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Author(s)	Jana, Partha Sarathi;Ghangrekar, Makarand Madhao;Leech, Dónal
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1 **Comparison of the performance of earthen plate and Nafion as membrane**
2 **separators in dual chamber microbial fuel cells**

3 **Partha Sarathi Jana¹, Makarand Madhao Ghangrekar² and Dónal Leech^{1*}**

4
5 ¹School of Chemistry & Ryan Institute

6 National University of Ireland Galway, Galway, Ireland

7 ²Department of Civil Engineering

8 Indian Institute of Technology Kharagpur, West Bengal, India

9
10 **Abstract**

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

21
22 **Keywords:** Proton exchange membrane, Microbial fuel cell, Earthen plate, Power density,
23 Chemical oxygen demand.

24 **1. Introduction**

25 Microbial fuel cell (MFC) is an emerging technology, which has been paid much attention in
26 recent years (Harnisch et al., 2008; Logan et al., 2006; Logan & Regan, 2006; Zhang et al., 2009;
27 Zuo et al., 2008), for application to wastewater treatment with simultaneous electricity
28 generation. An MFC is a bioelectrochemical system where bacteria catalyze the degradation of
29 organic matter under anaerobic conditions to convert the energy stored in chemical bonds of
30 organic compounds to electrical energy. The MFC performance is affected by many factors, such
31 as reactor configuration, type of electrode material and membrane separator, electrolyte solution
32 pH, temperature, substrate type and concentration, hydraulic retention time (HRT), inoculum
33 selection or enrichment, cathodic electron acceptor selection, etc. (Pant et al., 2012; Pant et al.,
34 2010b). In the past decade many advances have been made in MFC research aimed at enhancing
35 MFC power density output (Logan et al., 2006; Min et al., 2005; Park & Zeikus, 2003; Rabaey et
36 al., 2004). However, MFC construction, operation and maintenance cost still need to be
37 minimized to make this technology sustainable on economic grounds (Logan & Regan, 2006;
38 Zuo et al., 2008).

39 The characteristics of the membrane separator selected can significantly affect the
40 performance of an MFC (Zhang et al., 2009). Nafion is the most widely used membrane
41 separator because of the high ionic conductivity (Harnisch et al., 2008; Logan et al., 2006). The
42 high cost of Nafion however makes production cost of MFC commercially unacceptable to date
43 (Pant et al., 2010a). Many studies explore the use of alternate separators for MFC (Behera et al.,
44 2010a; Behera et al., 2010b; Jung et al., 2007; Logan et al., 2006; Martin et al., 2010; Min et al.,
45 2005; Park & Zeikus, 2003; Rabaey et al., 2004; Sun et al., 2009; Ter Heijne et al., 2006). For
46 example, the use of a salt bridge (Min et al., 2005), ultrex membrane (Rabaey et al., 2004), a

47 porcelain septum made from kaolin (Park & Zeikus, 2003), anion exchange membranes (Martin
48 et al., 2010), bipolar membranes (Ter Heijne et al., 2006), microfiltration membranes (Sun et al.,
49 2009), J-Cloths (Fan et al., 2007), a selenium HSF membrane (Logan et al., 2006), and
50 ultrafiltration discs (Lefebvre et al., 2011) have been reported for their use as separators in
51 MFCs. We recently (Behera et al., 2010a; Behera et al., 2010b) reported on the treatment of
52 synthetic and rice mill wastewater in fed-batch MFCs fabricated using an earthen pot acting as
53 both anode half-cell container, and a membrane separator, with the performance compared to
54 MFCs fabricated using a Nafion membrane separator (Jana et al., 2010). The earthen pot MFCs
55 demonstrated better performance in terms of organic matter removal and electricity generation
56 compared to the Nafion membrane, but the surface area available for ion transfer through the
57 wall of earthenware was much larger than that in the Nafion-based MFC, making comparison
58 difficult in that study. The thickness of the earthen pot membrane/anode container was also
59 shown to affect both MFC internal resistances, and as a consequence MFC power generation
60 (Behera & Ghangrekar, 2011). The present research focuses on an effort to better compare
61 performances of MFCs operated using the earthen pot as membrane separator to that of Nafion-
62 separated, MFCs by fabrication of polyacrylate MFCs with earthen plate separator of the same
63 exposed geometrical surface area to that of the Nafion separator. The comparison of MFC
64 performance is evaluated by operation of both types of MFC under continuous mode feeding of
65 acetate as synthetic waste, following initial batch incubation with acetate and anaerobic sludge,
66 as inoculum and using a model ferricyanide solution as oxidant in the catholyte.

