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ABSTRACT

Ceramic-based MFC designs have proven to be a low cost alternative for power production and wastewater treatment. The use of ionic liquids in ceramic MFCs is explored for the first time in the present work in order to improve power output. The ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[EMIM][Tf_2N]$, has been selected for this purpose due to its advantageous properties. The performance of activated carbon cathodes using polytetrafluoroethylene (PTFE) binder and different carbon diffusion layers (DL) (controls) are compared with two types of ionic

25 liquid-modified cathodes (test). This work continues to study the performance of

26 terracotta separators modified with the same ionic liquid, neat and also mixed

27 with PTFE. While the results show operational limitations when the IL is

28 integrated in the ceramic separator, there is a significant enhancement of the

29 MFC performance when added as part of the activated layer mixture of the

30 cathode, achieving up to 86.5 % more power output in comparison with IL-free

31 MFCs (from 229.78 µW to 428.65 µW). The addition of a layer of PTFE-mixed

32 ionic liquid spread on the activated layer of the cathode also leads to an

33 increase in power of approximately 37 %.

34

35 **Keywords: Ceramic separators; Microbial Fuel Cell; Ionic liquid; Activated**

36 **carbon cathodes; Activated sludge.**

37

38 **1. Introduction.**

39 Microbial Fuel Cells (MFCs) have been extensively investigated in recent years

40 since this technology offers promising prospects for bioenergy production from

41 wastewater. In the context of the current global energy crisis and growing

42 demands for water treatment, the scientific community sees the development of

43 this technology as a potential alternative that may help address such pressing

44 issues [1, 2]. Although the performance of this technology has increased almost

45 exponentially in the last two decades, there are some limitations associated with

46 the low levels of power density achieved and their operating and fabrication

47 costs [3]. Thus, the improvement of efficiency in MFC performance requires the

48 study of non-expensive materials and simpler designs [4, 5].

49 The great potential of MFC technology lies in the direct conversion of the

50 chemical energy stored in organic wastes and biomass into electricity, operating

51 at ambient conditions without additional energy requirements and with a net

52 balance of zero emissions [6]. In the process, electrons are released and

53 transported to the cathode through an external circuit while obtaining an

54 electrical current. In double and single-chamber MFCs the use of a membrane

55 or separator allows the ion exchange mechanism to take place while

56 maintaining the anode and cathode chambers physically separated [7]. The

57 selection of the appropriate separator is one of the key factors in designing

58 MFC devices. The high cost of proton exchange membranes based on

59 perfluored polymers such as Nafion reduces the efficiency of this technology

60 and, therefore, a wide range of separator materials have been investigated in

61 the last years, including cation and anion exchange membranes, glass fibers or

62 porous fabrics, among other alternatives [8]. Paper in combination with

63 conductive latex and microporous polymer-based carbon are other examples of

64 alternative separators made out of porous material being currently developed

65 [9,10]. Ceramic-based separators have proven to be a low cost alternative in

66 MFCs. Park *et al.* [11] used a porcelain-coated cathode as proton exchange

67 layer replacing expensive proton-selective membranes. Most recently, earthen

68 pot and terracotta have been evaluated as separators in MFCs showing their

69 capacity for proton transfer and power production [12, 13], reaching sufficient

70 power for practical applications in the absence of metal catalysts [14]. The use

71 of ceramic and precious metal-free MFCs has effected major cost reductions in

72 this technology. The thickness of the ceramic wall or the porosity are important

73 factors that affect the cell performance [13]. The electrode material is another

74 key factor directly affecting the performance of MFCs and their feasibility from

75 both an economic and long-term operation point of view [15]. Several types of

76 carbon-based materials such as carbon nanofibers (CNF), carbon nanotubes

77 (CNT) or activated carbon (AC) have been researched as electrode materials,

78 showing high surface area and catalytic activity for an effective oxygen

79 reduction reaction at the cathode [16-19]. Amongst them, activated carbon

80 offers competitive advantages such as low cost and high catalytic activity [14,

81 20].

82 The present work explores the enhancement of the power performance of

83 ceramic MFCs employing metal-free activated-carbon based electrodes through

84 the incorporation of ionic liquids as part of the cathode. It has been reported that

85 the potential of the cathode in ceramic-based MFCs can limit the power

86 production, thus demanding more emphasis for the improvement of the cathode

87 performance [12]. Because of the distinctive properties of ionic liquids, the

88 range of applications of this type of compounds has widened greatly in recent

89 years, including separation processes, chemical catalysis or biological systems

90 [21]. A typical IL is based on the combination of organic cations (e.g. N-

91 alkylpyridinium, N,N'-dialkylimidazolium) and a mono- or poly-atomic inorganic

92 anion (e.g. e.g. Cl^-, $AlCl_4^-$, PF_6^-) or, increasingly more common, an organic

93 anion (e.g. $(CF_3SO_2)_2N-$ = Tf_2N-, $(C_2F_5SO_2)_2N-$ = Pf_2N-) [22]. Their

94 environment-friendly characteristics, thermal stability, high ionic conductivity

95 and wide electrochemical window ($\approx$ 4-6 V) make them suitable candidates for

96 several electrochemical systems [23], having been employed in batteries and

97 capacitors, solid-state electrochemical actuators, electrochemical sensors and

98 fuel cells [22]. Several groups have also studied the performance of ionic liquids

99 as electrolytes in proton exchange membrane fuel cells (PEMFCs), including

100 MFCs [24-26]. The terracotta material itself has been used as an ion exchange

101 separator and MFC chassis. Some limitations have been posed by this type of

102 material, such as possible oxygen diffusion through the porous wall into the

103 anode chamber [12]. The present work also investigates the possibility of using

104 the ionic liquid as an electrolyte by directly applying it onto the ceramic

105 separator. Ionic liquids have been used as electrolytes in a wide range of

106 electrochemical processes and devices due to their good properties, being

107 characterised by negligible vapour pressure [27, 28]. These advantages have

108 made possible the replacement of conventional electrolytes with ionic liquids,

109 avoiding volatility and chemical stability problems [29]. In the present study, 1-

110 ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][Tf$_2$N], has

111 been selected to assess the use of ILs for improving the power performance in

112 ceramic MFCs for the first time. This imidadolizum-based IL was chosen due to

113 its advantageous properties such relatively high ionic conductivity compared

114 with the typical conductivity range for other ionic liquids (9 mS.cm-1 at RT [29]),

115 good chemical stability, low viscosity (37 cp at RT) and hydrophobic nature [28]

116 . The influence of the IL selected on the MFC performance is studied in terms of

117 power generation when added as part of the cathode and on the separator

118 (ceramic wall).

