breathing cathode demonstrated the second best performance, after Pt/C cathode, with a current around 2 A/m² at –0.300 V versus Ag/AgCl. The un-treated Vulcan XC-72R air-breathing cathode had a slightly lower performance (around 1 A/m² at –0.300 mV versus Ag/AgCl) in comparison with HNO₃ treated carbon. All other chemically treated air-breathing cathodes showed very poor performance with a maximum current density of 0.2 A/m² at –0.300 mV versus Ag/AgCl.

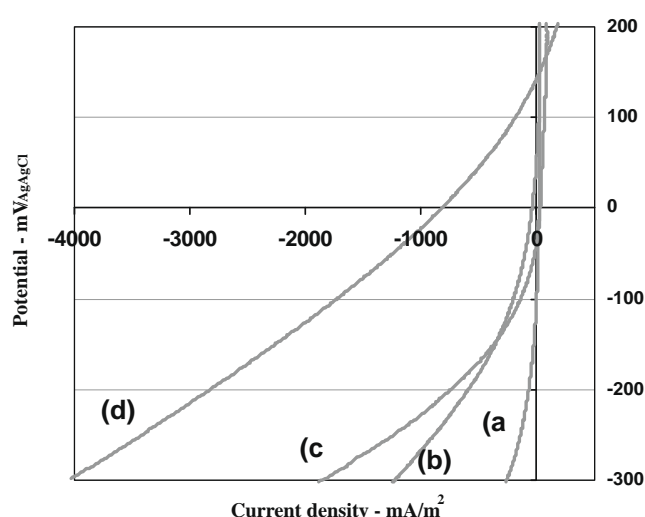


Fig. 1. Linear sweep of oxygen reduction with air-breathing cathode prepared from (a) un-treated carbon Vulcan XC-72R, (b) H₂O₂ treated carbon Vulcan XC-72R, (c) HNO₃ treated carbon Vulcan XC-72R, and (d) platinum supported on carbon Vulcan XC-72R. Scan rate 1 mV/s, phosphate buffer solution 50 mM, pH 6.0.

From the data presented in Fig. 1, we can conclude that the best performance after the Pt catalyst was delivered by HNO₃ treated carbon powder which is also in confirmation with the data obtained by SEM and EDX analyse. The better performance observed for HNO₃ treated carbon, in comparison with un-treated carbon, can be attributed to incorporation of oxygenated groups into the carbon black structure and also due to an increase of electrochemically active groups. The poor performance demonstrated by other air-breathing cathodes can be explained by the reduced real surface area correlated with some pore-blockage caused by certain oxygenate groups fixed at micro-pores entrance, probably blocking the diffusion of species into the micro-pores (Carmo et al., 2008).

Effect of pH on ORR was studied, in order to determine the optimum pH for energy harvesting using MFC. The linear sweep curves for ORR were recorded for different solution pH in the anodic compartment. Data presented in Fig. 2 shows that, for the noble catalyst air-breathing cathode, the highest performance improvement occurred when the pH was increased from 6 to 7.5. Almost no influence of pH change was found on the performance of un-treated Vulcan XC-72R carbon powder. The H₂O₂ treated carbon performance was slightly affected by the anodic pH. For HNO₃ treated carbon powder a slight increase in current was observed when the pH of anodic chamber was increased from 6 to 7.5. The Vulcan XC-72R carbon powder treated with H₂PO₄ and KOH, and H₂O₂ did not show any current during the electrochemical test (results not presented), and hence, it was decided not to use these materials for the cathode in the MFC.

3.3. MFC performances

Since the cathode made from Vulcan XC-72R carbon powder treated with nitric acid showed interesting performance concerning oxygen reduction, it was tested as an air-breathing cathode in a single-chamber MFC. To assess the real value added by HNO₃ treatment, two additional cells were constructed and studied in parallel. In the first MFC the air-breathing cathode was made using only un-treated carbon powder (Vulcan XC-72R), and in the second with a Pt-supported cathode, with a uniform distribution of 0.5 mg of catalyst per cm².

