

1           **ELECTRICITY PRODUCTION FROM HUMAN URINE IN CERAMIC**  
2           **MICROBIAL FUEL CELLS WITH ALTERNATIVE NON-FLUORINATED**  
3           **POLYMER BINDERS FOR CATHODE CONSTRUCTION**

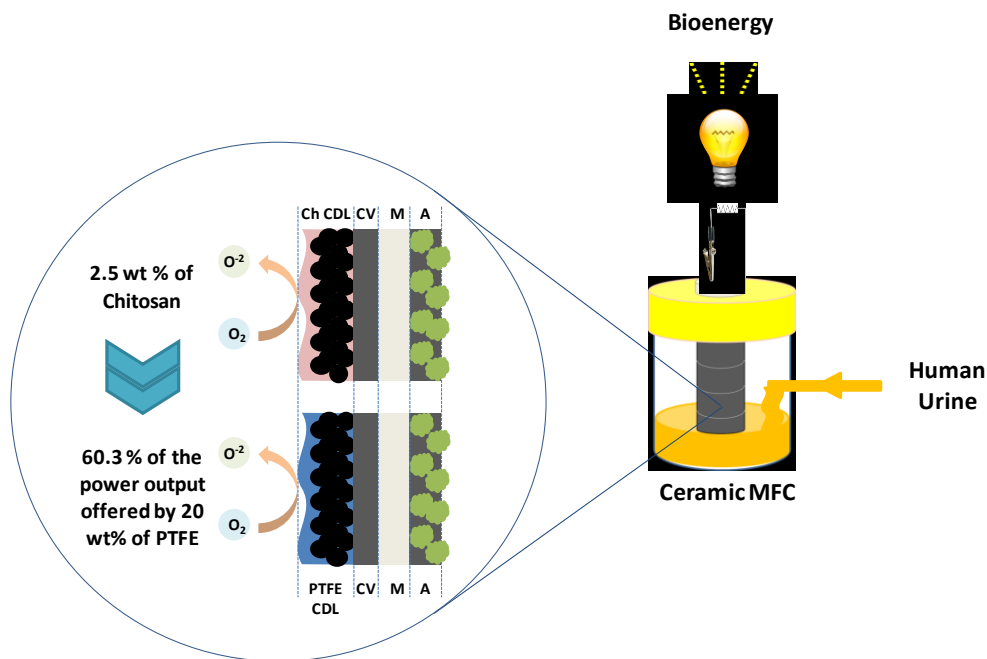
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5           **M.J. Salar-García<sup>1</sup>, V.M. Ortiz-Martínez<sup>1</sup>, I. Gajda<sup>2</sup>, J. Greenman<sup>2</sup>, F.J. Hernández-**  
6           **Fernández<sup>1</sup>, I.A. Ieropoulos<sup>2,\*</sup>.**

7           <sup>(1)</sup> Polytechnic University of Cartagena, Chemical and Environmental Engineering Department,  
8           Campus Muralla del Mar, C/Doctor Fleming S/N, E-30202 Cartagena, Murcia.

9           <sup>(2)</sup> Bristol BioEnergy Centre, Bristol Robotic Laboratory, Block T, UWE, Bristol, Coldharbour Lane,  
10          Bristol BS16 1QY, UK.

11                                   \* Corresponding author: E-mail: ioannis.ieropoulos@brl.ac.uk

12  
13          **GRAPHICAL ABSTRACT**



14                                   PTFE CDL: PTFE-Gas Diffusion Layer   Ch CDL: Chitosan-Gas Diffusion Layer   CV: Carbon Veil   M: Membrane   A: Anode

15          **HIGHLIGHTS**

- 16          •        Urine-fed ceramic MFCs for bioenergy production and urine treatment.
- 17          •        Alternative non-fluorinated polymers as binders in ceramic MFCs.

- 18 • Chitosan-based cathodes allow MFCs to reach a maximum power of 510  $\mu$ W.
- 19 • 60.3 % of the power output by PTFE obtained with 8 times less amount of
- 20 chitosan.