67 **2. Materials and Methods**

68 *2.1 Experimental set-up*

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

70 separated by the same exposed area of either a Nafion117 proton-exchange membrane (PEM,
71 Sigma Aldrich) or an earthen plate membrane (EP, 3.7 mm thick). The earthen plates were
72 prepared from soil (elemental composition: Al-32%, Si-47.80%, K-4.90%, Ca-1.20%, Ti-0.90%,
73 Fe-13%, similar to that used in previous studies of earthen pots as MFC containers and
74 membranes (Behera & Ghangrekar, 2011) sourced from Midnapore, India and baked at 550-
75 650°C for 6.0 hours, as described previously (Behera et al., 2010a) to provide plates of average
76 thickness of 3.7 mm. The cylindrical MFCs consisted of an outer catholyte chamber separated
77 from a rectangular polyacrylic inner anolyte chamber, with membranes glued to opposite
78 exposed areas in the faces of the inner chamber (Fig.1). Each membrane exposed 20 cm² surface
79 area to the anolyte, making the total exposed membrane surface area of 40 cm². The working
80 volume of the anolyte chamber of both types of MFCs was 350 mL, whilst that of the catholyte
81 chamber was 1200 mL.

82 Graphite plates of 70 cm² each were used as electrodes and placed in the anolyte
83 and catholyte, giving a total surface area of 140 cm² each for anode and cathode in all MFCs.
84 The electrodes were connected externally with titanium wire through a resistance of 100 Ω. The
85 acetate medium influent was supplied to the MFCs from the bottom of the anode chamber using
86 a peristaltic pump (Gilson, France) with effluent exiting the anode chamber at the top of the
87 reactor. The catholyte consisted of 50 mM ferricyanide in 100 mM phosphate buffer (pH of 7.0).

88 2.2 *MFC operation*

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

93 media containing acetate as a source of electron donor having COD of 1250 mg L^{-1} was used as
94 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
95 NaHCO_3 , 10 mL trace element solution and 10 mL vitamin solution (Katuri et al., 2012b)
96 prepared according to <http://www.dsmz.de> (medium No. 826). The feed pH was in the range of
97 7.2-7.5 throughout the experiments and the MFCs were operated at temperatures that varied from
98 28 to 32°C . Initially both the MFCs were operated under batch mode condition to encourage the
99 attachment of electrogenic bacteria to the graphite plate anodes. The first batch consisted of the
100 inoculum supplemented with 290 mL of acetate medium, with the two subsequent batches
101 prepared by replacement of half of the anolyte volume by new acetate medium (no additional
102 inoculums). After these three feed cycles, the MFCs were operated in continuous mode at
103 organic loading rate (OLR) of $2.5 \text{ kg COD m}^{-3}\text{d}^{-1}$, by maintaining a hydraulic retention time
104 (HRT) of 12 h using the peristaltic pump. After reaching a steady state voltage output across the
105 100Ω resistor, the performance of MFCs were evaluated by polarization experiments using a CH
106 instruments 650 (USA) potentiostat.

