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Study of the effects of ionic liquid-modified cathodes and ceramic separators on MFC performance

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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

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liquid-modified cathodes (test). This work continues to study the performance of terracotta separators modified with the same ionic liquid, neat and also mixed with PTFE. While the results show operational limitations when the IL is integrated in the ceramic separator, there is a significant enhancement of the MFC performance when added as part of the activated layer mixture of the cathode, achieving up to 86.5 % more power output in comparison with IL-free MFCs (from 229.78 µW to 428.65 µW). The addition of a layer of PTFE-mixed ionic liquid spread on the activated layer of the cathode also leads to an increase in power of approximately 37 %.

Keywords: Ceramic separators; Microbial Fuel Cell; Ionic liquid; Activated carbon cathodes; Activated sludge.

1. Introduction.

Microbial Fuel Cells (MFCs) have been extensively investigated in recent years since this technology offers promising prospects for bioenergy production from wastewater. In the context of the current global energy crisis and growing demands for water treatment, the scientific community sees the development of this technology as a potential alternative that may help address such pressing issues [1, 2]. Although the performance of this technology has increased almost exponentially in the last two decades, there are some limitations associated with the low levels of power density achieved and their operating and fabrication costs [3]. Thus, the improvement of efficiency in MFC performance requires the study of non-expensive materials and simpler designs [4, 5].

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The great potential of MFC technology lies in the direct conversion of the chemical energy stored in organic wastes and biomass into electricity, operating at ambient conditions without additional energy requirements and with a net balance of zero emissions [6]. In the process, electrons are released and transported to the cathode through an external circuit while obtaining an electrical current. In double and single-chamber MFCs the use of a membrane or separator allows the ion exchange mechanism to take place while maintaining the anode and cathode chambers physically separated [7]. The selection of the appropriate separator is one of the key factors in designing MFC devices. The high cost of proton exchange membranes based on perfluored polymers such as Nafion reduces the efficiency of this technology and, therefore, a wide range of separator materials have been investigated in the last years, including cation and anion exchange membranes, glass fibers or porous fabrics, among other alternatives [8]. Paper in combination with conductive latex and microporous polymer-based carbon are other examples of alternative separators made out of porous material being currently developed [9,10]. Ceramic-based separators have proven to be a low cost alternative in MFCs. Park *et al*. [11] used a porcelain-coated cathode as proton exchange layer replacing expensive proton-selective membranes. Most recently, earthen pot and terracotta have been evaluated as separators in MFCs showing their capacity for proton transfer and power production [12, 13], reaching sufficient power for practical applications in the absence of metal catalysts [14]. The use of ceramic and precious metal-free MFCs has effected major cost reductions in this technology. The thickness of the ceramic wall or the porosity are important factors that affect the cell performance [13]. The electrode material is another

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key factor directly affecting the performance of MFCs and their feasibility from both an economic and long-term operation point of view [15]. Several types of carbon-based materials such as carbon nanofibers (CNF), carbon nanotubes (CNT) or activated carbon (AC) have been researched as electrode materials, showing high surface area and catalytic activity for an effective oxygen reduction reaction at the cathode [16-19]. Amongst them, activated carbon offers competitive advantages such as low cost and high catalytic activity [14, 20].

The present work explores the enhancement of the power performance of ceramic MFCs employing metal-free activated-carbon based electrodes through the incorporation of ionic liquids as part of the cathode. It has been reported that the potential of the cathode in ceramic-based MFCs can limit the power production, thus demanding more emphasis for the improvement of the cathode performance [12]. Because of the distinctive properties of ionic liquids, the range of applications of this type of compounds has widened greatly in recent years, including separation processes, chemical catalysis or biological systems [21]. A typical IL is based on the combination of organic cations (e.g. N-alkylpyridinium, N,N'-dialkylimidazolium) and a mono- or poly-atomic inorganic anion (e.g. e.g. Cl^-, $AlCl_4^-$, PF_6^-) or, increasingly more common, an organic anion (e.g. $(CF_3SO_2)_2N–$ = $Tf_2N–$, $(C_2F_5SO_2)_2N–$ = $Pf_2N–$) [22]. Their environment-friendly characteristics, thermal stability, high ionic conductivity and wide electrochemical window (≈ 4-6 V) make them suitable candidates for several electrochemical systems [23], having been employed in batteries and capacitors, solid-state electrochemical actuators, electrochemical sensors and fuel cells [22]. Several groups have also studied the performance of ionic liquids

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as electrolytes in proton exchange membrane fuel cells (PEMFCs), including MFCs [24-26]. The terracotta material itself has been used as an ion exchange separator and MFC chassis. Some limitations have been posed by this type of material, such as possible oxygen diffusion through the porous wall into the anode chamber [12]. The present work also investigates the possibility of using the ionic liquid as an electrolyte by directly applying it onto the ceramic separator. Ionic liquids have been used as electrolytes in a wide range of electrochemical processes and devices due to their good properties, being characterised by negligible vapour pressure [27, 28]. These advantages have made possible the replacement of conventional electrolytes with ionic liquids, avoiding volatility and chemical stability problems [29]. In the present study, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][Tf_2N], has been selected to assess the use of ILs for improving the power performance in ceramic MFCs for the first time. This imidadolizum-based IL was chosen due to its advantageous properties such relatively high ionic conductivity compared with the typical conductivity range for other ionic liquids (9 mS.cm-1 at RT [29]), good chemical stability, low viscosity (37 cp at RT) and hydrophobic nature [28] . The influence of the IL selected on the MFC performance is studied in terms of power generation when added as part of the cathode and on the separator (ceramic wall).

