Comparison of the performance of earthen plate and Nafion as membrane separators in dual chamber microbial fuel cells

Partha Sarathi Jana[1], Makarand Madhao Ghangrekar[2] and Dónal Leech[1]*

[1]School of Chemistry & Ryan Institute

National University of Ireland Galway, Galway, Ireland

[2]Department of Civil Engineering

Indian Institute of Technology Kharagpur, West Bengal, India

Abstract

The performance of microbial fuel cells employing Nafion-117 or an earthen plate as membrane separators is compared using in identical up-flow dual-chambered cylindrical MFCs. The MFC configuration consisted of an outer cathode chamber separated by the membrane from a concentric rectangular inner anode chamber. These MFCs, operated under continuous mode at hydraulic retention time of 12 hr, achieved average chemical oxygen demand (COD) removal efficiency of 60% and 48%, for the Nafion and earthen plate separators, respectively. Whilst the microbial fuel cells based on the earthen plate separator generated slightly lower average (28%) and maximum (48%) power densities than that based on the Nafion separator, both achieve similar Coulombic efficiencies. The earthen plate separator is 99% cheaper than the Nafion membrane, showing promise as an alternate separator for application to MFC technology.

Keywords: Proton exchange membrane, Microbial fuel cell, Earthen plate, Power density, Chemical oxygen demand.

1. Introduction

Microbial fuel cell (MFC) is an emerging technology, which has been paid much attention in recent years (Harnisch et al., 2008; Logan et al., 2006; Logan & Regan, 2006; Zhang et al., 2009; Zuo et al., 2008), for application to wastewater treatment with simultaneous electricity generation. An MFC is a bioelectrochemical system where bacteria catalyze the degradation of organic matter under anaerobic conditions to convert the energy stored in chemical bonds of organic compounds to electrical energy. The MFC performance is affected by many factors, such as reactor configuration, type of electrode material and membrane separator, electrolyte solution pH, temperature, substrate type and concentration, hydraulic retention time (HRT), inoculum selection or enrichment, cathodic electron acceptor selection, etc. (Pant et al., 2012; Pant et al., 2010b). In the past decade many advances have been made in MFC research aimed at enhancing MFC power density output (Logan et al., 2006; Min et al., 2005; Park & Zeikus, 2003; Rabaey et al., 2004). However, MFC construction, operation and maintenance cost still need to be minimized to make this technology sustainable on economic grounds (Logan & Regan, 2006; Zuo et al., 2008).

The characteristics of the membrane separator selected can significantly affect the performance of an MFC (Zhang et al., 2009). Nafion is the most widely used membrane separator because of the high ionic conductivity (Harnisch et al., 2008; Logan et al., 2006). The high cost of Nafion however makes production cost of MFC commercially unacceptable to date (Pant et al., 2010a). Many studies explore the use of alternate separators for MFC (Behera et al., 2010a; Behera et al., 2010b; Jung et al., 2007; Logan et al., 2006; Martin et al., 2010; Min et al., 2005; Park & Zeikus, 2003; Rabaey et al., 2004; Sun et al., 2009; Ter Heijne et al., 2006). For example, the use of a salt bridge (Min et al., 2005), ultrex membrane (Rabaey et al., 2004), a

porcelain septum made from kaolin (Park & Zeikus, 2003), anion exchange membranes (Martin et al., 2010), bipolar membranes (Ter Heijne et al., 2006), microfiltration membranes (Sun et al., 2009), J-Cloths (Fan et al., 2007), a selemion HSF membrane (Logan et al., 2006), and ultrafiltration discs (Lefebvre et al., 2011) have been reported for their use as separators in MFCs. We recently (Behera et al., 2010a; Behera et al., 2010b) reported on the treatment of synthetic and rice mill wastewater in fed-batch MFCs fabricated using an earthen pot acting as both anode half-cell container, and a membrane separator, with the performance compared to MFCs fabricated using a Nafion membrane separator (Jana et al., 2010). The earthen pot MFCs demonstrated better performance in terms of organic matter removal and electricity generation compared to the Nafion membrane, but the surface area available for ion transfer through the wall of earthenware was much larger than that in the Nafion-based MFC, making comparison difficult in that study. The thickness of the earthen pot membrane/anode container was also shown to affect both MFC internal resistances, and as a consequence MFC power generation (Behera & Ghangrekar, 2011). The present research focuses on an effort to better compare performances of MFCs operated using the earthen pot as membrane separator to that of Nafion-separated, MFCs by fabrication of polyacrylate MFCs with earthen plate separator of the same exposed geometrical surface area to that of the Nafion separator. The comparison of MFC performance is evaluated by operation of both types of MFC under continuous mode feeding of acetate as synthetic waste, following initial batch incubation with acetate and anaerobic sludge, as inoculum and using a model ferricyanide solution as oxidant in the catholyte.