119

120 **2. Materials and methods.**

121 **2.1. MFC configuration and operation.**

122   Fig.1 shows a schematic representation of the Microbial Fuel Cells used in this

123   study. The units were set up with terracotta bottom sealed cylinders (Weston

124   Mill Pottery, Nottinghamshire, UK) of 10 cm length, with 3.5 cm and 4 cm, inner

125   and outer diameter, respectively, and wall thickness of 3 mm. The terracotta

126   material used is characterized by a water absorption amount (by weight) of 9.1

127   % (SD 0.4) [30]. The cylinders were placed in bottle-shaped plastic housing

128   covered on top with a layer of Parafilm®, which forms the anode compartment,

129   with a maximum fuel capacity of 160 ml. The anode electrode was a layer of

130   carbon fibre veil (loading 20 $g.m^{-2}$) in a rectangular shape with a total macro

131   surface area of 2430 cm^2 (PRF Composite Materials, Dorset, UK), folded and

132   wrapped around the outside of the terracotta caves and held with nickel-

133   chromium wire; the latter also served as the current collector and connection

134   point. MFCs were fed with full strength or 1:10 diluted activated sewage sludge

135   (Wessex Water Scientific Laboratory, Cam Valley, Saltford, UK) in distilled

136   water and supplemented with sodium acetate anhydrous (Fisher chemical,

137   Loughborough, UK) to ensure sufficient carbon energy for the microorganisms

138   during the operation of the MFCs. Two conditions of substrate concentration (20

139   and 100 mM) were employed in order to study the effects of substrate

140   concentration on power performance and, in turn, compare this with that of the

141   ionic liquid. The MFCs employed were operated in batch mode and loaded with

142   an external resistance of 100 Ω. The anode of each MFC was matured for two

143   weeks, prior to starting the experiments, by periodically feeding the anode with

144   a solution of sludge and acetate (100 mM).

145   **[INSERT FIGURE 1]**

146   **2.2. Preparation of the cathodes and the ceramic separators.**

147 Several activated carbon-based cathodes were fabricated and their

148 performance was compared in terms of power production. The general way to

149 prepare the cathodes involves hot pressing a mixture of 80 g of activated

150 carbon (AC) powder (G. Baldwin and Co., London, UK) and 20 wt% of

151 polytetrafluoroethylene (PTFE) in 120 ml of deionized water, onto the diffusion

152 layer (carbon veil or carbon cloth), which was previously coated with PTFE (60

153 % PTFE dispersion in water, Sigma Aldrich, UK), as described in [14]. The final

154 dimensions of the cathodes were 9x10 cm and the final loading of activated

155 carbon was approximately 60 mg.cm^{-2} per cathode. Once the AC mixture is dry,

156 the cathodes are placed inside the terracotta cylinders (cathode compartment),

157 with the side of the AC loading in contact with the inner wall of the ceramic

158 cylinder and the diffusion layer exposed to air. As a preliminary study, the

159 behaviour of two types of carbon materials were tested as substratum/diffusion

160 layers namely, carbon veil (cathode-1) (20 g.m^{-2}, air permeability 420

161 cm^3/cm^2/sec, PRF Composite Materials, Dorset, UK) and carbon cloth (cathode-

162 2) (120 g.m^{-2}, air permeability 100 cm^3/cm^2/sec, 100% activated, Zorflex$^®$,

163 Feluy, Belgium).

164 The performance of the ionic liquid 1-ethyl-3-methylimidazolium

165 bis(trifluoromethylsulfonyl)imide) [EMIM][Tf$_2$N] (Ionic Liquids Technologies,

166 Heilbronn, Germany), was first investigated in the ceramic MFCs as part of the

167 cathode. Two cathode structures were fabricated for this purpose. The first

168 modified type was prepared by mixing AC, PTFE and deionised water as

169 described above and hot pressing the mixture onto carbon veil. Once the

170 cathode is dry, a layer of ionic liquid mixed with PTFE (60 % dispersion in

171 water) is applied uniformly over the side of the AC mixture (cathode-3). The

172   second modified type of AC-based cathode was prepared by mixing AC, PTFE,

173   deionised water and the ionic liquid under study at the same time, and then hot

174   pressing the final mixture onto carbon veil until the cathode is dry (cathode-4).

175   The fabrication of the cathodes was manual and thus it is difficult to provide an

176   accurate thickness, which ranged between 1.5-2 mm, at a fixed carbon loading

177   of 60 mg.cm^{-2} for all cathodes prepared.

178   The inner wall of the terracotta cylinders, which acts as separator between the

179   cathode and the anode chamber of the MFCs set up [31], was modified with

180   [EMIM][Tf$_2$N] and the effects on power output were compared with the

181   performance of the terracotta separator in the absence of ionic liquid over the

182   ceramic surface (separator-1). Thus, [EMIM][Tf$_2$N] was applied onto the inner

183   ceramic wall in contact with the catholyte. The ceramic materials were modified

184   by two methods resulting in two types of test to be investigated: (i) by uniformly

185   applying a layer of ionic liquid soaked in PTFE onto the whole of the inner wall

186   of the terracotta cylinder with a brush (separator-2) and (ii) by uniformly

187   applying a layer of ionic liquid but without PTFE (separator-3). In both cases,

188   the separators were left to dry overnight. All the configurations including ionic

189   liquid were prepared with a total amount of 1.5 g per cathode or separator. As

190   the amount of ionic liquid deposited is low compared with the high surface area

191   of the cathode chamber and some part is absorbed by the porous material, the

192   increase in separator thickness is negligible (approximately 200 μ for the case

193   of separator-2 due to the inclusion of PTFE). There was a total of six set-ups for

194   investigating the performance of the ionic liquid [EMIM][Tf$_2$N] in ceramic MFCs

195   (Table 1). It must be noted that the configurations named "cathode-1" and

196   "separator-1" are equivalent and served as the controls for the conditions

197 modified in the experiments. Three replicates of each type of MFC were built.

198 Fig. 2 shows a basic representation of the structure of the cathodes and the

199 separators researched.

200 **[INSERT TABLE 1]**

201 **[INSERT FIGURE 2]**

202 **2.3. Data and analysis.**

203 Voltage measurements (V) were recorded by ADC-24 Data Logger (Pico

204 Technology Cambridge shire, UK). The performance of the ceramic MFCs

205 assembled with different cathode and separator structures was analysed in

206 terms of power production. Polarisation and power curves were determined by

207 successively lowering the external resistive loads (R_L) from ≈ 1 MΩ to 11.78 Ω,

208 every 3 minutes, using an automatic load-controlled measurement tool [32]. Six

209 measurements were taken for each resistance at 30 second intervals. Current

210 and power output were calculated by $V = I x R_L$ and $P = V^2/R_L$, respectively.

211 Internal resistance (R_{int}) of MFCs was calculated by $R_{int} = (OCV/I) − R_L$ applied

212 at the point of peak power, which is the point of maximum power transfer, where

213 OCV is the voltage in open-circuit conditions, I is the current under the external

214 load resistor and R_L is the external load resistor [33].