## 21 **ABSTRACT**

22 Polytetrafluoroethylene (PTFE) is one of the most common binders employed to  
23 prepare cathode electrodes in microbial fuel cells (MFCs) and yet this fluorinated  
24 polymer is neither sustainable nor environmental friendly. In this work, four non-  
25 fluorinated polymers have been tested as alternative binders to PTFE in ceramic MFCs.  
26 The performance of ceramic MFCs using carbon-based cathodes containing silicone,  
27 polyvinyl chloride, Ludox<sup>®</sup> (colloidal silica) and chitosan, was compared with the  
28 performance of MFCs using cathodes prepared with PTFE. The results obtained  
29 confirm that polyvinylchloride, Ludox<sup>®</sup> and chitosan are suitable materials to be used  
30 as binders for MFC cathode construction. Amongst them, Ludox<sup>®</sup> and chitosan are the  
31 most sustainable options due to their chemical nature. Cathodes prepared with 2.5 wt  
32 % of chitosan - 8 times less than the amount needed for PTFE – in MFCs reached a  
33 maximum power of 510  $\mu$ W, which represents 60.3 % out of the power output from  
34 MFCs with PTFE-based cathodes. In terms of urine treatment capacity, the chemical  
35 oxygen demand (COD) removal was similar across the systems tested, due to the short  
36 retention time. However, chitosan-based MFCs reached COD removal rates of up to 26  
37 %, which was slightly higher than the COD removal rate measured for MFCs using  
38 PTFE-cathodes (23.5 %).

39

40 *Keywords: Ceramic microbial fuel cells; binders; non-fluorinated polymers; bioenergy*  
41 *production.*

## 42 **1. INTRODUCTION**

43 Since their discovery, ceramic materials have been employed in a wide variety of  
44 applications including building, decoration and technological applications such as  
45 electrochemical devices. Amongst the most common ceramic materials, ceramic  
46 membranes have been widely used in ultrafiltration, electrocoagulation and  
47 electrochemical processes due to their adaptable selectivity properties and high  
48 stability and resistance to oxidation [1-3]. The use of ceramic membranes in fuel cells  
49 for energy production has also become commonplace. In 1937, Baur and Preis [4]  
50 pioneered the use of ceramic membranes in solid-oxide fuel cells (SOFCs). This  
51 technology consists of a solid construction made of three ceramic layers comprising an  
52 electrolyte sandwiched between two electrodes. Ceramic materials are suitable in  
53 SOFCs due to their stability at high operation temperatures and the possibility of  
54 modifying their porosity and permeability properties [4].

55 Fuel cell technology allows the chemical energy contained in a substrate to be directly  
56 transformed into electricity by using chemical reactions. A widespread use of this  
57 technology could help mitigate climate change since fuel cells generate clean energy  
58 with low CO<sub>2</sub> emissions. Although different fuel cells can vary significantly in operation,  
59 they essentially consist of the same main components: i) an anode, at which the  
60 substrate is oxidized while producing protons and electrons, ii) a cathode, at which  
61 protons and electrons are combined and iii) an electrolyte, for the selective transport  
62 of ions from the anode to the cathode [5, 6]. Fuel cells can be divided into two main  
63 categories, namely chemical fuel cells and biofuel cells, depending on the nature of the  
64 chemical reactions involved. Biofuel cells can be further categorised into enzymatic  
65 fuel cells, bioelectrochemical fuel cells and organelle fuel cells. Microbial Fuel Cells

66 (second category) work on microbial metabolism to generate electricity, which offers  
67 the double advantage of producing electricity whilst treating a wide range of organic  
68 substrates, including wastewater and urine. Neat human urine has been previously  
69 shown to work as an excellent fuel for electricity production in MFCs [7], which was  
70 the main reason for choosing urine in the present study.

71 Despite the multiple benefits of microbial fuel cells, scale-up remains a challenge due  
72 to the high cost of the materials commonly involved such as precious catalysts and  
73 commercial proton exchange separators [8]. In this sense, ceramic membranes have  
74 proven to be a suitable alternative to expensive commercial membranes with  
75 numerous advantages including low cost, abundance in nature, high thermal and  
76 chemical stability and low maintenance requirements. Ceramic materials have been  
77 applied in several MFC configuration types in a wide variety of shapes, not only as  
78 separators but also for electrode construction. These ceramic materials include  
79 earthenware, clayware and terracotta [9-11]. The application of porcelain material as  
80 proton exchange membrane was first reported by Park and Zeikus [12]. Over the  
81 subsequent years, the use of ceramic-based membranes exponentially increased in  
82 this field due to the aforementioned advantages [13- 16].