107 2.3 *Analyses and calculations*

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

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

125 **3. Results and Discussion**

126 *3.1 MFC operation*

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

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

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

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

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

163

164 3.2 *Organic matter removal*

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

176 3.3 *Polarization studies*

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

184 and EP-MFC, respectively. The earthen plate membrane is substantially thicker (~3.7 mm) than
185 the Nafion 117 (~0.17 mm), which might contribute towards the higher internal resistance for
186 these cells. In comparison to the results reported here, Jung et al. (Jung et al., 2007) report
187 internal resistances of dual chamber MFCs using a range of membrane separators to be from
188 1239 to 1344 Ω , depending on factors such as electrode spacing (Kong et al., 2010) and
189 membrane, with higher internal resistance resulting in MFC with lower power densities in this
190 configuration. Lower internal resistances of 84-98 Ω , and higher power densities, were obtained
191 for MFCs in a single chamber, air-breathing cathode configuration with much closer electrode
192 spacing (Katuri et al., 2012a). Using a dual chamber Nafion-separated MFC system, similar to
193 the configuration in this report, Katuri et al. (Katuri et al., 2012a) report a maximum power
194 density of 6.4 W m^{-3} based on anolyte volume for the MFC operating on slaughterhouse
195 wastewaters, whilst Kong et al. (Kong et al., 2010) observed maximum power density of 4.35 W
196 m^{-3} using acetate as feed. Improvement in power density may be achieved, as reported recently
197 by Zhang et al. (Zhang et al., 2011), by use of high surface area anodes and glass fiber as a
198 separator in a single chamber air-breathing cathode MFC configuration, providing a power
199 density of 75 W m^{-3} .

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

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

214 **4. Conclusion**

215 Nafion is the most widely used fuel cell membrane as it provides high ionic conductivity, but
216 with limitations of high cost, fouling and deformation This study demonstrated by comparison to
217 Nafion, that an earthen plate membrane may provide a low-cost and more durable alternative to
218 Nafion in continuous flow MFCs. The MFC using Nafion membrane as separator showed
219 slightly better performance in terms of organic matter removal and electricity generation than the
220 MFC based on earthen plate membrane separators, whilst both show comparable Coulombic
221 efficiency. The performance of earthen plate MFC may be enhanced by increasing the membrane
222 surface area or decreasing the membrane thickness. The 40 cm² Nafion117 membranes used in
223 the present experiment costs approximately €30.0 whilst the same area of the earthen plate costs
224 approximately €0.025, making it 99% cheaper. Utilization of such low cost separators may
225 contribute to further developing economical MFC technology.

226

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334

335

336

337 Figure legends

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

341
342 **Fig.2.** Voltage generation response as a function of time for the PEM-MFC (grey) and the EP-
343 MFC (black). Arrows indicate replacement with fresh feed and star indicates the time when the
344 reactors were switched from batch to continuous mode operation.

345
346 **Fig.3.** Cyclic voltammograms (1 mV/s) of anodic biofilm, recorded in-situ on the 19th day of
347 operation of the cells under 100 Ω external resistors, for the PEM-MFC (grey) and EP-MFC
348 (black) systems.

349
350 **Fig.4.** A comparison of the change in pH of the catholyte chamber, initially containing distilled
351 deionized water, as a function of time upon introduction of 1 M sulphuric acid into the anolyte
352 chamber for PEM (grey) and earthen plate (black) MFCs.

353
354 **Fig.5.** COD removal efficiency (open) and voltage generation across the 100 Ω resistance
355 (closed) of PEM-MFC (grey circles) and EP-MFC (black triangles) as a function of time during
356 continuous feed of MFCs (commenced at day 7).