215 Measurements of pH and conductivity of each MFC were performed during the

216 experiments with a Hanna-8424 pH-meter (Hanna Instrument, UK) and 470-

217 Jenway conductivity meter (Camlab, UK), respectively.

218

219 **3. Results and Discussion**

220 *3.1. Carbon veil vs. carbon cloth*

221 As a preliminary study, the performance of two types of carbon materials,

222 carbon veil (cathode-1) and carbon cloth (cathode-2), were tested as diffusion

223 layers in MFCs fed with full strength activated sludge supplemented with

224 acetate (20 mM). Figure 3 depicts the polarisation and power curves with

225 standard error mean bars shown for the three replicates of each type of

226 cathode. The results from the triplicate tests, clearly show that the MFCs

227 working with carbon veil reached higher power levels than those with carbon

228 cloth. The maximum power and current values achieved by carbon veil

229 cathodes were 274.07 µW and 1154.88 µA, respectively, which were on

230 average more than double than those obtained with carbon cloth cathodes,

231 135.69 µW at 509.96 µA. Although the average value of OCV for the carbon

232 cloth (541 mV) was higher compared with that obtained with carbon veil (498

233 mV), the faster rate of change (steeper slope) suggests higher ohmic

234 resistance, which leads to a faster decrease in cell voltage. In fact, internal

235 resistance (R_{int}) in the case of carbon cloth-based MFCs, 539.1 Ω (calculated

236 according to the method described in section 2.3) is more than double the value

237 of R_{int} for the case of carbon veil-based MFCs, 225.5 Ω. The improved

238 performance of the carbon veil is strengthened by its lower cost, compared to

239 the carbon cloth [14]. These results were achieved with a total cathode area of

240 90 cm^2 in both cases. Although the carbon density is much higher for carbon

241 cloth, 120 g.m^{-2} with a thickness of 0.5 mm *vs.* 20 g.m^{-2} and 0.19 mm thickness

242 for carbon veil, the oxygen-permeability of carbon cloth is actually lower

243 according to the air permeability (section 2.2). The added advantage of carbon

244 veil is improved material integrity with minimal additional weight and thickness.

245 Consequently, carbon veil was selected as supporting and diffusion material for

246 the preparation of the cathodes when studying the influence of ionic liquids in

247 the subsequent experimental steps.

248

249 **[INSERT FIGURE 3]**

250

251 3.2. *Cathodes modified with ionic liquid.*

252

253 The voltage response of the MFCs using different cathode configurations

254 (cathode-1, cathode-3 and cathode-4) is shown in Fig. 4A. After the anode

255 maturing period with the cathode-1 in all MFCs, this type of cathode was

256 removed and replaced by the cathode types 3 and 4 in the appropriate

257 replicates. All anode compartments were emptied and replenished with 160 ml

258 of wastewater diluted 1:10 in deionised water and supplemented with acetate

259 with a final concentration of 20 mM. Fig. 4A shows the temporal voltage

260 response after the anolyte replenishment. For the sake of simplicity, the bar

261 errors for the replicates are not shown in Figure 4A, which is solely intended to

262 offer the voltage trends. Standard error mean values are however shown in

263 Figure 4B, which depicts the power levels achieved by each type of cathode.

264 The voltage response of the cells shows that the group of MFCs stabilises at

265 approximately 103, 129 and 167 mV for cathode-1, cathode-3 and cathode-4,

266 respectively, after 3 days (4305 min, without considering the anode maturing

267 period). The trend of maximum power follows the same order as the voltage

268 response, $P_{max\ cathode-4} > P_{max\ cathode-3} >> P_{max\ cathode-1}$. These results suggest that

269 the MFCs using the ionic liquid 1-ethyl-3-methylimidazolium

270 bis(trifluoromethylsulfonyl)imide, [EMIM][Tf$_2$N] were significantly improved in

271 terms of power performance. MFC replicates using cathode-4, with the ionic

272 liquid as part of the mixture of the activated layer, reached a maximum power of

273 428.65 μW at a current of 2238.51 μA; the corresponding power and current

274 levels for the control replicates were 229.78 μW at 1016.22 μA. This shows that

275 the inclusion of the ionic liquid almost doubles the level of power and current

276 produced (an increase of up to 86.5%). When the ionic liquid was uniformly

277 spread over the activated carbon layer soaked in PTFE (cathode-3), the

278 performance of the MFCs also improved with values of 314.87 μW and 1668.04

279 μA of maximum power and current, respectively (Fig.4B), which represents an

280 increase of ≈ 37 % over the maximum power obtained in the absence of ionic

281 liquid (cathode-1).

282

283   **[INSERT FIGURE 4]**

284

285 As seen in Figure 4, the effect of the ionic liquid used as part of the cathode is

286 visible for both cases when it is included in the mixture that forms the activated

287 carbon deposited on the carbon veil layer (cathode-4) and as a PTFE-soaked

288 layer over the carbon activated mixture once deposited on the electrode

289 (cathode-3). However as shown above, the level of power generated by MFCs

290 using the first configuration is higher. Although Figure 4 shows that MFCs using

291 Cathode-1 reached the highest OCV (476 mV), there is a rapid decrease of

292 voltage as current increases, whilst for the case of cathode-3 and cathode-4,

293 the slope for ohmic resistance is less steep, resulting in higher current and

294 power output and indicating improvement due to the addition of IL. As shown in

295   Table 2, the estimated values of R_{int} are higher for the MFCs working with

296   cathode-1 (245.9 Ω) compared with cathode-3 (119.6 Ω) and cathode-4

297   modifications (85.6 Ω). MFCs and fuel cells in general are subject to internal

298   losses such as activation, ohmic and mass-transfer over-potentials. The ohmic

299   losses in an MFC include both the electrode resistance to the flow of electrons,

300   and the cation-exchange-separator resistance to the flow of ions within the

301   anode and cathode electrolytes if present [34]. Through the application of the

302   ionic liquid in ceramic MFCs is expected to boost the ion transport from the

303   anode to the cathode through the ceramic separator [3], significantly improving

304   the level of power generated. The hydrophobic nature of the ionic liquid

305   [EMIM][Tf$_2$N] also allows the stability of the cathode performance [28].

306   Focusing on the comparison between cathode-3 and cathode-4, the way of

307   incorporating the ionic liquid described for cathode-3 implies the inclusion of an

308   additional layer of PTFE between the separator and the activated mixture itself.

309   It has been previously reported that the presence of an appropriate amount of

310   PTFE inside an activated carbon mixture for cathode construction results in a

311   more porous and highly textured mix, compared with a solely AC-based

312   cathode, enhancing oxygen diffusion and ion exchange [20]. However, cathode-

313   3 configuration also implies the superficial addition of PTFE (to soak the ionic

314   liquid) covering the surface of the catalyst that may improve the contact

315   between the separator and the carbon cathode, but also can lead to a reduction

316   of the cathode active area and thus the deterioration of the MFC performance

317   [35]. This may explain why the cathode-4, with the ionic liquid integrated in the

318   activated layer and not involving the addition of an extra PTFE layer,

319   outperforms the rest of the cathode configurations, as supported by the data of

320   maximum power and internal resistance provided above.