2. Materials and Methods

2.1 Experimental set-up

The study was carried out in two identical up-flow dual chambered polyacrylic MFCs

separated by the same exposed area of either a Nafion117 proton-exchange membrane (PEM, Sigma Aldrich) or an earthen plate membrane (EP, 3.7 mm thick). The earthen plates were prepared from soil (elemental composition: Al-32%, Si-47.80%, K-4.90%, Ca-1.20%, Ti-0.90%, Fe-13%, similar to that used in previous studies of earthen pots as MFC containers and membranes (Behera & Ghangrekar, 2011) sourced from Midnapore, India and baked at 550-650°C for 6.0 hours, as described previously (Behera et al., 2010a) to provide plates of average thickness of 3.7 mm. The cylindrical MFCs consisted of an outer catholyte chamber separated from a rectangular polyacrylic inner anolyte chamber, with membranes glued to opposite exposed areas in the faces of the inner chamber (Fig.1). Each membrane exposed 20 cm^2 surface area to the anolyte, making the total exposed membrane surface area of 40 cm^2. The working volume of the anolyte chamber of both types of MFCs was 350 mL, whilst that of the catholyte chamber was 1200 mL.

Graphite plates of 70 cm^2 each were used as electrodes and placed in the anolyte and catholyte, giving a total surface area of 140 cm^2 each for anode and cathode in all MFCs. The electrodes were connected externally with titanium wire through a resistance of 100 Ω. The acetate medium influent was supplied to the MFCs from the bottom of the anode chamber using a peristaltic pump (Gilson, France) with effluent exiting the anode chamber at the top of the reactor. The catholyte consisted of 50 mM ferricyanide in 100 mM phosphate buffer (pH of 7.0).

2.2 MFC operation

The MFCs were inoculated with anaerobic sludge collected from an anaerobic digester (Mutton Island wastewater treatment center, Galway). The granular sludge was crushed in a grinder for 10 seconds and 60 mL of the resultant sludge was added to the anode chamber to establish a sludge loading rate at 0.75 kg COD kg VSS^{-1} (Behera & Ghangrekar, 2009). Synthetic

media containing acetate as a source of electron donor having COD of 1250 mg L^{-1} was used as feed. The acetate medium also contained (per L): 0.1 g KCl, 0.15 g NH_4Cl, 0.6 g Na_2HPO_4, 2.5 g $NaHCO_3$, 10 mL trace element solutionand 10 mL vitamin solution (Katuri et al., 2012b) prepared according to http://www.dsmz.de (medium No. 826). The feed pH was in the range of 7.2-7.5 throughout the experiments and the MFCs were operated at temperatures that varied from 28 to 32^oC. Initially both the MFCs were operated under batch mode condition to encourage the attachment of electrogenic bacteria to the graphite plate anodes. The first batch consisted of the inoculum supplemented with 290 mL of acetate medium, with the two subsequent batches prepared by replacement of half of the anolyte volume by new acetate medium (no additional inoculums). After these three feed cycles, the MFCs were operated in continuous mode at organic loading rate (OLR) of 2.5 kg COD $m^{-3}d^{-1}$, by maintaining a hydraulic retention time (HRT) of 12 h using the peristaltic pump. After reaching a steady state voltage output across the 100 Ω resistor, the performance of MFCs were evaluated by polarization experiments using a CH instruments 650 (USA) potentiostat.

2.3 Analyses and calculations

The cell voltages were recorded continuously using a digital multimeter with data acquisition unit (Pico data logger, UK) throughout the batch and continuous feed experiments by connecting anode and cathode across a 100 Ω external resistor. Current (*I)* was calculated using Ohm's law ($I = V/R$) and MFC power was estimated by $P = IV$, where I is cell current and V is the cell voltage. Polarization studies were carried out by linear sweep voltammetry at a scan rate of 1 mVs^{-1} in a two electrode assembly system. Power density was estimated by normalization to the geometric anode surface area. Internal resistance of the MFCs was estimated from the slope of the linear portion of the plot of voltage versus current (Picioreanu et al., 2007).