357
358 **Fig.6** In-situ polarization curves, recorded on day 25, cell voltage and power density versus
359 current density for PEM (grey closed) and earthen plate (black open) MFCs

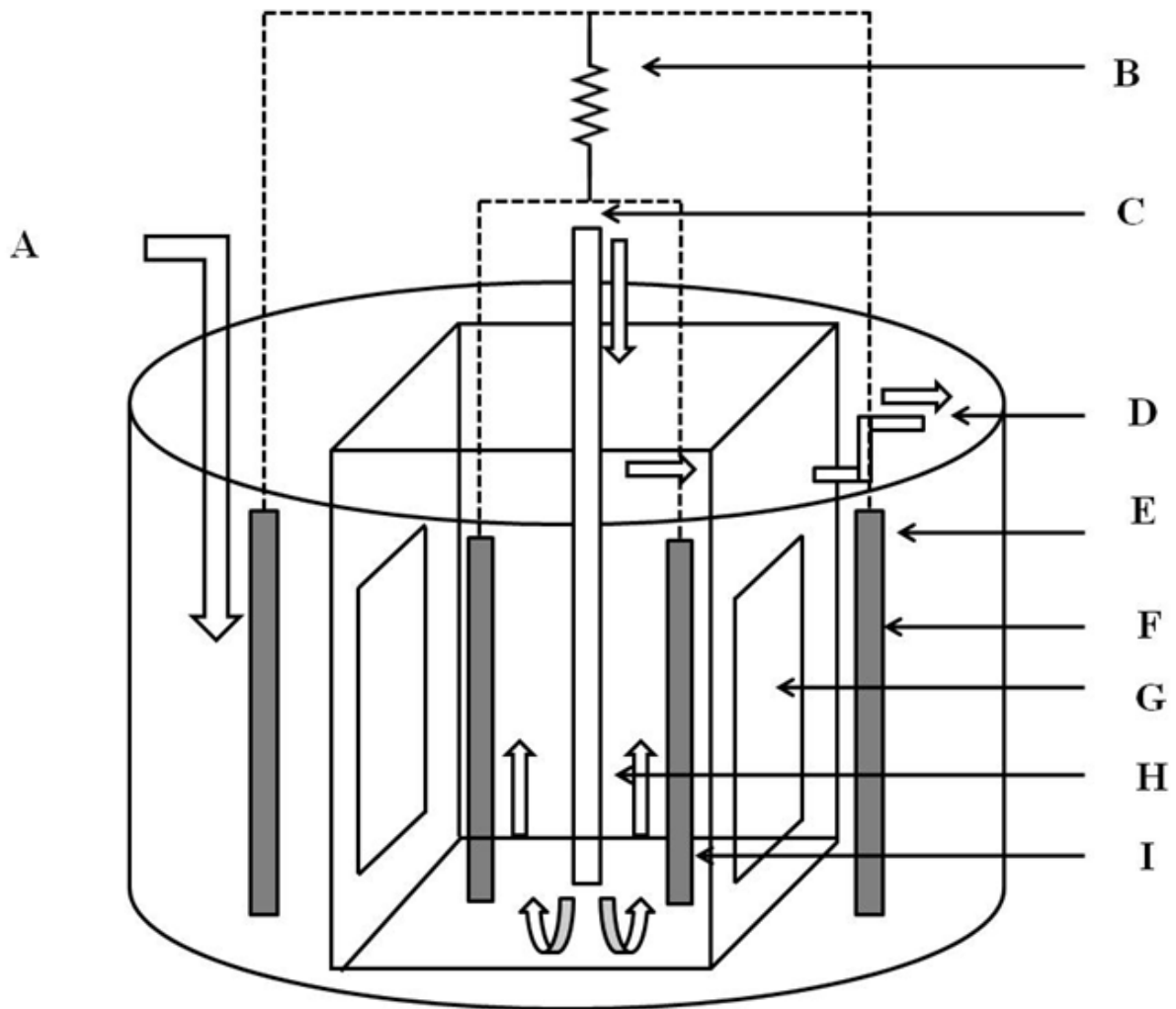
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361
362 Table 1. Comparison of performance of PEM-MFC and EP-MFC