321

322   *3.3 Ceramic separator modified with ionic liquid.*

323

324   Several recent reports focused on the study of ionic liquids as electrolyte in

325   ionic exchange membranes for their application in MFCs [36]. The use of the

326   ionic liquid acting as an electrolyte was also included in this study through as

327   part of the separator by modifying the inner wall of the caves in two ways, (1) as

328   a layer of IL and PTFE directly applied on the ceramic material (separator-2)

329   and (2) as a layer of IL only (separator-3). As described in the previous section,

330   polarisation measurements were taken after establishing a stable voltage

331   response, once the MFCs were refilled with 160 ml of anolyte (described in

332   Materials and Methods). Figure 5 shows the power curves of the MFCs

333   incorporating these modifications, compared with those obtained with the

334   control set (separator-1). In this case, no improvement in the efficiency of the

335   MFCs working with a layer of PTFE-mixed IL spread over the inner ceramic wall

336   (separator-2) is observed or the level of power is severely limited when only the

337   IL is applied in the absence of PTFE (separator-3).

338

339   It must be noted that, for both types of modification i.e. separator-2 and

340   separator-3, the polarisation curves exhibit an irregular behaviour in the sector

341   after reaching the maximum power. This phenomenon has been previously

342   explored and described as overshoot due to the simultaneous decrease in

343   power and current, and has been associated with the underperformance of the

344 MFCs [30]. The overshoot phenomenon was not observable in the power

345 curves of the control set, even when the performance of these MFCs could be

346 improved by incorporating ionic liquid as part of the electrode. Therefore, the

347 occurrence of overshoot is not directly associated with the presence of a limiting

348 element such a low conductivity catholyte, but possibly with the presence of an

349 inhibiting component in the system. The overshoot phenomenon can be

350 attributed to the presence of the ionic liquid directly applied onto the ceramic

351 wall. But still, the MFCs replicates working with the separator-2, in presence of

352 PTFE, offer levels of power closer to those given by the control set (209.04 µW

353 *vs*. 229.78 µW).

354 When calculating the values of R_{int} of the MFCs using the different separator

355 configurations, it was found a significant increase in R_{int} for separator-3 (473.1

356 Ω) compared with that of separator-1 (245.9 Ω), and it was also higher for

357 separator-2 (288.6 Ω). In the case of separator-3, the lower regression

358 coefficient is due to the lack of stability of the MFC systems due to the

359 overshoot phenomenon. The ion exchange capacity of the ceramic material is

360 due to its hydrophilic nature and high cation exchange capacity [13]. When the

361 ionic liquid in the absence of PTFE is applied to the ceramic wall and is let to

362 dry, a certain amount of the catholyte is absorbed by the ceramic material,

363 penetrating the pores on the inner wall of the terracotta cylinder. Since the

364 performance of this type of MFCs lies on the transport of ions from the anode to

365 the cathode through the ceramic separator, the effects of depositing the ionic

366 liquid directly onto the separator can be observed in the values of internal

367 resistance and power output [37]. If the ionic is deposited on the ceramic wall

368 soaked with PTFE forming a mixture to fix the ionic liquid on the surface of the

369 ceramic wall, the blocking effect may be relieved compared to separator-2,

370 although internal resistance is still affected compared to separator-1 and no

371 improvement in power performance is observed. These results indicate that it is

372 not possible to improve the MFC performance in terms of power output by

373 integrating the electrolyte in the ceramic separator of the system by the

374 methods here described.

375

376 **[INSERT FIGURE 5]**

377

378 *3.4. Influence of the substrate concentration.*

379

380 In order to study the influence of the concentration of the substrate on the

381 power output and compare it with the effect of the ionic liquid, the MFCs

382 working with cathode-3 and cathode-4 and the control set were run at two

383 values of acetate concentration (20 and 100 mM), shown in Figure 6B. Voltage

384 and power values for the concentration of 20 mM correspond to the value given

385 in section 3.2. Figure 6C and D show the power and polarisation measurement

386 for the cathodes modified with ionic liquid (cathode-3 and cathode-4), including

387 the results for the MFCs working with the ionic liquid-free cathode at 100 mM as

388 control. The increase in the power output due to the addition of acetate is 26.1

389 % on overage for the replicates using the cathode-1 (see Fig. 6.B), whilst the

390 increase due to the use of the ionic liquid is over 86% for the best case (see

391 Fig. 6.D). The comparison between the power curves of the replicates at 100

392 mM shows that the trend of maximum power levels at such concentration is the

393 same as is at 20 mM, $P_{max\ cathode-4} > P_{max\ cathode-3} \gg P_{max\ cathode-1}$ (see Table 2).

394 Regarding the replicates with ionic liquid, the higher percentage of increase in

395 power level is observed for cathode-3, with cathode-4 outperforming all the

396 other designs. These results also suggest that the cathode performance can be

397 one of the limiting factors in this type of MFCs in terms of power production,

398 since even the maximum power value achieved by the MFCs in the absence of

399 ionic liquid (cathode-1) at 100 mM (acetate), 289.73 µW, is almost half the best

400 result obtained with the ionic liquid present in the activated layer (cathode-4) at

401 20 mM, 428.65 µW (see Table 2). Moreover, although Figures 6.C and 6.D

402 show a higher value of OCV for cathode-1 (454 mV) compared to both cathode-

403 3 (376 mV at 20 mM and 414 mV at 100 mM) and cathode-4 (373 mV at 20 mM

404 and 404 mV at 100 mM), the differences observed in the slopes of the

405 polarization curves indicate a faster decrease in voltage, as current increases

406 for cathode-1. This results in an increase of the internal resistance (see Table

407 2), which remains much lower for cathode-4 and cathode-3 for both 20 and 100

408 mM.

409

410 **[INSERT FIGURE 6]**

411

412 **[INSERT TABLE 2]**

413

414 *3.5. Catholyte production.*

415

416 The operation of the MFC design used for this research implies the generation

417 of a certain amount of catholyte as a consequence of the transport of ion

418 species and water from the anode chamber through the ceramic wall. The

419   catholyte generated in the MFCs was of a transparent appearance. This type of

420   cylindrical ceramic-based MFC allows the production of catholyte of high salt

421   concentration whilst the recovery of clean water from the anode takes places by

422   electro-osmosis [37]. Figure 7 shows the amount of catholyte generated, pH

423   and conductivity after ≈ 5400 min. of operation by the main MFC configurations

424   studied, for the 20 mM acetate concentration case. As can be seen, there are

425   significant differences in the volume of catholyte generated, and it can be

426   assumed that the amount of catholyte generated directly depends on the level

427   of MFC performance as a consequence of the ion exchange through the

428   separator. These differences are not visible in the measurements of pH and

429   conductivity, which remained within the range of 10.6-12.1 for pH and 10.1-11.2

430     $mS.cm^{-1}$ for conductivity, although the values of pH are slightly higher for the

431   catholyte samples generated by the cathode-3 and cathode-4.