2. Materials and methods.

2.1. MFC configuration and operation.

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Fig.1 shows a schematic representation of the Microbial Fuel Cells used in this study. The units were set up with terracotta bottom sealed cylinders (Weston Mill Pottery, Nottinghamshire, UK) of 10 cm length, with 3.5 cm and 4 cm, inner and outer diameter, respectively, and wall thickness of 3 mm. The terracotta material used is characterized by a water absorption amount (by weight) of 9.1 % (SD 0.4) [30]. The cylinders were placed in bottle-shaped plastic housing covered on top with a layer of Parafilm®, which forms the anode compartment, with a maximum fuel capacity of 160 ml. The anode electrode was a layer of carbon fibre veil (loading 20 $g.m^{-2}$) in a rectangular shape with a total macro surface area of 2430 cm^2 (PRF Composite Materials, Dorset, UK), folded and wrapped around the outside of the terracotta caves and held with nickel-chromium wire; the latter also served as the current collector and connection point. MFCs were fed with full strength or 1:10 diluted activated sewage sludge (Wessex Water Scientific Laboratory, Cam Valley, Saltford, UK) in distilled water and supplemented with sodium acetate anhydrous (Fisher chemical, Loughborough, UK) to ensure sufficient carbon energy for the microorganisms during the operation of the MFCs. Two conditions of substrate concentration (20 and 100 mM) were employed in order to study the effects of substrate concentration on power performance and, in turn, compare this with that of the ionic liquid. The MFCs employed were operated in batch mode and loaded with an external resistance of 100 Ω. The anode of each MFC was matured for two weeks, prior to starting the experiments, by periodically feeding the anode with a solution of sludge and acetate (100 mM).

[INSERT FIGURE 1]

2.2. Preparation of the cathodes and the ceramic separators.

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Several activated carbon-based cathodes were fabricated and their performance was compared in terms of power production. The general way to prepare the cathodes involves hot pressing a mixture of 80 g of activated carbon (AC) powder (G. Baldwin and Co., London, UK) and 20 wt% of polytetrafluoroethylene (PTFE) in 120 ml of deionized water, onto the diffusion layer (carbon veil or carbon cloth), which was previously coated with PTFE (60 % PTFE dispersion in water, Sigma Aldrich, UK), as described in [14]. The final dimensions of the cathodes were 9x10 cm and the final loading of activated carbon was approximately 60 $mg.cm^{-2}$ per cathode. Once the AC mixture is dry, the cathodes are placed inside the terracotta cylinders (cathode compartment), with the side of the AC loading in contact with the inner wall of the ceramic cylinder and the diffusion layer exposed to air. As a preliminary study, the behaviour of two types of carbon materials were tested as substratum/diffusion layers namely, carbon veil (cathode-1) (20 $g.m^{-2}$, air permeability 420 $cm^3/cm^2/sec$, PRF Composite Materials, Dorset, UK) and carbon cloth (cathode-2) (120 $g.m^{-2}$, air permeability 100 $cm^3/cm^2/sec$, 100% activated, Zorflex®, Feluy, Belgium).

The performance of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) [EMIM][Tf_2N] (Ionic Liquids Technologies, Heilbronn, Germany), was first investigated in the ceramic MFCs as part of the cathode. Two cathode structures were fabricated for this purpose. The first modified type was prepared by mixing AC, PTFE and deionised water as described above and hot pressing the mixture onto carbon veil. Once the cathode is dry, a layer of ionic liquid mixed with PTFE (60 % dispersion in water) is applied uniformly over the side of the AC mixture (cathode-3). The

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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_2N] 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_2N] 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_2N] 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

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modified in the experiments. Three replicates of each type of MFC were built. Fig. 2 shows a basic representation of the structure of the cathodes and the separators researched.

[INSERT TABLE 1]

[INSERT FIGURE 2]

2.3. Data and analysis.

Voltage measurements (V) were recorded by ADC-24 Data Logger (Pico Technology Cambridge shire, UK). The performance of the ceramic MFCs assembled with different cathode and separator structures was analysed in terms of power production. Polarisation and power curves were determined by successively lowering the external resistive loads (R_L) from ≈ 1 MΩ to 11.78 Ω, every 3 minutes, using an automatic load-controlled measurement tool [32]. Six measurements were taken for each resistance at 30 second intervals. Current and power output were calculated by $V = IxR_L$ and $P = V^2/R_L$, respectively. Internal resistance (R_{int}) of MFCs was calculated by $R_{int} = (OCV/I) – R_L$ applied at the point of peak power, which is the point of maximum power transfer, where OCV is the voltage in open-circuit conditions, I is the current under the external load resistor and R_L is the external load resistor [33].

Measurements of pH and conductivity of each MFC were performed during the experiments with a Hanna-8424 pH-meter (Hanna Instrument, UK) and 470-Jenway conductivity meter (Camlab, UK), respectively.

3. Results and Discussion

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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.

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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, $P_{max\ cathode\text{-}4} > P_{max\ cathode\text{-}3} >> P_{max\ cathode\text{-}1}$. These results suggest that
269 the MFCs using the ionic liquid 1-ethyl-3-methylimidazolium

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bis(trifluoromethylsulfonyl)imide, [EMIM][Tf_2N] were significantly improved in terms of power performance. MFC replicates using cathode-4, with the ionic liquid as part of the mixture of the activated layer, reached a maximum power of 428.65 µW at a current of 2238.51 µA; the corresponding power and current levels for the control replicates were 229.78 µW at 1016.22 µA. This shows that the inclusion of the ionic liquid almost doubles the level of power and current produced (an increase of up to 86.5%). When the ionic liquid was uniformly spread over the activated carbon layer soaked in PTFE (cathode-3), the performance of the MFCs also improved with values of 314.87 µW and 1668.04 µA of maximum power and current, respectively (Fig.4B), which represents an increase of ≈ 37 % over the maximum power obtained in the absence of ionic liquid (cathode-1).