83 Regarding the cathodic catalyst, platinum is often employed in MFCs due to its  
84 biocompatibility, stability and high performance. However, its high cost has promoted  
85 the development of alternative materials such as activated carbon (AC) for this  
86 purpose. It has been reported that MFCs using AC-based cathodes can have similar  
87 performance levels to those achieved by MFCs employing platinum [17, 18]. In  
88 addition, polytetrafluoroethylene (PTFE) and Nafion® are amongst the most  
89 widespread binders used to fix the AC active layer to an electrode support material.

90 Whilst Nafion<sup>®</sup> is a hydrophilic cation-conducting polymer based on sulfonate groups,  
91 PTFE is a hydrophobic non-ionic polymer based on fluorinated groups [19], whose cost  
92 can be 500 times lower than that of Nafion<sup>®</sup>. However, the performance of PTFE-based  
93 electrodes is generally lower by comparison [20]. Recently, Guerrini *et al.* 2015 [21]  
94 analysed the effect of PTFE in the external gas diffusion layer of air-breathing cathodes  
95 employed in membraneless MFCs. The authors prepared cathodes based on different  
96 amount of binder. Cyclic voltametry tests reported that the lower the PTFE content,  
97 the higher cathodic electrochemical active area. Therefore, the lowest amount of PTFE  
98 allowed MFCs to reach the best performance. On the other side, extremely high  
99 content of PTFE in the cathode has a negative effect on the MFC behaviour.

100 Novel fabrication methods have been developed in order to improve the efficiency of  
101 PTFE as a binder for electrodes [22]. Despite the advantage of low cost, this fluorinated  
102 binder is regarded as toxic and it is therefore necessary to find other environmental-  
103 friendly alternatives.

104 In this work, four non-fluorinated and low cost polymers have been tested as  
105 alternative binders for cathode construction in ceramic MFCs fed with human urine.  
106 Several amounts (by weight) of polyvinyl chloride (PVC), Ludox<sup>®</sup> (colloidal silica),  
107 silicone and chitosan have been investigated to determine the best alternative to PTFE.

108 Chitosan is the n-deacetylated derivative of chitin (acetylation degree < 0.35), one of  
109 the most abundant natural polysaccharides. It is generally found in crustacean shells  
110 from crabs, shrimp or insects. This bio-polymer is neither soluble in water nor in most  
111 of organic and alkali solvents. The chitosan structure is based on three different polar  
112 functional groups: i) hydroxyl (-OH); ii) primary amine (-NH<sub>2</sub>); iii) ether (C-O-C). The  
113 most promising characteristic is the possibility of improving its mechanical and

114 chemical properties by chemical crosslinking reactions. These techniques allow its ionic  
115 conductivity to be improved and thus chitosan is appropriate for preparing electrodes  
116 or membranes for MFCs [23, 24, 25]. Several reports have demonstrated the  
117 numerous advantages of chitosan as binder. Choudhury *et al.* [26] employed  
118 glutaraldehyde cross-linked chitosan as binder to prepare electrodes for direct  
119 borohydride fuel cells (DBFCs). They observed that the performance of DBFCs is better  
120 when the electrodes contain chitosan instead of Nafion<sup>®</sup>, the amount required to  
121 prepare the electrodes being also lower.

122 In addition to bonding catalyst particles, chitosan has been used to improve their  
123 properties. Epichlorohydrin cross-linked chitosan was employed by Phompan and  
124 Hansupala [27] to entrap a mixture of platinum and carbon. Their results demonstrate  
125 that chitosan extends the three-phase boundary of the carbon agglomerate, reducing  
126 the activation overpotential and enhancing the performance of hydrogen proton  
127 exchange membrane fuel cells.

128 In the case of microbial fuel cells, chitosan has been employed to prepare membranes  
129 and anodes, but only a few studies have reported its use for cathode construction.

130 In the case of Ludox<sup>®</sup>, this material has started to be used as a binder in different  
131 processes recently. Peters *et al.* [28] used Ludox<sup>®</sup> AS-40 as a binder to deposit zeolites  
132 on ceramic membranes for pervaporation purposes. Ludox<sup>®</sup> AS-40 enhances the  
133 bonding of zeolite crystal on aluminosilicate based substrates. One of the most  
134 important advantages of the use of colloidal silica as a binder is its long term stability  
135 and none self-gelating tendency [29]. Rodrigues *et al.* [30] also employed silica  
136 colloidal (Ludox<sup>®</sup> HS-40) as binder to synthesize monolithic catalysts based on  
137 10Ni/CeSiO<sub>x</sub>. This material was successfully used for the partial oxidation of ethanol,

138 allowing a high amount of syngas to be obtained. Ludox® has not been previously  
139 employed in MFCs.