432

433   **[INSERT FIGURE 7]**

434   **4. Conclusions**

435

436   The present work has investigated the application of ionic liquids in ceramic-

437   based MFCs in order to improve the level of power generation. For this

438   purpose, activated-carbon cathodes and terracotta separators were modified

439   with [EMIM][Tf$_2$N] in pure form or soaked with PTFE. The results prove that with

440   the inclusion of the ionic liquid as part of the cathode a significant increase of

441   over 86% in power output is achieved. Amongst the methods tested, the mixture

442   of a certain amount of ionic liquid, activated carbon and PTFE forming one layer

443   pressed onto the diffusion layer (carbon veil) has shown to be the best option,

444 whilst the modification of the ceramic wall with [EMIM][Tf$_2$N] leads to the

445 deterioration of MFC performance. These results also hold true for a higher

446 concentration of the substrate. The MFCs using IL in the optimal way also

447 generated higher volumes of catholyte. Given the wide range of ionic liquids

448 available, further research may be needed to find the most appropriate ILs to be

449 applied in ceramic MFCs and optimise their use in this technology. In this

450 context, protic ionic liquids are of special interest in the field of MFCs, since the

451 ratio of proton conductivity to total ionic conductivity is an important parameter

452 in determining the performance of a fuel cell electrolyte. The study of the

453 transport of different ion species through the separator in the presence of ionic

454 liquid is an another important factor from the point of view of the

455 characterization of the ceramic material, and hence future work is needed to

456 gain a better understanding of its performance, as well as how it may affect the

457 synthesised catholyte composition.

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Figure captions.

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Fig. 1. Ceramic MFC set-up.

Fig. 2. Configuration of the cathodes and the separators studied. IL is represented by the positive and negative charges.

Fig. 3. Polarisation and power curves of the MFCs with carbon veil (cathode-1) and carbon cloth (cathode-2).

Fig. 4. A) Voltage response of different MFCs cathode configurations. B) Polarisation and power curves of MFCs working with cathode-1 (without ionic liquid), cathode-3 (ionic liquid layer) and cathode-4 (ionic liquid mixture), including SEM error bars for replicates.

Fig. 5. Polarisation and power curves of MFCs working with separator-1, separator-2 and separator-3 configurations, including error bars for replicates.

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Fig. 6. A) Voltage response of the different MFCs cathode configurations at 100 mM acetate concentration. B, C and D) Effect of the substrate concentration on the power performance.

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Fig. 7. Volume, pH and conductivity of the catholyte generated by the MFCs.

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605 **Figures.**

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Anode: $CH_3COO^- + 2H_2O \longrightarrow 2CO_2 + 7H^+ + 8e^-$ Cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
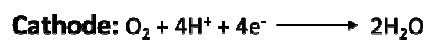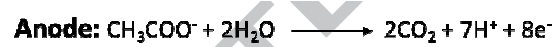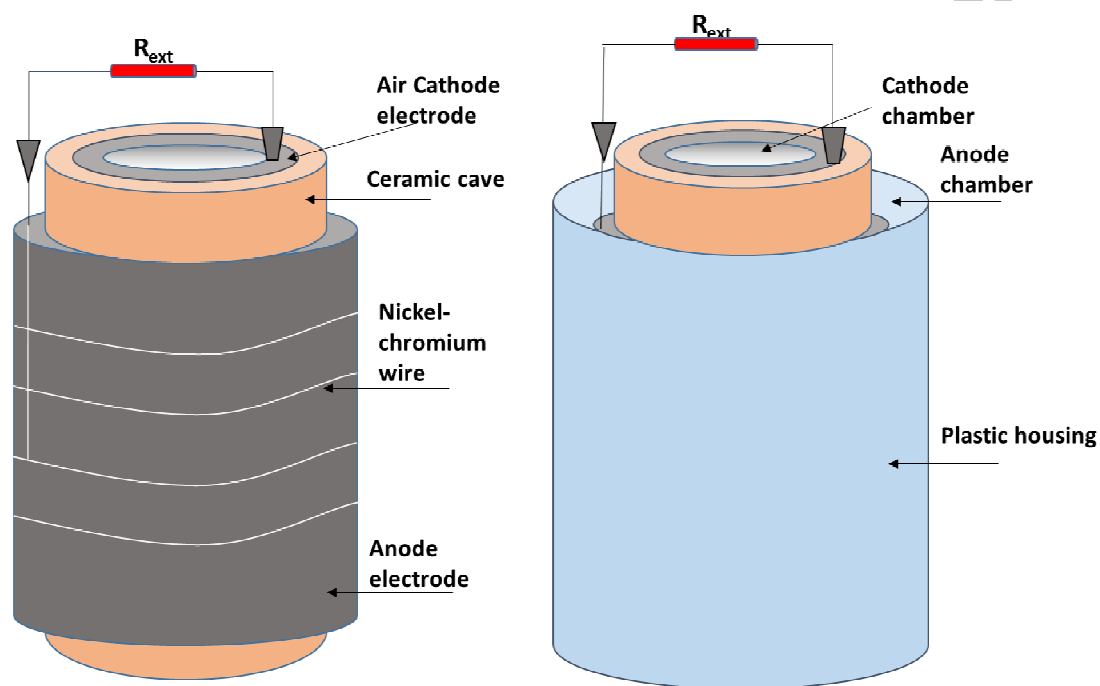
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608   **Fig. 1**