[INSERT FIGURE 4]

As seen in Figure 4, the effect of the ionic liquid used as part of the cathode is visible for both cases when it is included in the mixture that forms the activated carbon deposited on the carbon veil layer (cathode-4) and as a PTFE-soaked layer over the carbon activated mixture once deposited on the electrode (cathode-3). However as shown above, the level of power generated by MFCs using the first configuration is higher. Although Figure 4 shows that MFCs using Cathode-1 reached the highest OCV (476 mV), there is a rapid decrease of voltage as current increases, whilst for the case of cathode-3 and cathode-4, the slope for ohmic resistance is less steep, resulting in higher current and power output and indicating improvement due to the addition of IL. As shown in

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Table 2, the estimated values of R_{int} are higher for the MFCs working with cathode-1 (245.9 Ω) compared with cathode-3 (119.6 Ω) and cathode-4 modifications (85.6 Ω). MFCs and fuel cells in general are subject to internal losses such as activation, ohmic and mass-transfer over-potentials. The ohmic losses in an MFC include both the electrode resistance to the flow of electrons, and the cation-exchange-separator resistance to the flow of ions within the anode and cathode electrolytes if present [34]. Through the application of the ionic liquid in ceramic MFCs is expected to boost the ion transport from the anode to the cathode through the ceramic separator [3], significantly improving the level of power generated. The hydrophobic nature of the ionic liquid [EMIM][Tf_2N] also allows the stability of the cathode performance [28].

Focusing on the comparison between cathode-3 and cathode-4, the way of incorporating the ionic liquid described for cathode-3 implies the inclusion of an additional layer of PTFE between the separator and the activated mixture itself. It has been previously reported that the presence of an appropriate amount of PTFE inside an activated carbon mixture for cathode construction results in a more porous and highly textured mix, compared with a solely AC-based cathode, enhancing oxygen diffusion and ion exchange [20]. However, cathode-3 configuration also implies the superficial addition of PTFE (to soak the ionic liquid) covering the surface of the catalyst that may improve the contact between the separator and the carbon cathode, but also can lead to a reduction of the cathode active area and thus the deterioration of the MFC performance [35]. This may explain why the cathode-4, with the ionic liquid integrated in the activated layer and not involving the addition of an extra PTFE layer,

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outperforms the rest of the cathode configurations, as supported by the data of maximum power and internal resistance provided above.

3.3 Ceramic separator modified with ionic liquid.

Several recent reports focused on the study of ionic liquids as electrolyte in ionic exchange membranes for their application in MFCs [36]. The use of the ionic liquid acting as an electrolyte was also included in this study through as part of the separator by modifying the inner wall of the caves in two ways, (1) as a layer of IL and PTFE directly applied on the ceramic material (separator-2) and (2) as a layer of IL only (separator-3). As described in the previous section, polarisation measurements were taken after establishing a stable voltage response, once the MFCs were refilled with 160 ml of anolyte (described in Materials and Methods). Figure 5 shows the power curves of the MFCs incorporating these modifications, compared with those obtained with the control set (separator-1). In this case, no improvement in the efficiency of the MFCs working with a layer of PTFE-mixed IL spread over the inner ceramic wall (separator-2) is observed or the level of power is severely limited when only the IL is applied in the absence of PTFE (separator-3).

It must be noted that, for both types of modification i.e. separator-2 and separator-3, the polarisation curves exhibit an irregular behaviour in the sector after reaching the maximum power. This phenomenon has been previously explored and described as overshoot due to the simultaneous decrease in power and current, and has been associated with the underperformance of the

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MFCs [30]. The overshoot phenomenon was not observable in the power curves of the control set, even when the performance of these MFCs could be improved by incorporating ionic liquid as part of the electrode. Therefore, the occurrence of overshoot is not directly associated with the presence of a limiting element such a low conductivity catholyte, but possibly with the presence of an inhibiting component in the system. The overshoot phenomenon can be attributed to the presence of the ionic liquid directly applied onto the ceramic wall. But still, the MFCs replicates working with the separator-2, in presence of PTFE, offer levels of power closer to those given by the control set (209.04 µW *vs*. 229.78 µW).

When calculating the values of R_{int} of the MFCs using the different separator configurations, it was found a significant increase in R_{int} for separator-3 (473.1 Ω) compared with that of separator-1 (245.9 Ω), and it was also higher for separator-2 (288.6 Ω). In the case of separator-3, the lower regression coefficient is due to the lack of stability of the MFC systems due to the overshoot phenomenon. The ion exchange capacity of the ceramic material is due to its hydrophilic nature and high cation exchange capacity [13]. When the ionic liquid in the absence of PTFE is applied to the ceramic wall and is let to dry, a certain amount of the catholyte is absorbed by the ceramic material, penetrating the pores on the inner wall of the terracotta cylinder. Since the performance of this type of MFCs lies on the transport of ions from the anode to the cathode through the ceramic separator, the effects of depositing the ionic liquid directly onto the separator can be observed in the values of internal resistance and power output [37]. If the ionic is deposited on the ceramic wall soaked with PTFE forming a mixture to fix the ionic liquid on the surface of the

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ceramic wall, the blocking effect may be relieved compared to separator-2, although internal resistance is still affected compared to separator-1 and no improvement in power performance is observed. These results indicate that it is not possible to improve the MFC performance in terms of power output by integrating the electrolyte in the ceramic separator of the system by the methods here described.