MFCs	Voltage with 100 Ω 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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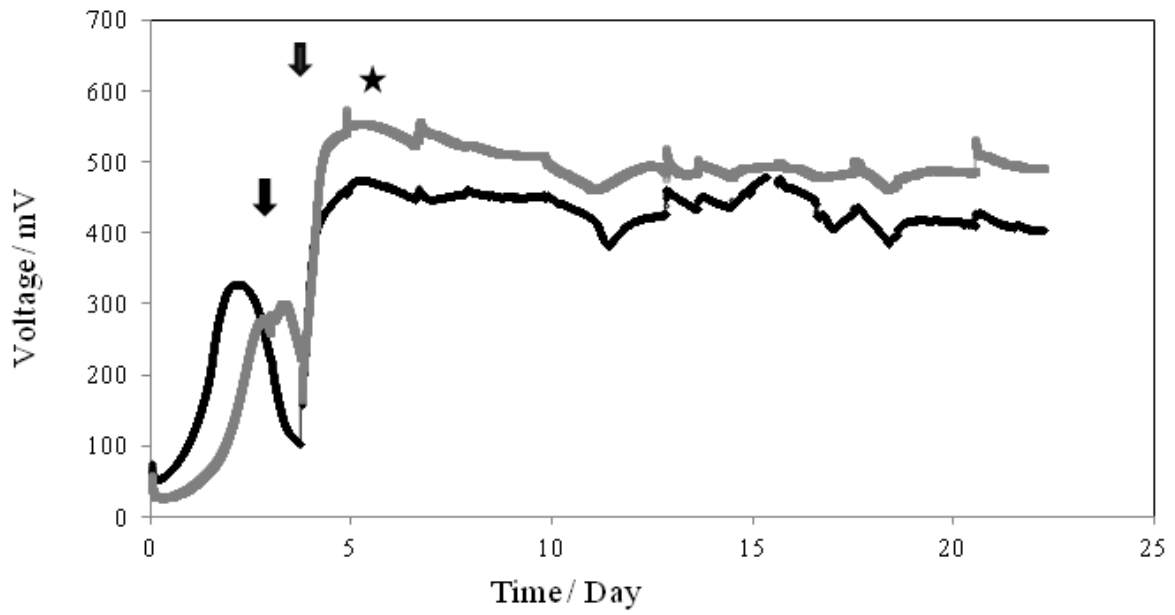
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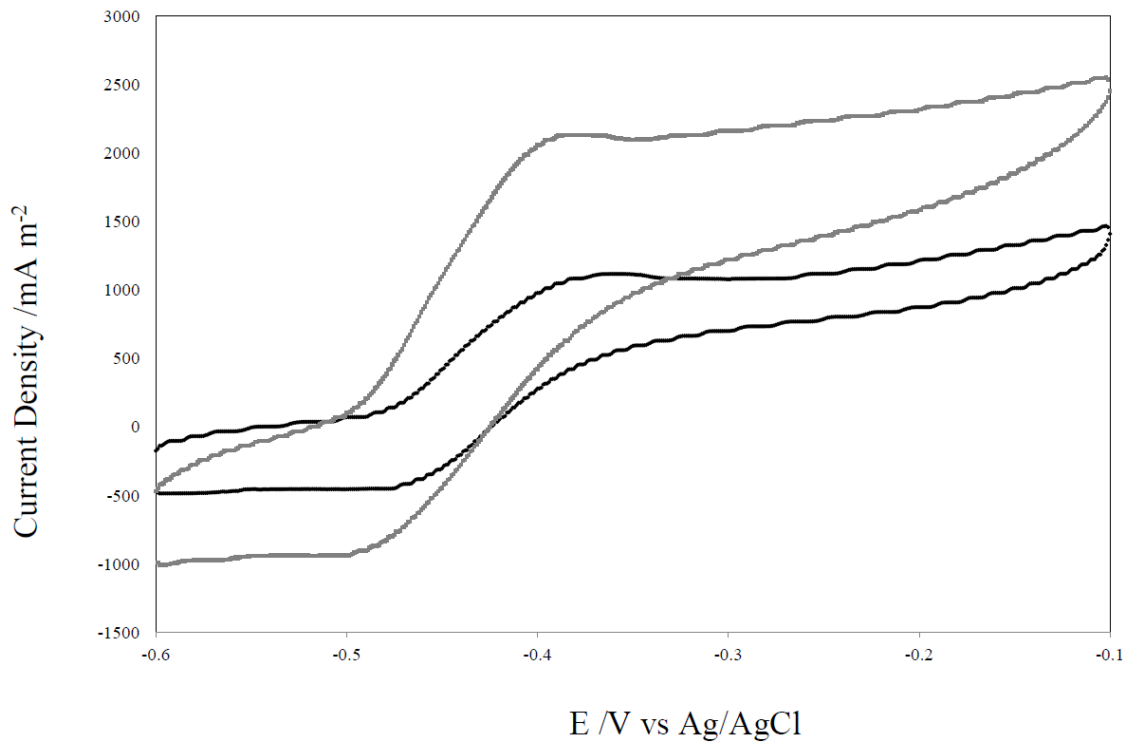
366 Fig. 1.