Starting from the first day, these MFCs were connected with an external resistor of 100 Ω. After one week of operation, the open

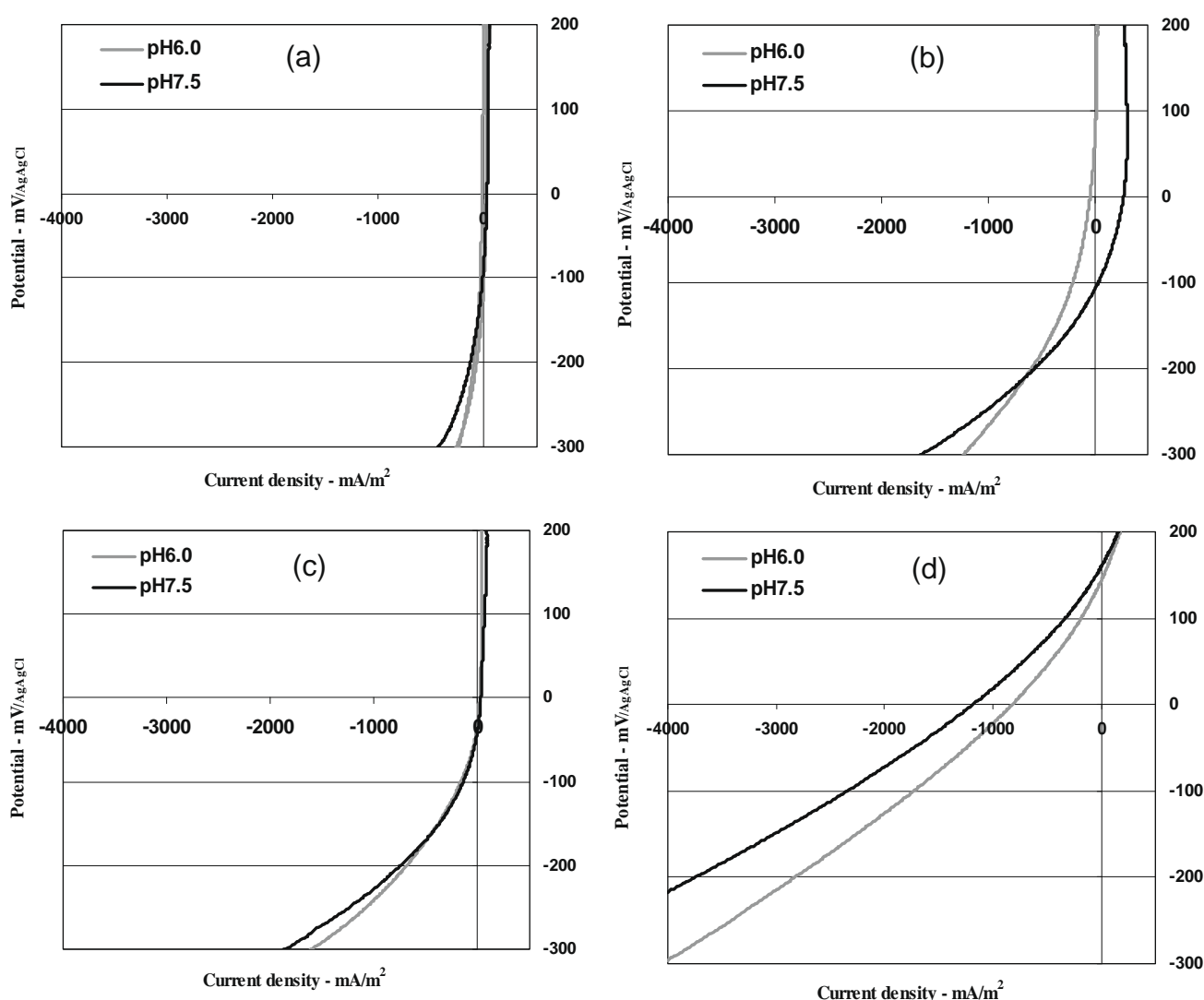


Fig. 2. Effect of pH on non-catalyzed oxygen reduction – linear sweep of oxygen reduction with air-breathing cathode prepared from (a) un-treated carbon Vulcan XC-72R, (b) H_2O_2 treated carbon Vulcan XC-72R, (c) HNO_3 treated carbon Vulcan XC-72R, and (d) platinum supported on carbon Vulcan XC-72R. Scan rate 1 mV/s, phosphate buffer solution 50 mM.

circuit voltage (OCV) reached 340, 370 and 520 mV for MFC equipped with un-treated Vulcan XC-72R, HNO_3 treated Vulcan and Pt-supported air-cathode, respectively. MFCs performances were first evaluated during this start-up period by recording cell polarization curves (Fig. 3). At this step, the power density obtained from the MFCs equipped with cathodes constructed using un-treated XC-72R and HNO_3 treated Vulcan were comparable. Maximum power densities of about 20–27 mW/m^2 were obtained.