[INSERT FIGURE 5]

3.4. Influence of the substrate concentration.

In order to study the influence of the concentration of the substrate on the power output and compare it with the effect of the ionic liquid, the MFCs working with cathode-3 and cathode-4 and the control set were run at two values of acetate concentration (20 and 100 mM), shown in Figure 6B. Voltage and power values for the concentration of 20 mM correspond to the value given in section 3.2. Figure 6C and D show the power and polarisation measurement for the cathodes modified with ionic liquid (cathode-3 and cathode-4), including the results for the MFCs working with the ionic liquid-free cathode at 100 mM as control. The increase in the power output due to the addition of acetate is 26.1 % on overage for the replicates using the cathode-1 (see Fig. 6.B), whilst the increase due to the use of the ionic liquid is over 86% for the best case (see Fig. 6.D). The comparison between the power curves of the replicates at 100 mM shows that the trend of maximum power levels at such concentration is the same as is at 20 mM, $P_{max\ cathode\text{-}4} > P_{max\ cathode\text{-}3} >> P_{max\ cathode\text{-}1}$ (see Table 2).

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Regarding the replicates with ionic liquid, the higher percentage of increase in power level is observed for cathode-3, with cathode-4 outperforming all the other designs. These results also suggest that the cathode performance can be one of the limiting factors in this type of MFCs in terms of power production, since even the maximum power value achieved by the MFCs in the absence of ionic liquid (cathode-1) at 100 mM (acetate), 289.73 µW, is almost half the best result obtained with the ionic liquid present in the activated layer (cathode-4) at 20 mM, 428.65 µW (see Table 2). Moreover, although Figures 6.C and 6.D show a higher value of OCV for cathode-1 (454 mV) compared to both cathode-3 (376 mV at 20 mM and 414 mV at 100 mM) and cathode-4 (373 mV at 20 mM and 404 mV at 100 mM), the differences observed in the slopes of the polarization curves indicate a faster decrease in voltage, as current increases for cathode-1. This results in an increase of the internal resistance (see Table 2), which remains much lower for cathode-4 and cathode-3 for both 20 and 100 mM.

[INSERT FIGURE 6]

[INSERT TABLE 2]

3.5. Catholyte production.

The operation of the MFC design used for this research implies the generation of a certain amount of catholyte as a consequence of the transport of ion species and water from the anode chamber through the ceramic wall. The

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catholyte generated in the MFCs was of a transparent appearance. This type of cylindrical ceramic-based MFC allows the production of catholyte of high salt concentration whilst the recovery of clean water from the anode takes places by electro-osmosis [37]. Figure 7 shows the amount of catholyte generated, pH and conductivity after ≈ 5400 min. of operation by the main MFC configurations studied, for the 20 mM acetate concentration case. As can be seen, there are significant differences in the volume of catholyte generated, and it can be assumed that the amount of catholyte generated directly depends on the level of MFC performance as a consequence of the ion exchange through the separator. These differences are not visible in the measurements of pH and conductivity, which remained within the range of 10.6-12.1 for pH and 10.1-11.2 $mS.cm^{-1}$ for conductivity, although the values of pH are slightly higher for the catholyte samples generated by the cathode-3 and cathode-4.

[INSERT FIGURE 7]

4. Conclusions

The present work has investigated the application of ionic liquids in ceramic-based MFCs in order to improve the level of power generation. For this purpose, activated-carbon cathodes and terracotta separators were modified with [EMIM][Tf_2N] in pure form or soaked with PTFE. The results prove that with the inclusion of the ionic liquid as part of the cathode a significant increase of over 86% in power output is achieved. Amongst the methods tested, the mixture of a certain amount of ionic liquid, activated carbon and PTFE forming one layer pressed onto the diffusion layer (carbon veil) has shown to be the best option,

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whilst the modification of the ceramic wall with [EMIM][Tf_2N] leads to the deterioration of MFC performance. These results also hold true for a higher concentration of the substrate. The MFCs using IL in the optimal way also generated higher volumes of catholyte. Given the wide range of ionic liquids available, further research may be needed to find the most appropriate ILs to be applied in ceramic MFCs and optimise their use in this technology. In this context, protic ionic liquids are of special interest in the field of MFCs, since the ratio of proton conductivity to total ionic conductivity is an important parameter in determining the performance of a fuel cell electrolyte. The study of the transport of different ion species through the separator in the presence of ionic liquid is an another important factor from the point of view of the characterization of the ceramic material, and hence future work is needed to gain a better understanding of its performance, as well as how it may affect the synthesised catholyte composition.

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Figure captions.

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.

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.