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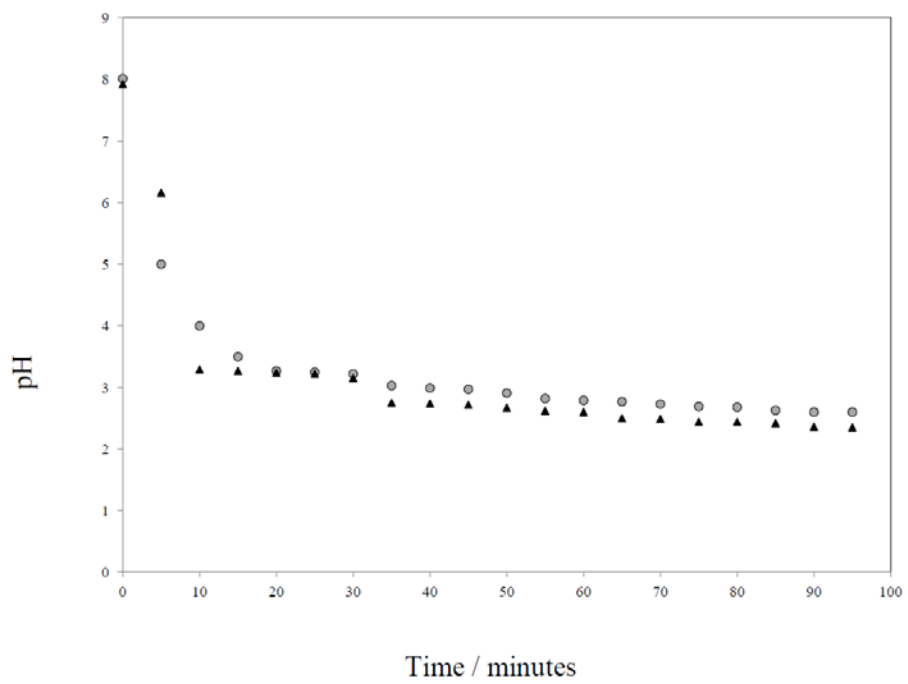
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369 Fig 2.