The SS, VSS, and COD levels were monitored according to APHA standard methods (APHA, 1998). Chemical compositions of earthen plates were estimated from Scanning Electron Microscopy (SEM, Hitachi SU-70) images with Energy Dispersive X-ray Microanalysis (EDX, Oxford Instruments). The Coulombic efficiency (*CE*) was estimated using the ratio of charge produced (by integrating the measured current over time) to theoretical charge on the basis of consumed COD, with the theoretical charge production estimated as (F x n x w)/M, where F is Faraday's constant, n is the number of moles of electrons produced per mole of substrate (= 4 for wastewater COD), w is the daily COD load consumed in gram and M is molar mass of oxygen (Logan et al., 2006).

3. Results and Discussion

3.1 MFC operation

After inoculation, a gradual increase in the voltage produced across the 100 Ω external resistance load was observed in both the MFCs over the first 48 hrs, with a slight delay in response of the Nafion, proton-exchange membrane based MFC (PEM-MFC) compared to that for the earthen plate based MFC (EP-MFC), leading to generation of a maximum voltage of ~0.3 V over the first batch feed cycle, Figure 2. In this set-up, it is presumed that the cathode does not limit the current, as the ferricyanide catholyte was supplemented periodically over the time course of the experiments resulting in a constant electron acceptor concentration close to 50 mM, as reported previous (Herrero-Hernandez et al., 2013; Katuri et al., 2012a; Kong et al., 2010). After two further batch fed cycles, represented by the arrows in Figure 2, the feed was switched to continuous mode on the 7^{th} day of operation, providing 20 mM acetate to the chamber at such a flow rate to provide a HRT of 12 hrs. The measured cell voltage for both types of MFC stabilized after this, with average sustainable current generation of 5.14 mA and 4.34 mA for the

PEM-MFC and EP-MFC, respectively, across 100 Ω external resistances over the 7 to 26 days of continuous feed time period (Figure 2). The cells thus provided average power densities of 190 mW/m^2 and 138 mWm^{-2}, respectively, under these steady-state conditions. Under these conditions both cells establish the same OCV of 0.68 V. This OCV is close to the 0.76 V observed by Kong et al. and others (Kong et al., 2010; Venkata Mohan et al., 2008) for a PEM-MFC fed with acetate and using potassium ferricyanide solution as catholyte.

To examine the catalytic activity of the anodic biofilm slow scan cyclic voltammograms were recorded *in situ* in the cell culture medium. Sigmoidal shaped voltammograms shown in Figure 3 permit estimation, from the first derivative of the CVs (not shown), of acetate oxidation centered at −0.44 vs. Ag/AgCl. The sigmoidal shaped CV is indicative of catalytic oxidation of the substrate by the biofilm and heterogeneous electron transfer to the electrode, with similar responses reported on for acetate oxidation by anodic biofilms of *Geobacter sulfurreducens* (Katuri et al., 2010; Katuri et al., 2012b; Marsili et al., 2010) and by mixed culture biofilms (Liu et al., 2008). From the difference in the ferricyanide reduction potential in buffer of ~+0.24 V vs. Ag/AgCl and that of the redox couple centred at −0.44 vs. Ag/AgCl an estimate of the cell voltage of ~0.68 V is obtained, agreeing well with the OCV measured for both cells.

Efficient proton and ion transfer between anolyte and catholyte is important in MFC systems, to maintain electroneutrality during current flow and power production. The ability of the earthen plate membrane to permit ion-exchange was therefore evaluated and compared to that of the Nafion PEM. For this experiment, 1 M H_2SO_4 was added to the anolyte chamber of both MFCs and the pH change in the catholyte, initially containing distilled deionized water was measured as a function of time. The catholyte pH decreased with time as protons migrated from

anolyte to catholyte with the extent of proton exchange through the earthen plate membrane similar to that observed for proton exchange through the Nafion separator (Fig 4).

3.2 Organic matter removal

Initially both MFCs were operated in batch mode to avoid the washout of the sludge inoculum and thus encourage attachment of bacteria to the anode surface. After ~7 days of operation in batch mode, MFC operation was switched to continuous mode at an OLR of 2.5 kg $CODm^{-3}d^{-1}$. Steady state conditions for stable substrate degradation, represented by COD removal, and electricity generation were already established at this stage (Figure 5). During the subsequent steady state operation in continuous feed mode over an 18 day period, the PEM-MFC demonstrated an average COD removal efficiency of 60%, compared to an average COD removal efficiency of 48% for the EP-MFC. It should be noted that the earthen plate material has also been found to be permeable to oxygen (Behera & Ghangrekar, 2011), which could be one reason for the relatively lower COD removal efficiency for the EP-MFC compared to the for PEM-MFC.