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

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605 **Figures.**

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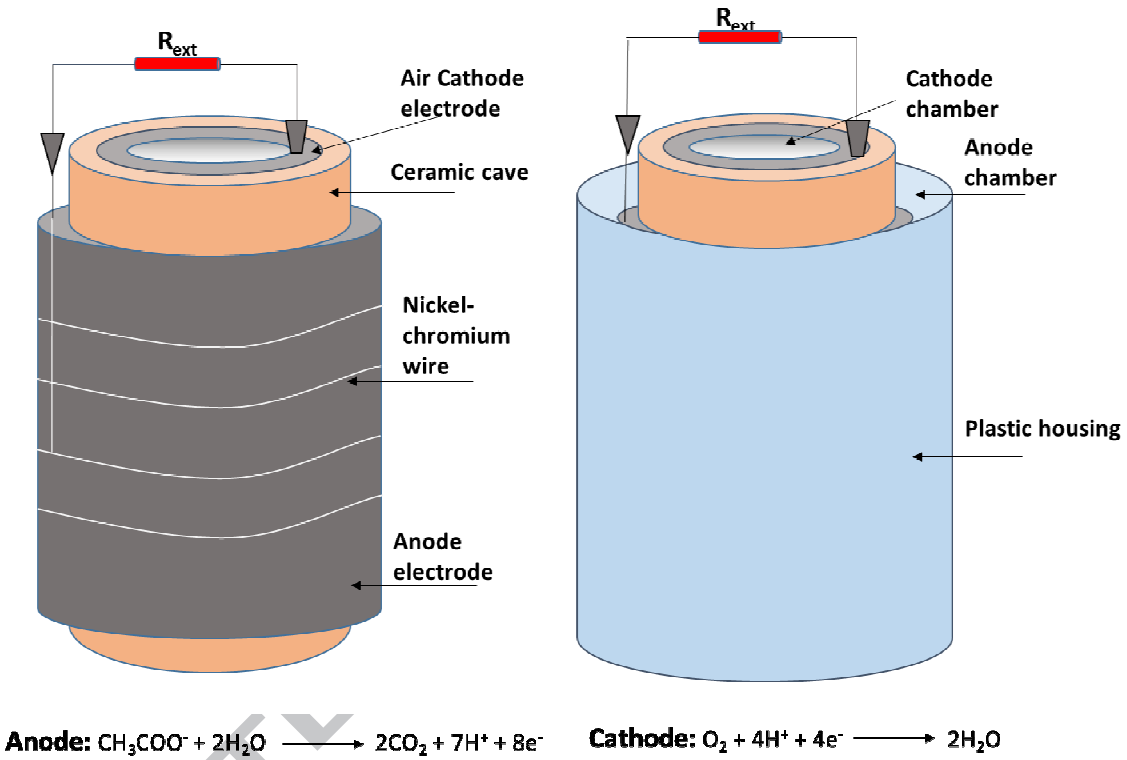

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608 **Fig. 1**

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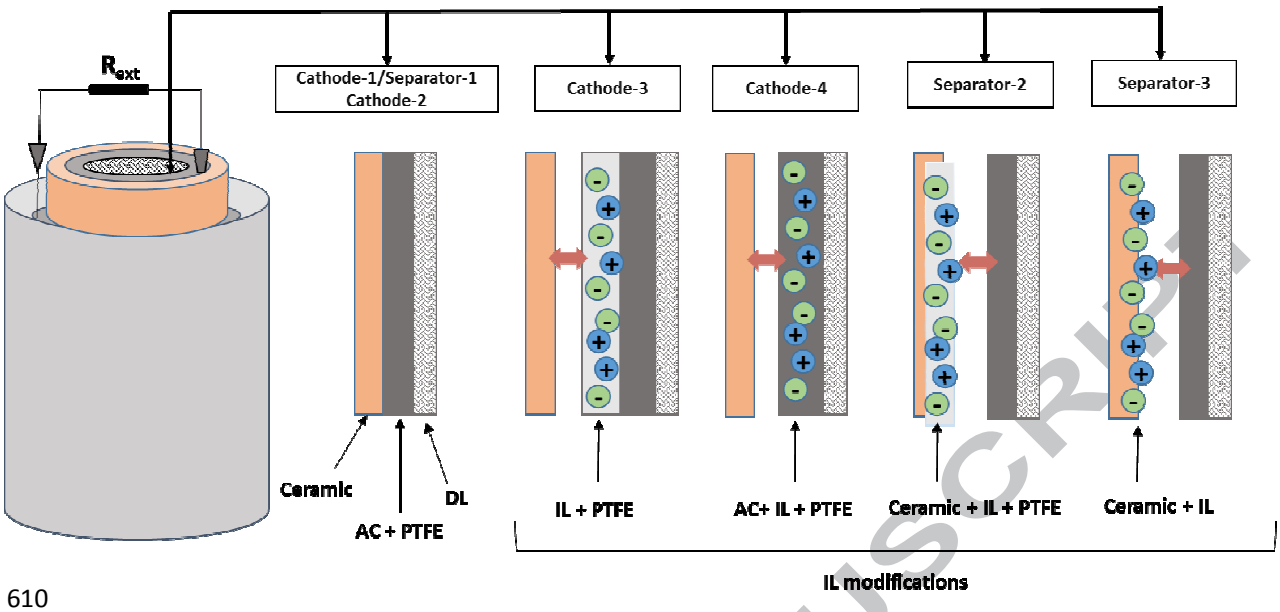