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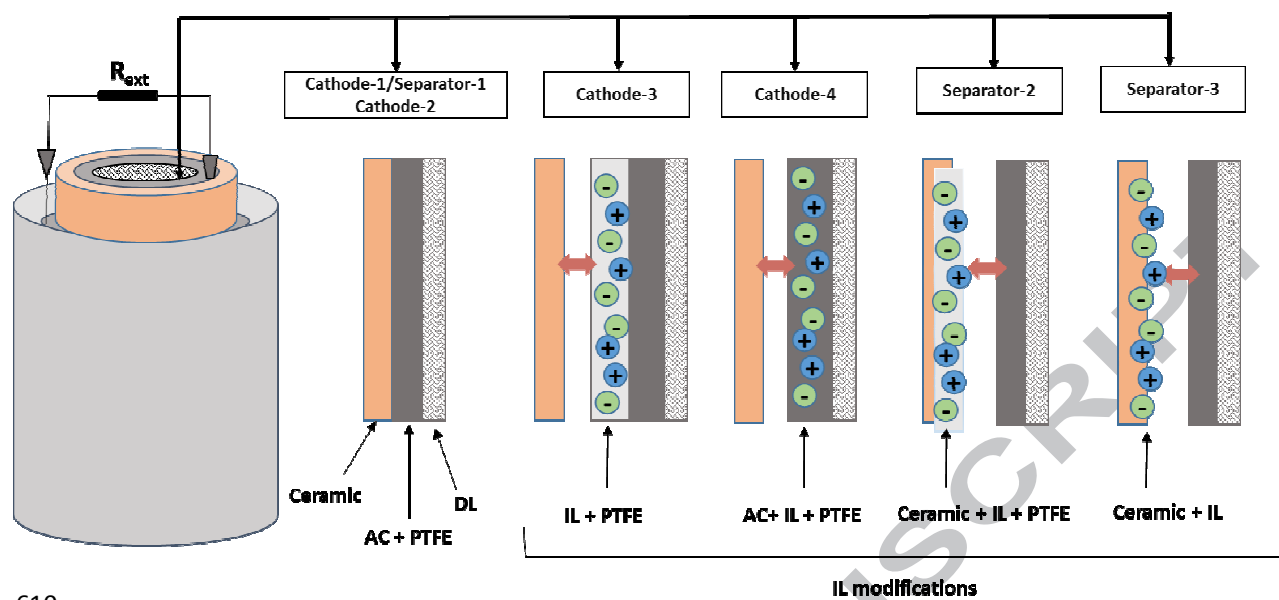**Fig. 2.**

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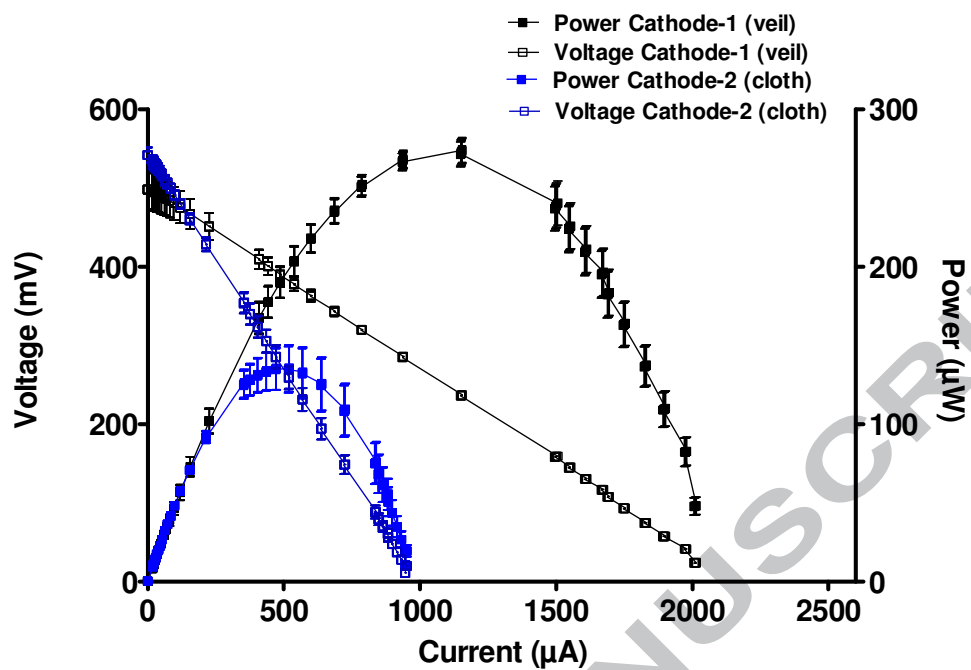**Fig. 3.**

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Fig. 4.