3.3 Polarization studies

At the end of the continuous feed period (day 25) polarization studies were carried out for the MFCs by slow scan linear sweep voltammetry yielding the polarization curves (Figure 6) with a maximum power density of 250 mWm^{-2} at 35Ω resistance for the PEM-MFCand 145 mWm^{-2} at 67 Ω resistance for the EP-MFC. Maximum volumetric power density of 10.0 Wm^{-3} and 5.8 Wm^{-3} were estimated based on anolyte volume from the polarization curves for the PEM-MFC and EP-MFC, respectively. Internal resistances of 36 Ω and 70 Ω were estimated from the slope of the linear portion of the plot of cell voltage versus current (Figure 6), for the PEM-MFC

and EP-MFC, respectively. The earthen plate membrane is substantially thicker (~3.7 mm) than the Nafion 117 (~0.17 mm), which might contribute towards the higher internal resistance for these cells. In comparison to the results reported here, Jung et al. (Jung et al., 2007) report internal resistances of dual chamber MFCs using a range of membrane separators to be from 1239 to1344 Ω, depending on factors such as electrode spacing (Kong et al., 2010) and membrane, with higher internal resistance resulting in MFC with lower power densities in this configuration. Lower internal resistances of 84-98 Ω, and higher power densities, were obtained for MFCs in a single chamber, air-breathing cathode configuration with much closer electrode spacing (Katuri et al., 2012a). Using a dual chamber Nafion-separated MFC system, similar to the configuration in this report, Katuri et al. (Katuri et al., 2012a) report a maximum power density of 6.4 W m^{-3} based on anolyte volume for the MFC operating on slaughterhouse wastewaters, whilst Kong et al. (Kong et al., 2010) observed maximum power density of 4.35 W m^{-3} using acetate as feed. Improvement in power density may be achieved, as reported recently by Zhang et al. (Zhang et al., 2011), by use of high surface area anodes and glass fiber as a separator in a single chamber air-breathing cathode MFC configuration, providing a power density of 75 W m^{-3}.

Table 1 shows the comparison of the performance of the EP-MFC and PEM-MFC. From the polarization curve and the data in Table 1 the EP-MFC generates ~40% less maximum power density, with an internal cell resistance 48% higher than the PEM-MFC. Over the 18 day period of steady state operation in continuous feed the Coulombic efficiency difference less than 10% is estimated for both the PEM-MFC and the EP-MFC under the 100 Ω resistance load. Many different membrane separator configurations have been studied in MFCs, such as the use of single chamber porous air cathode (Park & Zeikus, 2003), tubular air cathode system with an

outer cathode and an inner anode (Rabaey et al., 2005), and more recently (Zhang et al., 2010) nylon and glass fiber filter separators in air-cathode single-chamber microbial fuel cells. A potential disadvantage to all these configurations is the susceptibility of the membrane separators to degradation (Zhang et al., 2009) or mechanical deformation (Zhang et al., 2011) over long periods. The use of an earthen plate separator as an alternative membrane provides a low cost and durable option, with little loss in performance compared to the same exposed area of a Nafion PEM as a benchmark.

4. Conclusion

Nafion is the most widely used fuel cell membrane as it provides high ionic conductivity, but with limitations of high cost, fouling and deformation This study demonstrated by comparison to Nafion, that an earthen plate membrane may provide a low-cost and more durable alternative to Nafion in continuous flow MFCs. The MFC using Nafion membrane as separator showed slightly better performance in terms of organic matter removal and electricity generation than the MFC based on earthen plate membrane separators, whilst both show comparable Coulombic efficiency. The performance of earthen plate MFC may be enhanced by increasing the membrane surface area or decreasing the membrane thickness. The 40 cm^2 Nafion117 membranes used in the present experiment costs approximately €30.0 whilst the same area of the earthen plate costs approximately €0.025, making it 99% cheaper. Utilization of such low cost separators may contribute to further developing economical MFC technology.

5. Acknowledgments

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Figure legends

Fig.1. Schematic diagram of the MFCs used in the study: (A) $K_3Fe(CN)_6$ catholyte influent, (B) External resistance load, (C) Cell culture medium influent, (D) Cell culture medium effluent, (E) Catholyte chamber, (F) Cathode, (G) membrane, (H) Anolyte chamber, and (I) Anode.