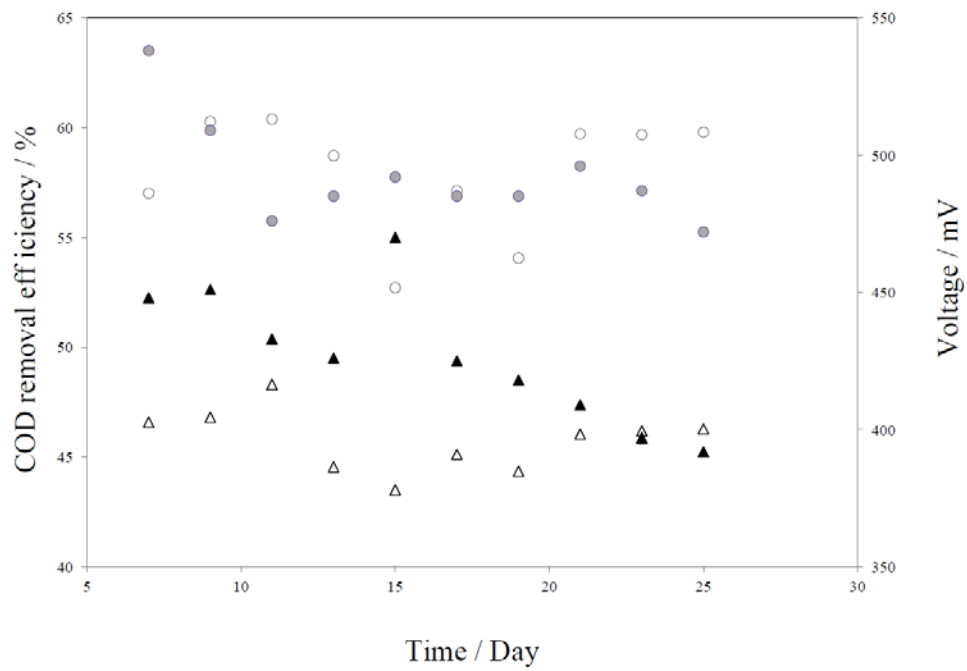
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371 Fig 3.



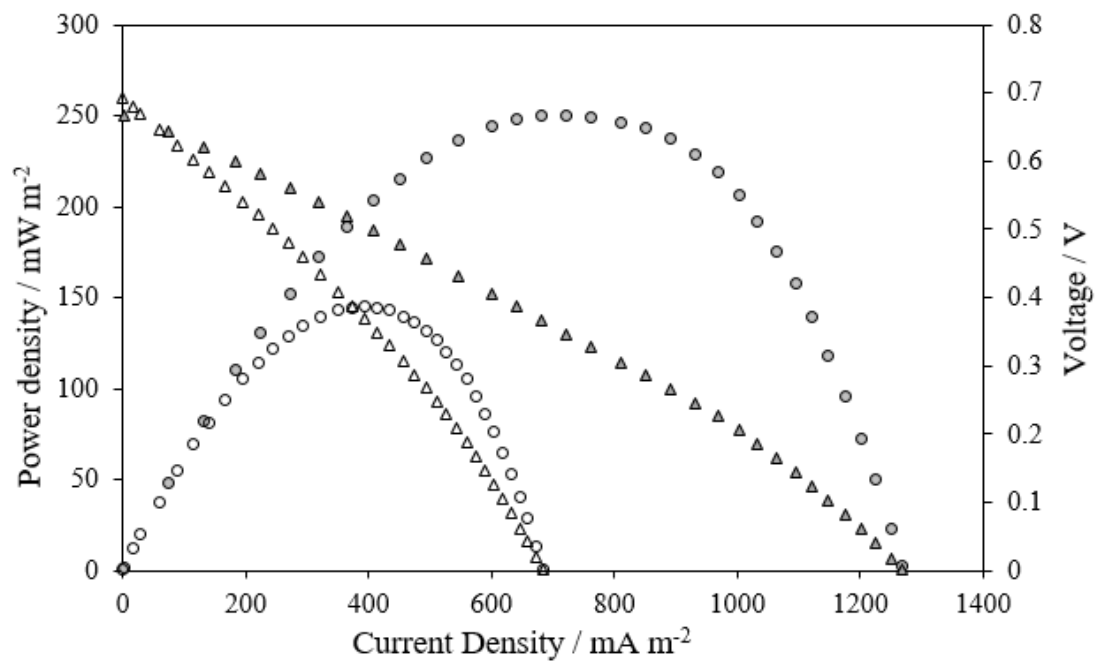
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373 Fig 4.



374

375 Fig 5.



376

377 Fig 6.