140

## 141 2. MATERIALS AND METHODS

### 142 2.1. MFC configuration and operation mode

143 Single-chamber air-cathode microbial fuel cells were used in these tests. The units  
144 consisted of 5 cm tall white fine fire clay cylinders sealed at the bottom with an  
145 internal and external diameter of 1.75 cm and 2.2 cm, respectively (Roca S.L., Spain).  
146 This structure acted as the separator between the anode and the cathode. A piece of  
147 carbon veil (loading of 20 g.m<sup>-2</sup>) folded and wrapped around the outside surface of the  
148 ceramic cylinder with a total surface area of 420 cm<sup>2</sup> was used as the anode (PRF  
149 Composite Materials, Dorset, UK). A long piece of nickel-chromium wire was wrapped  
150 around the electrode to physically hold it against the ceramic body, and which also  
151 served as the current collector and connection point. The cathode was made from a  
152 layer of carbon veil (25 cm<sup>2</sup>) (Gas Diffusion Layer) coated with a mixture of activated  
153 carbon and each of the subject binders, to form the conductive layer. The blend was  
154 spread onto the surface of the carbon veil layer and allowed to air dry in the case of  
155 chitosan, Ludox®, PVC and silicone-cathodes and heat-pressed in the case of PTFE-  
156 cathodes. The electrode was placed inside the ceramic cylinder and the conductive  
157 layer was in direct contact with the separator. The unit was placed in bottle-shaped  
158 plastic containers (Sarstedt, Australia) that held the substrate of the system (50 mL).  
159 The MFCs were loaded with an external resistance of 500 Ω during the maturing  
160 process. After this period, this initial resistance load was replaced by 100 Ω to assess

161 the performance of the binders. Figure 1 shows a schematic representation of the  
162 main components and the assembly process of the ceramic MFCs employed.

163 ***[Insert Figure 1]***

164 The fuel cells were matured for 15 days in batch mode. During this process, all MFCs  
165 were assembled with cathodes containing PTFE as the binder to ensure that the  
166 systems have the same start-up conditions. The units were fed with activated sewage  
167 sludge (Wessex Water Scientific Laboratory, Cam Valley, Saltford, UK). After 5 days,  
168 half the substrate volume was replaced with a mixture of sludge and neat human urine  
169 (1:1 vol/vol) collected from the public toilets of T-Block (Bristol Robotic Laboratory,  
170 Frenchay Campus, University of the West of England, Bristol, UK). Two days later, half  
171 the substrate was again replaced with fresh mixture of sludge and urine. After this  
172 period, the substrate was substituted completely by human urine. Once the anode was  
173 matured, the fuel cells were run in continuous flow mode at a feed rate of 216 mL.day<sup>-1</sup>  
174 <sup>1</sup> (hydraulic retention time of 5.55 h) and the cathodes were replaced by new ones  
175 containing the subject binders.

176

## 177 **2.2. Binder selection**

178 All cathode types were prepared with a load of 0.13 g.cm<sup>-2</sup> of activated carbon. Five  
179 types of polymer were tested as binders for the preparation of the active layer of the  
180 cathode: polytetrafluoroethylene (PTFE), silicone, polyvinylchloride (PVC), silica dioxide  
181 (Ludox®) and chitosan. The proportion of each polymer in the cathode mixture was  
182 also optimised. Binders and other reagents were purchased from Sigma-Aldrich (UK).  
183 The investigated amounts of each type of binder (wt percentage of the amount of  
184 activated carbon) are specified below:



185 • PTFE (60 wt % dispersed in water) for MFC cathode construction was tested at  
186 concentrations of 10, 20, 34 and 60 wt %.

187 • A two-component commercial silicone rubber PlatSil 73 (Mouldlife, UK) was used  
188 as binder in the MFC cathodes at 20 wt %. Component A and component B were mixed  
189 in equal proportion.