Fig.2. Voltage generation response as a function of time for the PEM-MFC (grey) and the EP-MFC (black). Arrows indicate replacement with fresh feed and star indicates the time when the reactors were switched from batch to continuous mode operation.

Fig.3. Cyclic voltammograms (1 mV/s) of anodic biofilm, recorded in-situ on the 19th day of operation of the cells under100 Ω external resistors, for the PEM-MFC (grey) and EP-MFC (black) systems.

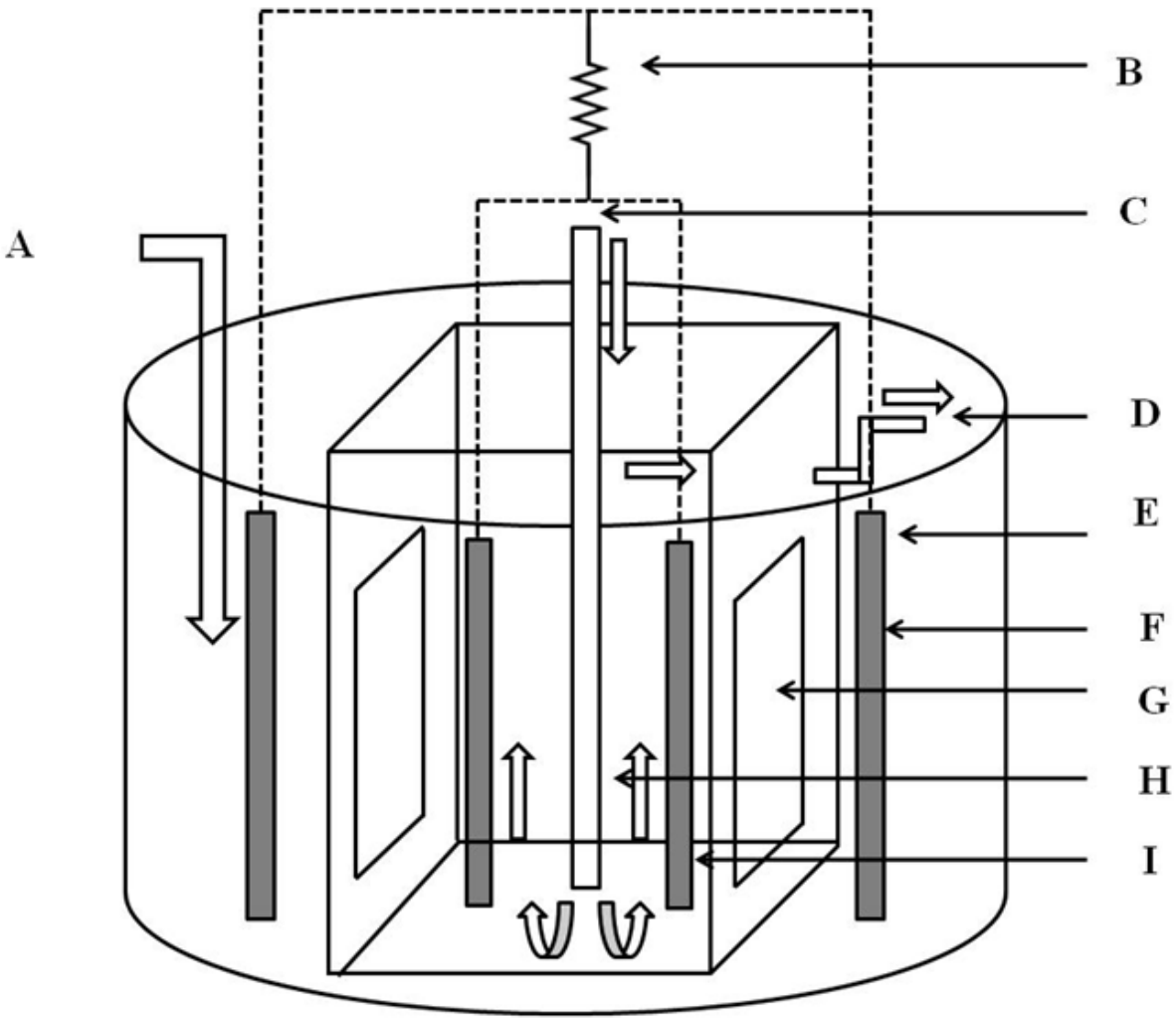
Fig.4. A comparison of the change in pH of the catholyte chamber, initially containing distilled deionized water, as a function of time upon introduction of 1 *M* sulphuric acid into the anolyte chamber for PEM (grey) and earthen plate (black) MFCs.