After 6 weeks, OCVs stabilized at 507, 481 and 640 mV for un-treated, HNO_3 treated and Pt-Vulcan XC-72R cathode MFCs, respectively, and steady-state behaviours were reached (Table 2). Two consecutive scans were performed and almost similar behaviour was obtained. With acclimatised reactors, as expected, the highest power density of 217 mW/m^2 was produced using the Pt catalyst; while MFC equipped with HNO_3 treated Vulcan cathode produced 170 mW/m^2 . The performance of the MFC with a cathode of un-treated Vulcan powder was poor, reaching only a power density of 51 mW/m^2 and a maximum current density of 352 mA/m^2 . Power densities produced using HNO_3 treated Vulcan XC-72R carbon powder were comparable with Pt/C cathode MFC performance. At current densities less than 500 mA/m^2 , the Pt/C cathode cell had

the better performance, whilst at current densities over 500 mA/m^2 the HNO_3 treated carbon cathode showed better performance. The maximum current density obtained with this cathode was 1115 mA/m^2 and thus it performed better than the MFC using platinumised cathode (Table 2). MFCs equipped with HNO_3 treated Vulcan XC-72R and Pt/C cathodes achieved the highest Coulombic efficiency (62%). Over 87% COD was removed from synthetic wastewater in all tested MFCs.

3.4. Behaviours of electrodes potentials

During generation of the MFCs polarization curves on week 6, values of both the anodic and cathodic potential were recorded and are reported in Fig. 4. The current–potential curves of bioanodes obtained after 6 weeks showed “zero-current” at potential between –580 and –530 mV versus Ag/AgCl, instead of +100 mV versus Ag/AgCl before anodic biofilm formation. Such a negative “zero-current” potential value is a significant advantage in an MFC. These bioanodes generated current density up to 500 mA/m^2 , at –250 mV versus Ag/AgCl considering a total projected sur-

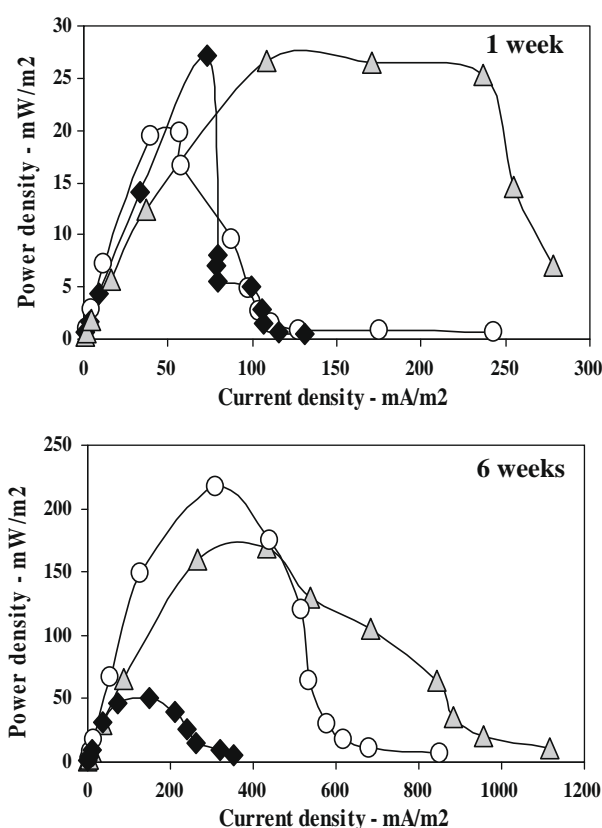


Fig. 3. Curves of polarization obtained from three single MFCs using un-treated Vulcan XC-72R (◆), HNO₃ treated Vulcan (▲), and Pt/Vulcan (○) as cathode materials after 1 and 6 working weeks under 1000 Ω resistance.

Table 2
Summary of MFC performances.

Cell	Treatment	OCV (mV)	Current density (mA/m ²)	Power density (mW/m ²)	CE (%)
A	–	507	352	51	25.5
B	HNO ₃	481	1115	170	61.8
C	+Pt	640	849	217	61.2

OCV: open circuit voltage and CE: Coulombic efficiency.

face area of 12.5 cm², with exception of bioanode that formed in the MFC equipped with the un-treated Vulcan XC-72R cathode.