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611 **Fig. 2.**

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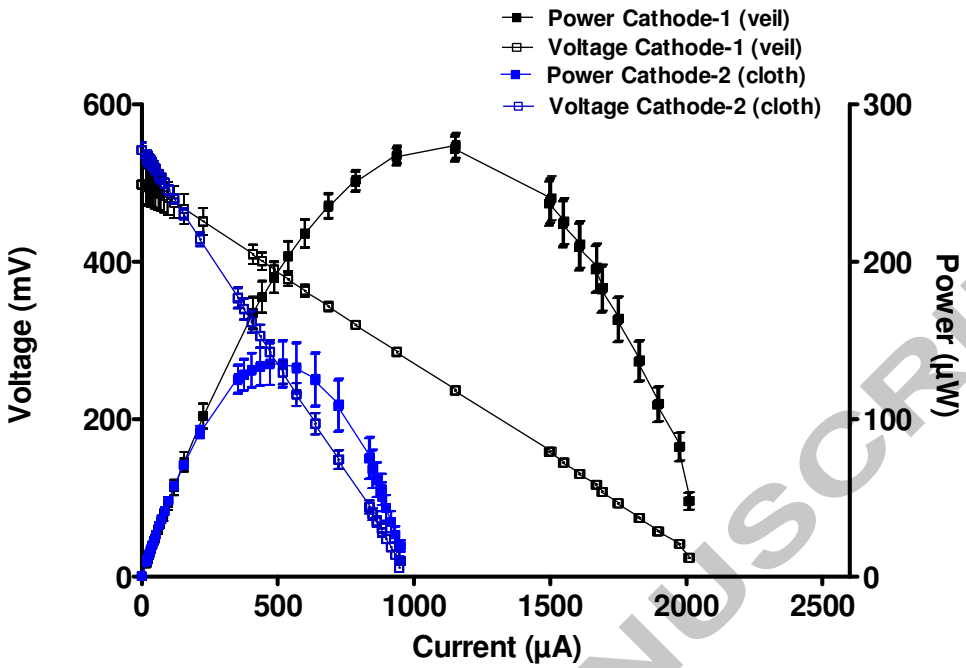

Fig. 3.

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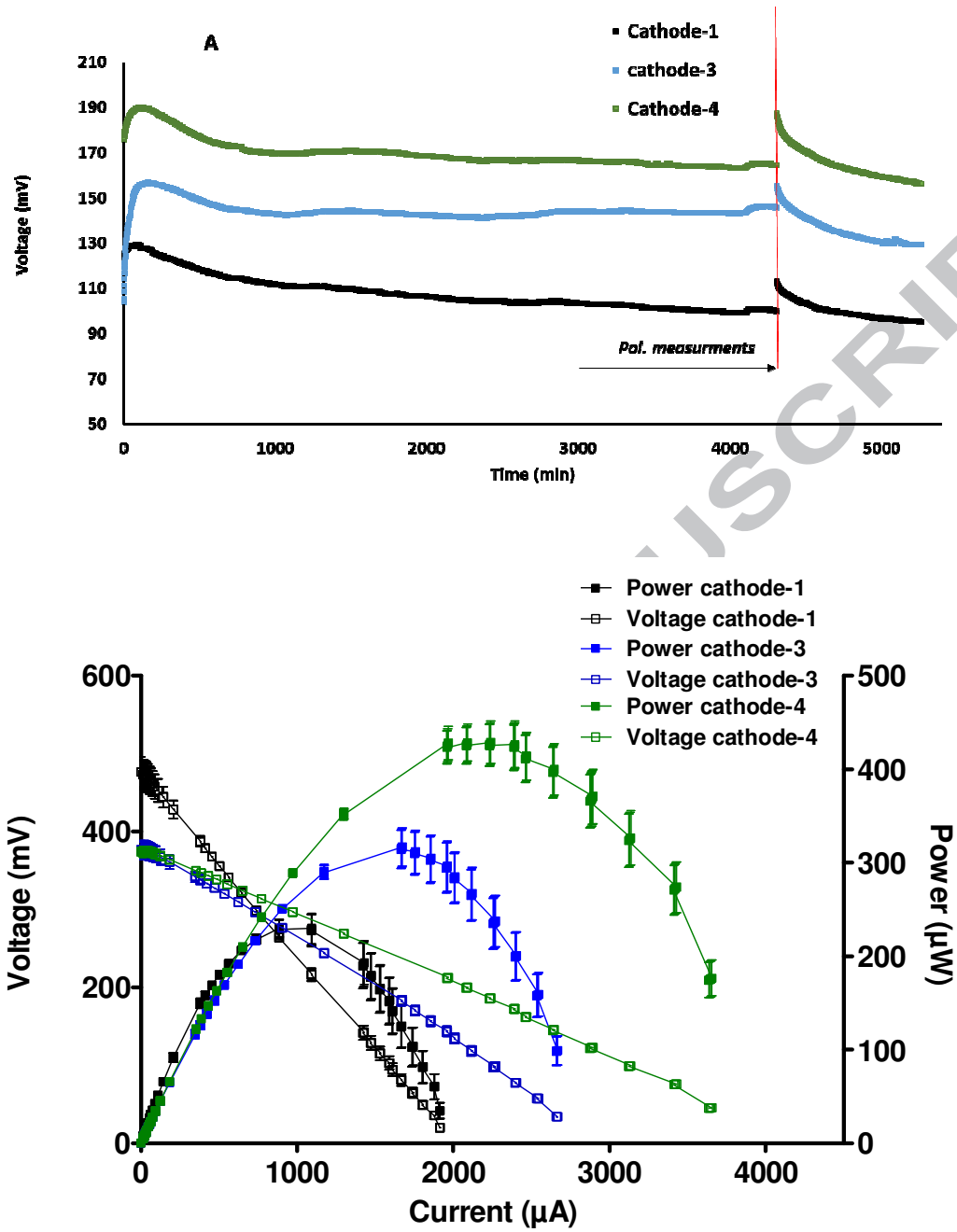

Fig. 4.