Fig.5. COD removal efficiency (open) and voltage generation across the 100 Ω resistance (closed) of PEM-MFC (grey circles) and EP-MFC (black triangles) as a function of time during continuous feed of MFCs (commenced at day 7).

Fig.6 In-situ polarization curves, recorded on day 25, cell voltage and power density versus current density for PEM (grey closed) and earthen plate (black open) MFCs

Table 1. Comparison of performance of PEM-MFC and EP-MFC

MFCs	Voltage with 100Ω load (V)	Power density with 100 Ω load (mW m^{-2})	Maximum Power density (optimum resistance) (mW m^{-2})	Volumetric power density with 100 Ω load (W m^{-3})	Maximum volumetric power density (optimum resistance) (W m^{-3})	Internal Resistance (Ω)
PEM-MFC	0.52	190	250(35 Ω)	7.6	10.0(35 Ω)	36
EP-MFC	0.44	138	145(67 Ω)	5.5	5.8(67 Ω)	70



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366 Fig. 1.

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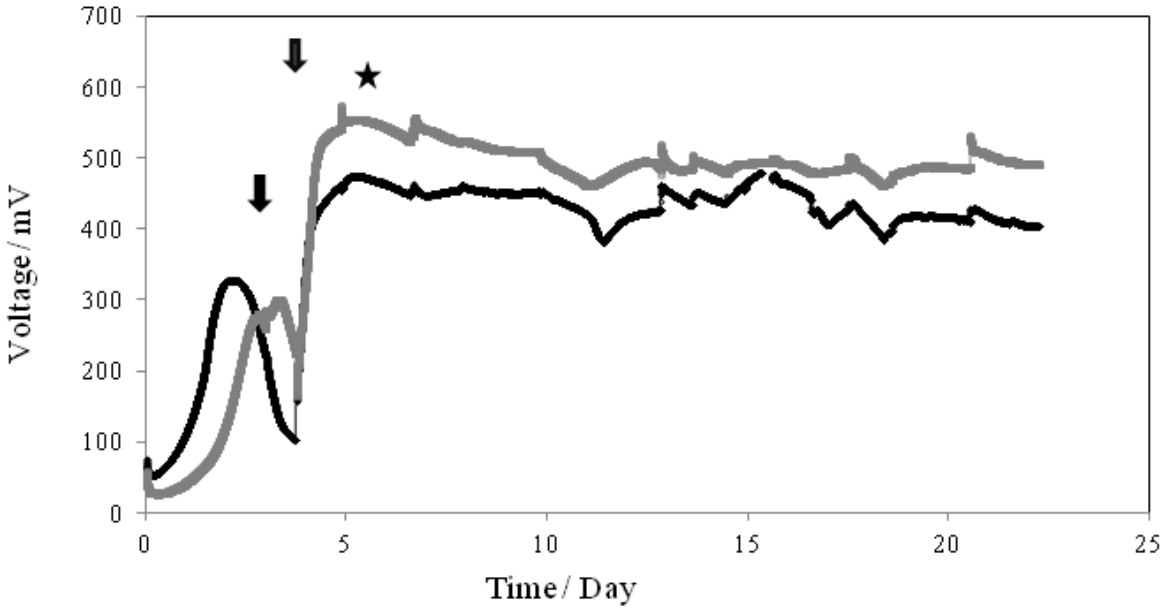