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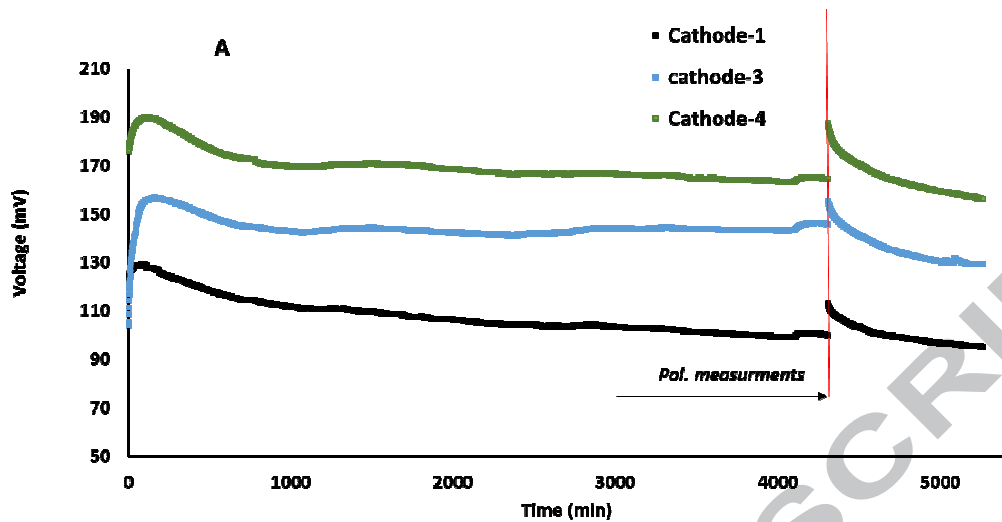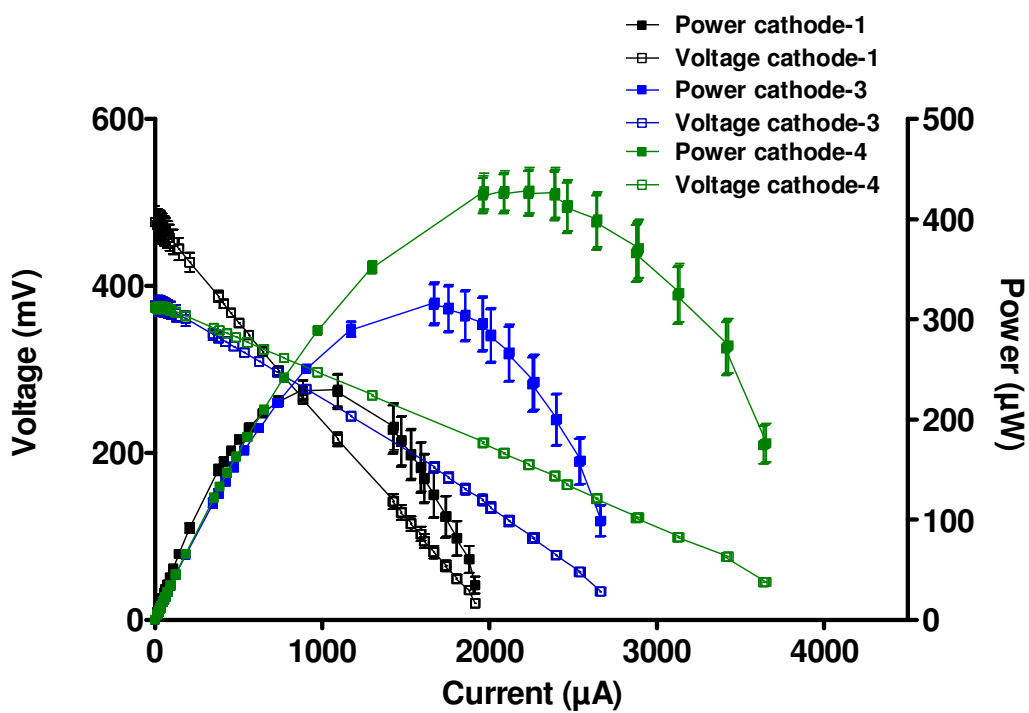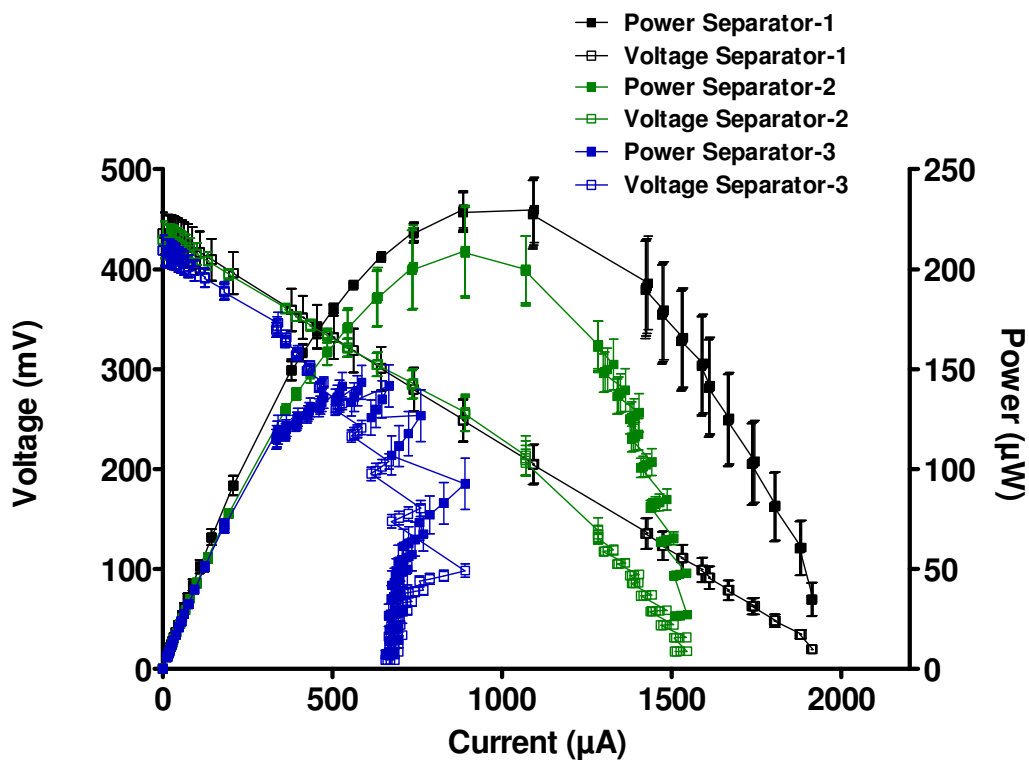
Fig. 5.

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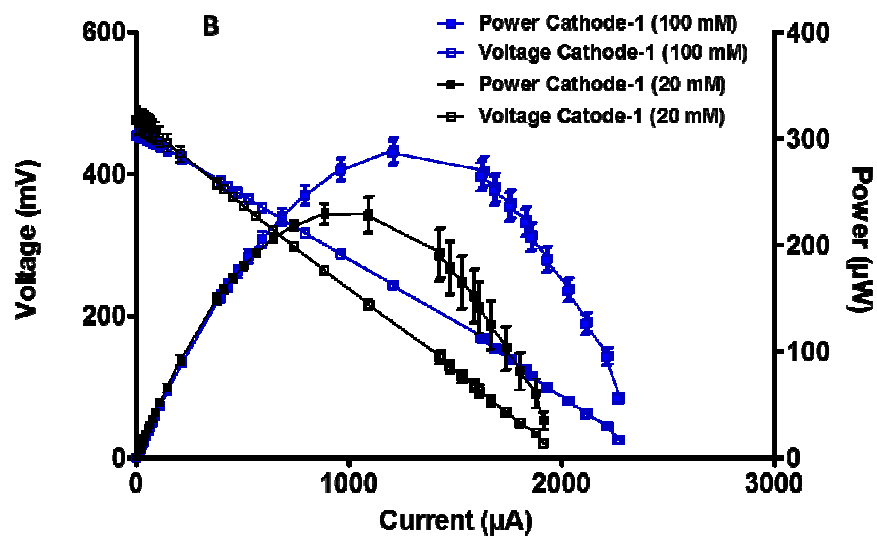659
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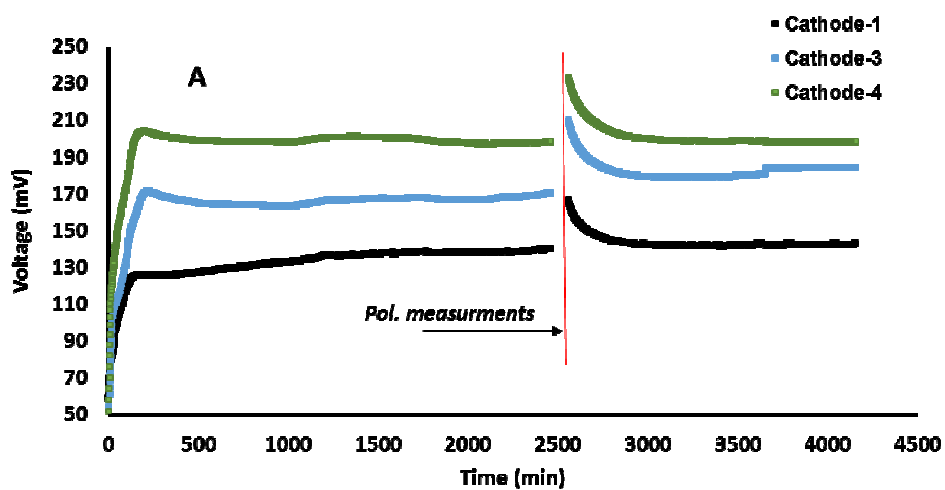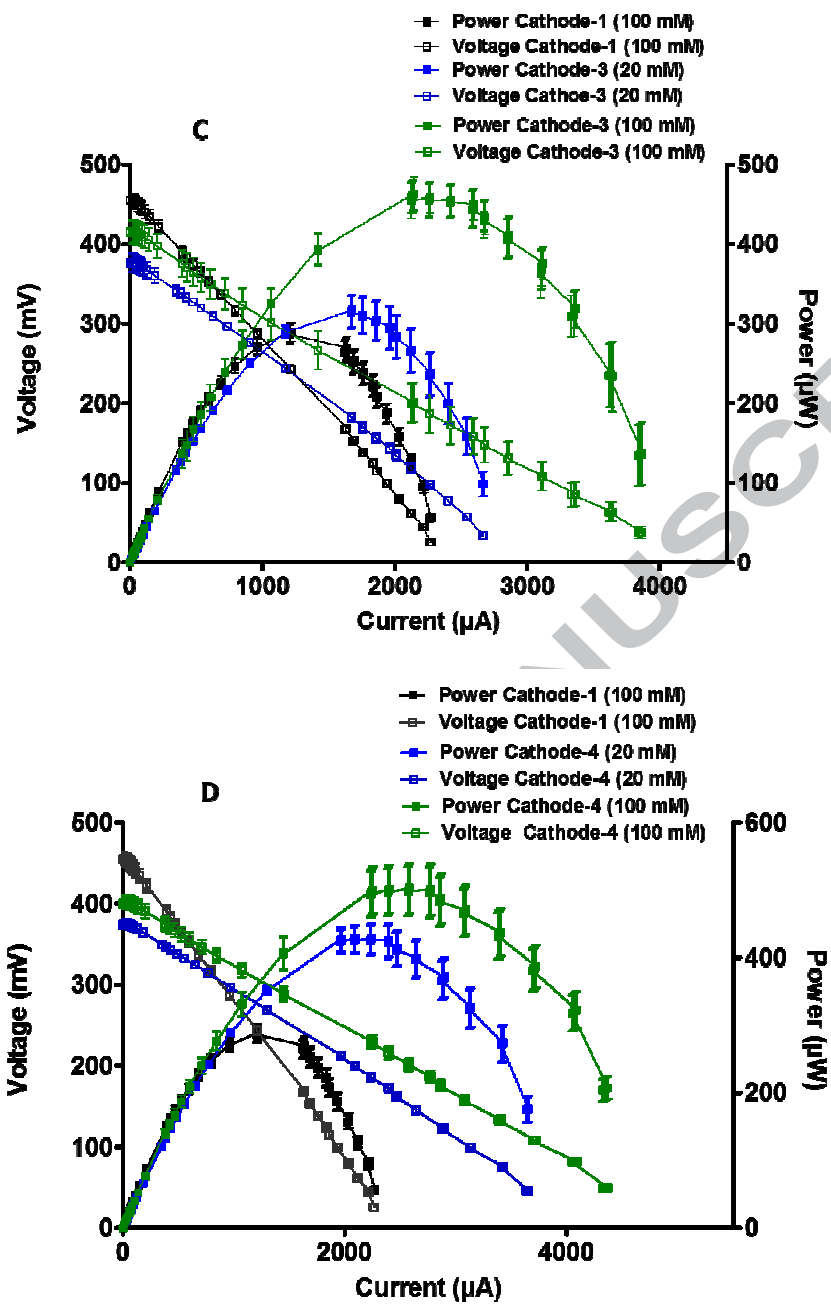