In fact, in the case of un-treated Vulcan XC-72R cathode, the faster decrease in cathodic potential from open circuit potential (OCP) to short-circuit potential indicated the poor reaction kinetics on classical graphite material (Fig. 4). The high activation energy of ORR on graphite material can explain this high cathodic overpotential observed with the un-treated Vulcan XC-72R cathode. The HNO₃ treatment of Vulcan XC-72R lowered the cathodic overpotential proving the decrease of activation energy needed for ORR. Moreover, even if the OCP of HNO₃ treated cathode is about –200 mV, more negative than the Pt-supported cathode (Fig. 4), its overpotential was lower than that observed with the platinum cathode, confirming the positive effect of the acidic treatment on oxygen reduction catalysis.

As explained by Freguia et al. (2007), the ORR overpotential can be reduced either by using a catalyst to reduce the activation energy or by increasing the specific surface area of the graphite material (Freguia et al., 2007). Many studies have reported solutions to increase the rates of ORR involving innovative and cheap catalysts (Aelterman et al., 2008; Cheng et al., 2006; Clauwaert et al., 2007;

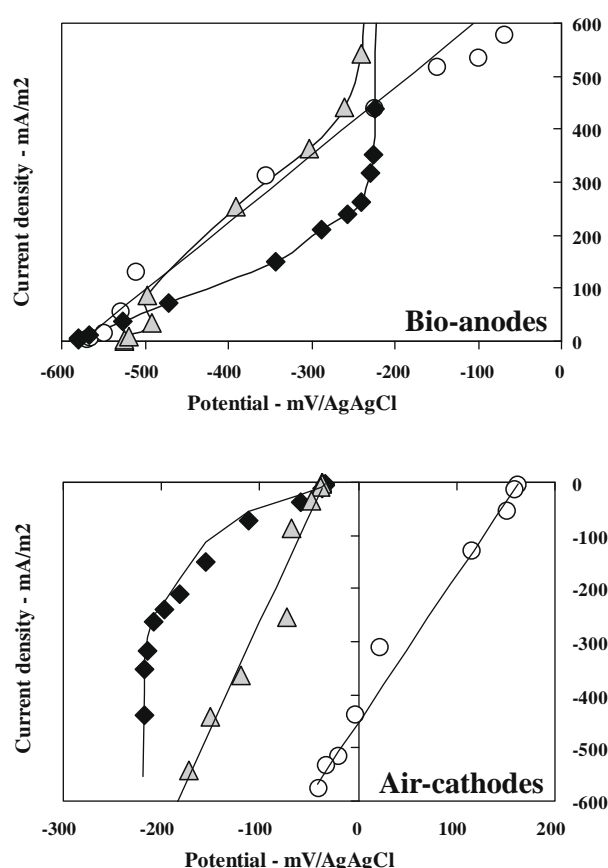


Fig. 4. Current density versus potential of the bioanodes and potential of the air-cathodes after 6 working weeks under 1000 Ω resistance: (◆) un-treated Vulcan XC-72R, (▲) HNO₃ treated Vulcan, and (○) platinum.

Freguia et al., 2007; Sun et al., 2009). Recently, Zhang et al. compared the performance of manganese dioxides (MnO₂) to Pt as catalyst material in an air-cathode MFC systems constructed with *Klebsiella pneumoniae* biofilm (Zhang et al., 2009). Maximum power density of 466 mW/m³, using MnO₂ as catalyst, is reported which is four-times higher than that obtained with non-catalyzed cathode (102 mW/m³). However, the power generated by this MnO₂ based MFC was only 64% of the performance of Pt-catalyzed MFC (726 ± 19 mW/m³). In a study with graphite-granules, Freguia et al. (2007) have demonstrated the possibility to sustain stable high performance output of a MFC integrated with catalyst-free material as cathode (Freguia et al., 2007).

In the present work, it has been shown that chemical treatment with nitric acid played a role not only in modifying the specific surface area (Erable et al., 2009) but also in improving the catalytic property of the graphite material, since the current densities comparable to that of a Pt-supported carbon cathode were observed. Improved performance of MFC with chemically modified carbon cathode demonstrates that the research should not be only focus on new catalyst development at neutral pH, but should also include development of new high surface area materials with better catalytic property by chemical modification.

4. Conclusions

It has been shown that chemical treatment with HNO₃ played significant role in modifying the specific surface and in improving the catalytic property of the Vulcan XC-72R carbon powder. During electrochemical analysis the best performance, after the Pt

catalyst, was delivered by HNO₃ treated carbon powder (2 A/m² at –0.300 V versus Ag/AgCl), followed by slightly lower performance by using un-treated Vulcan XC-72R. Performance of HNO₃ treated carbon was not much affected by anodic solution pH between 6 and 7.5. Such chemically modified carbon material can become a cheaper alternative for expensive platinum based catalyst used in MFC cathode construction.

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