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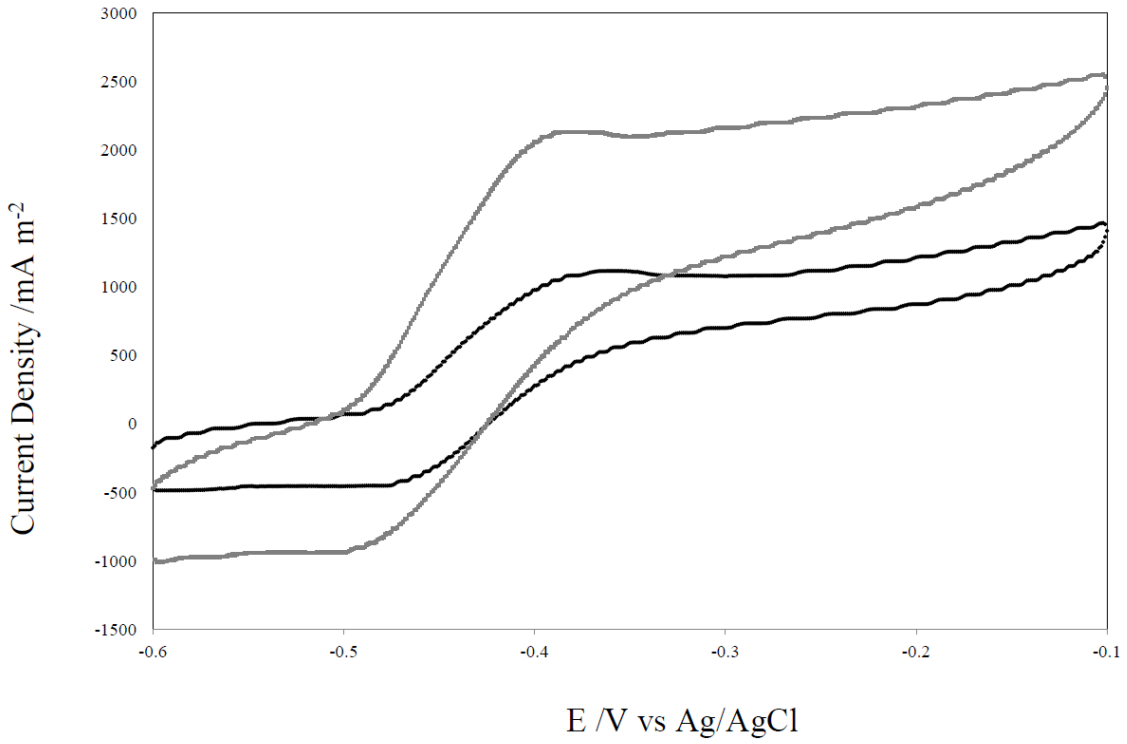
369 Fig 2.



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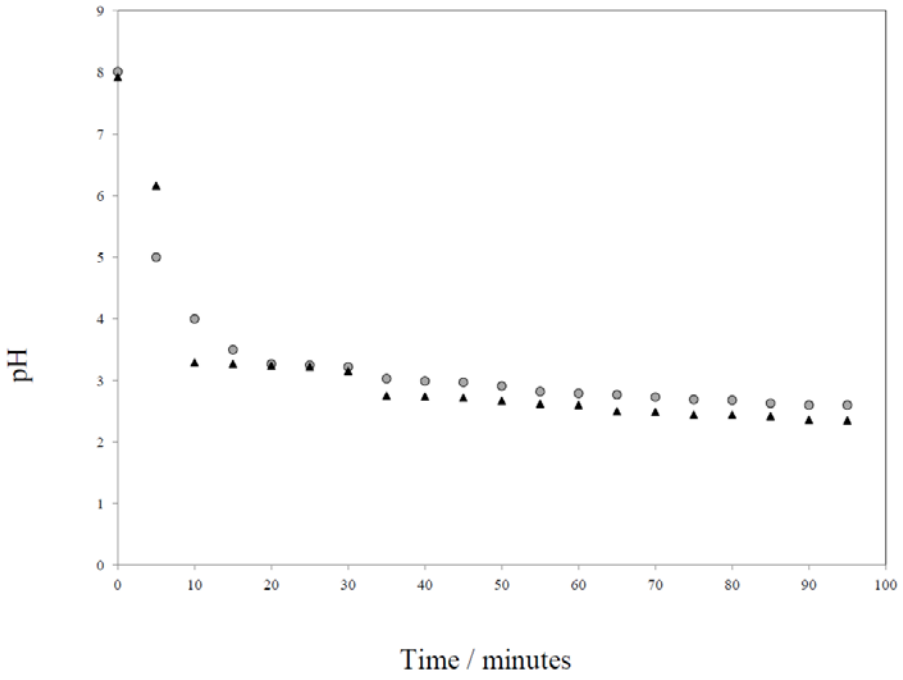