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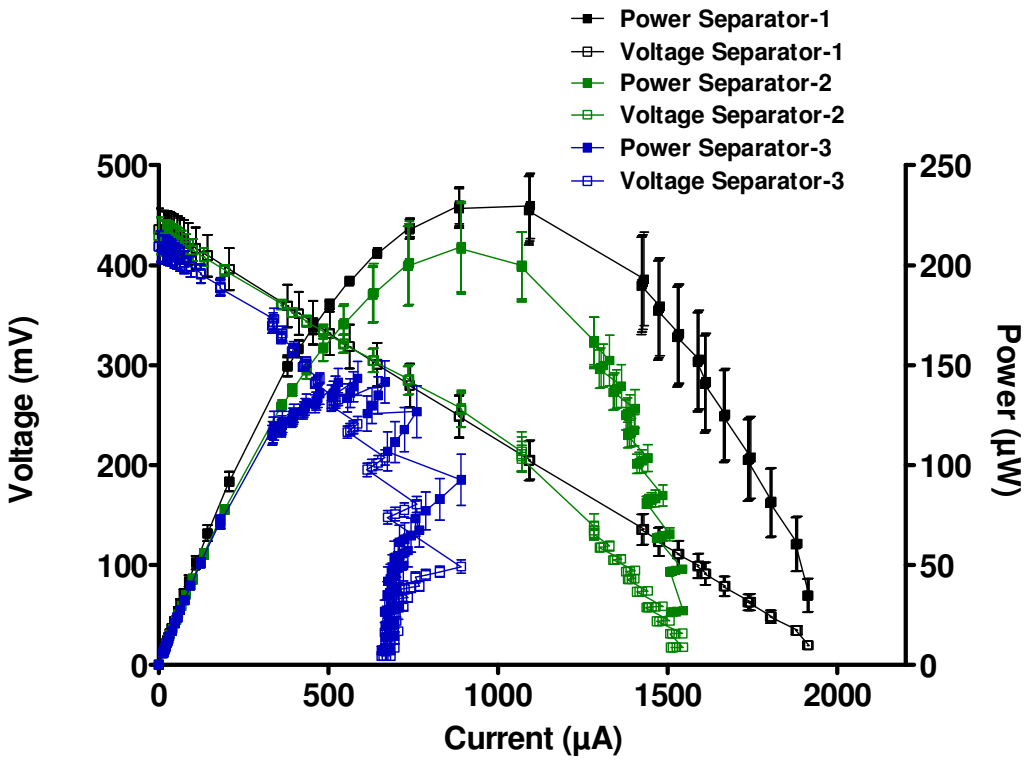

Fig. 5.

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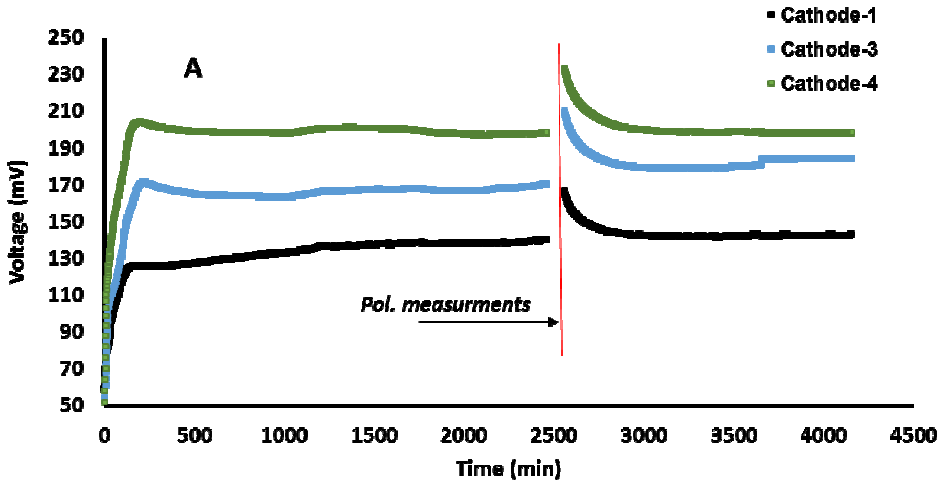

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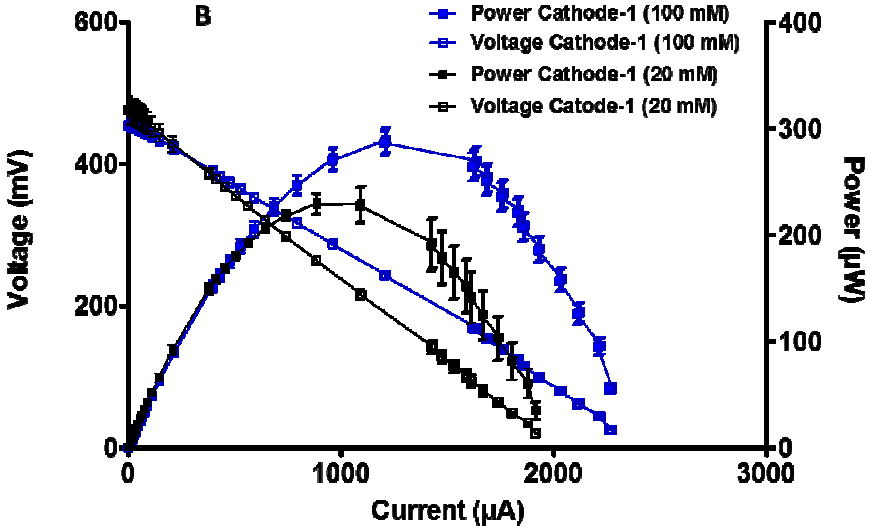