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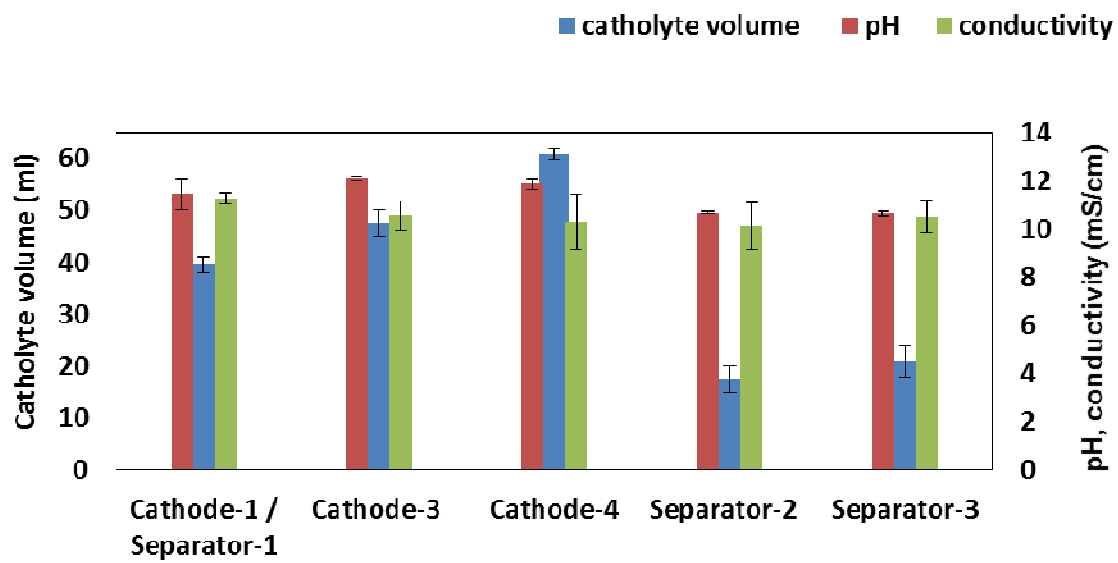671

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676   **Fig. 6.**
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Fig. 7.

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690 **Tables.**

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692 **Table 1.** Six types of MFCs studied.

693 **Table 2**. Maximum power output and associated electrical current.

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MFC type	Diffusion Layer	Cathode	Inner Ceramic Wall
Cathode-1 / **Separator-1**	Carbon veil	AC + PTFE	Clean
Cathode-2	Carbon cloth	AC + PTFE	Clean
Cathode-3	Carbon veil	$[AC + PTFE]_{Mixture} + [IL + PTFE]_{Layer}$	Clean
Cathode-4	Carbon veil	$[AC + PTFE + IL]_{Mixture}$	Clean
Separator-2	Carbon veil	AC + PTFE	IL + PTFE
Separator-3	Carbon veil	AC + PTFE	IL

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696 **Table 1.**

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	20 mM acetate (1:10)			100 mM acetate (1:10)		
	Pmax (µW)	I (mA)	R_{int} (Ω)	Pmax (µW)	I (mA)	Ri_{nt} (Ω)
Cathode-1	229.78	1016.22	245.9	289.73	1211.82	169.2
Cathode-3	314.87	1668.4	119.6	459.22	2229.93	93.5
Cathode-4	428.65	2238.51	85.6	502.92	2581.63	75.5

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702 **Table 2**.

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Highlights

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- **IL-modified cathodes improve the performance of ceramic MFCs.**

- **[EMIM][Tf$_2$N]-based MFCs offer 86 % more power output compared with IL-free MFCs.**

- **Optimal performance of ILs as part of the activated layer of the cathode.**

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