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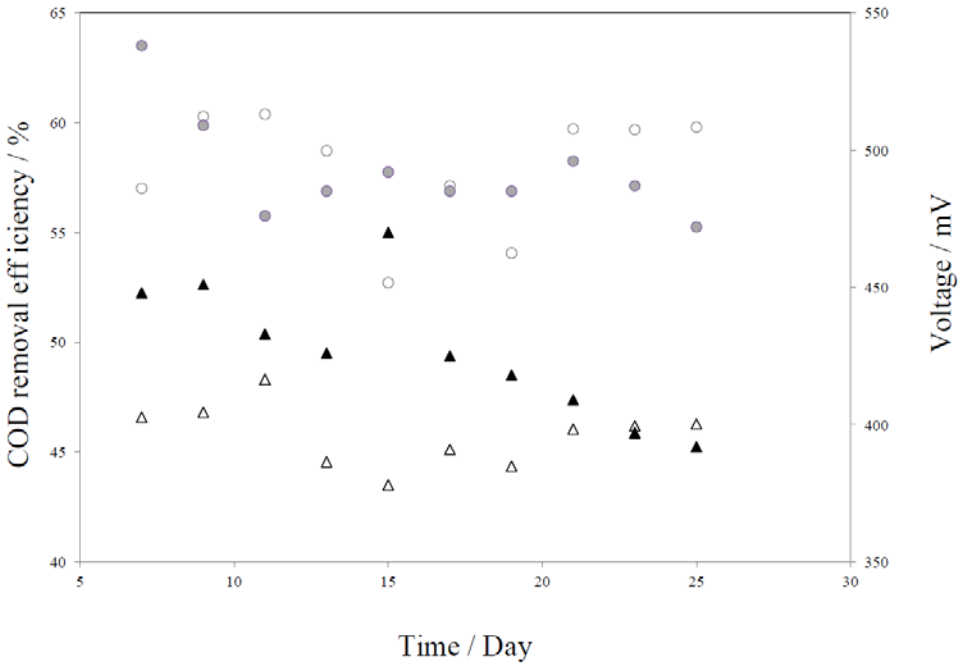
373 Fig 4.



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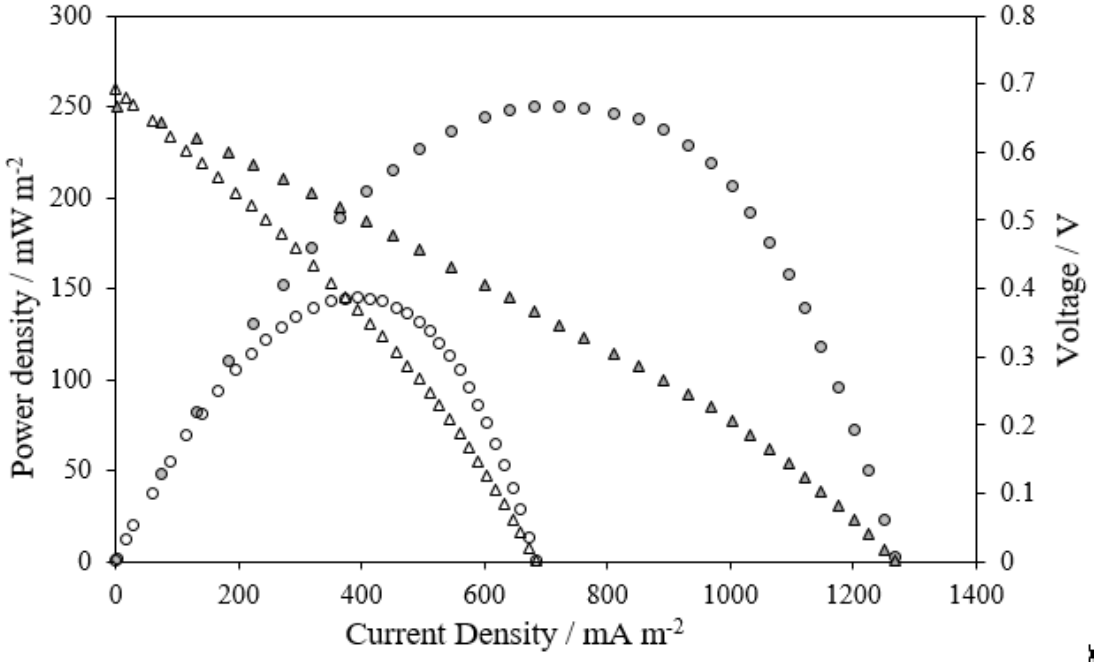
375 Fig 5.


Power density / mW m-2
Voltage / V
Current Density / mA m-2
0
50
100
150
200
250
300
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
200
400
600
800
1000
1200
1400

376

377 Fig 6.