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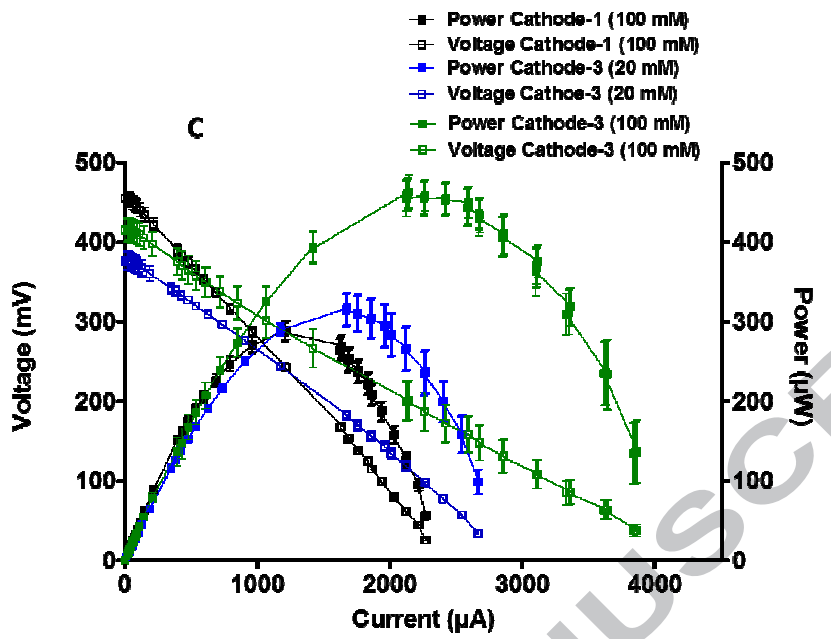

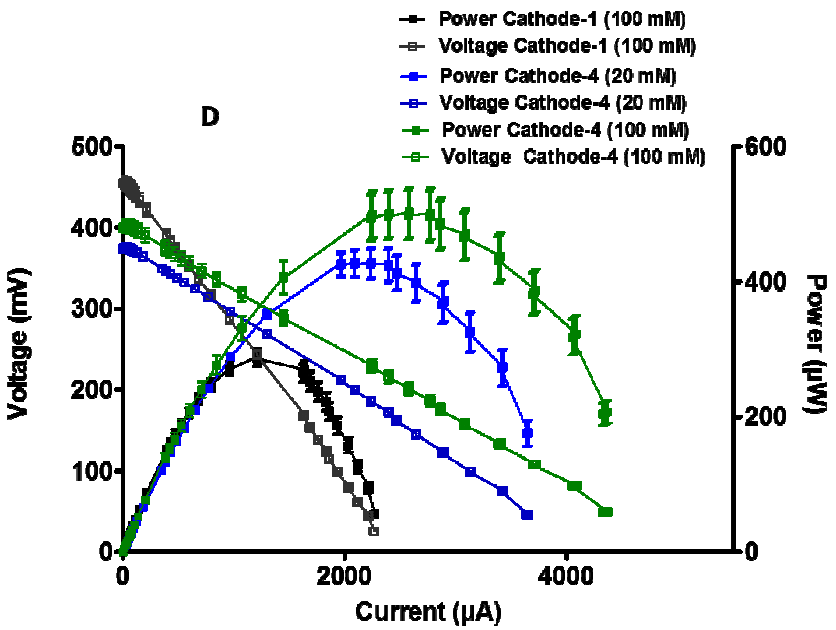

Fig. 6.

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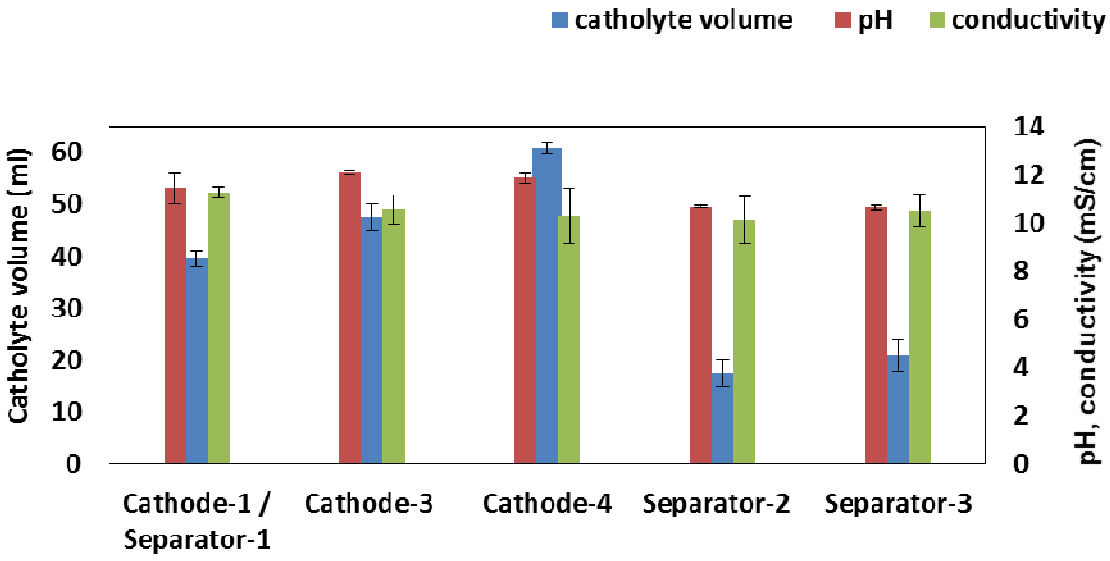

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688 **Fig. 7.**

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Tables.

Table 1. Six types of MFCs studied.

Table 2. Maximum power output and associated electrical current.

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

Table 1.

	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

Table 2.

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Highlights

- **IL-modified cathodes improve the performance of ceramic MFCs.**
- **[EMIM][Tf_2N]-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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