190 • PVC powder was first dissolved in tetrahydrofuran. The final amounts of PVC in  
191 the activated layer of the cathodes were 10, 20 and 34 wt %. It was not possible to test  
192 higher percentages of PVC due to the high viscosity of the resulting final mixtures,  
193 which prevented handling and folding to the cylindrical shape of the MFCs.

194 • Commercial colloidal silica dioxide Ludox<sup>®</sup>TM-50 (50 wt % suspended in water)  
195 was provided by Sigma-Aldrich (UK). This material was only tested at 60 wt % since it  
196 was the minimum amount of Ludox<sup>®</sup> to obtain a suitable consistency of paste to be  
197 used as conductive layer.

198 • Chitosan, a biopolymer made out of crab shells, was dissolved in a water solution  
199 of acetic acid 3 v/v. The amount selected to prepare the cathodes was 2.5 wt % due to  
200 the high viscosity of the final mixtures of chitosan/activated carbon at higher  
201 percentages.

202

### 203 **2.3. Analytical method**

204 Power output vs time was monitored by a 16-channel ADC-24 Picolog recorder data  
205 logger (Pico Technology Ltd, Cambridgeshire, UK). An automatic resistorstat tool was  
206 used to perform polarisation tests by varying the external resistance load from 999999  
207 to 0  $\Omega$  (including open circuit voltage) [31]. The urine treated (anode chamber) was  
208 characterized by measuring its pH and conductivity (Hanna 8424 pHmeter, Hanna

209 Instrument, UK and 470 Jenway conductivity meter, Camlab, UK, respectively).  
210 Chemical oxygen demand (COD) removal was determined with the dichromate  
211 oxidation method-based vials (COD HR, Camlab, UK) and a MD 200 photometer  
212 (Lovibond, UK). The evolution of the amount of ammonium in the treated urine was  
213 also measured with a HI 733 Ammonia High Range colorimeter (Hannah Instruments).

214

#### 215 **2.4. SEM-EDX characterization**

216 The morphological appearance and the chemical composition of each cathode type  
217 was determined by scanning electron microscopy (SEM) and energy-dispersive X-Ray  
218 (EDX) using a HITACHI S-3500N microscope coupled to a BRUKER AXS in high vacuum  
219 and in variable pressure modes.

220

### 221 **3. RESULTS AND DISCUSION**

222 **The SEM-EDX images of the cathodes prepared with the optimal amounts of the**  
223 **respective binders are shown in supporting material.** Although all of them show  
224 homogeneous surfaces, several differences can be observed in terms of surface  
225 appearance. Cathodes containing 20 wt % of silicone as binder display smooth  
226 surfaces, while those based on 10 wt % of PVC and 2.5 wt % of chitosan have slightly  
227 rougher surface appearances. Regarding the cathodes prepared with 20 wt % of PTFE  
228 and 60 wt % of Ludox<sup>®</sup>, they show the most granulated surface forming a spongy  
229 structure. On the other hand, EDX spectra confirm the presence of the binders  
230 investigated in respective cathodes (see supporting material). For instance, Figure B'  
231 shows the characteristic peaks of polytetrafluoroethylene such as carbon and fluoride,  
232 and Figure D' contains the peaks belonging to Ludox<sup>®</sup> (silica and oxygen).

233 Once the surface area and the composition of each cathode were characterised, their  
234 effects on the MFC performance were investigated. Figure 2 shows the polarisation  
235 and power curves including standard error mean bars determined on the basis on the  
236 three replicates set up for each cathode condition. These figures contain both the  
237 effect of the type and the percentage of the binder used on the MFC performance. The  
238 results from the triplicate tests clearly show that MFCs containing 20 wt % of PTFE  
239 reached higher power output than those with cathodes prepared at 10, 34, 60 wt % of  
240 PTFE. This behaviour was also observed on the polarisation curves, where 20 wt %  
241 PTFE<sup>®</sup>-based cathodes show lower ohmic losses compared to rest of the PTFE  
242 concentrations studied. Lower than 60% amounts of binder resulted in lower power  
243 maxima achieved by the devices. However, the reduction of power output was more  
244 marked for concentrations of PTFE above 20 wt %, probably because the structure is  
245 blocked by higher amounts of binder.

246 Regarding the PVC-based cathodes, there is an inverse relationship between the MFC  
247 performance and the amount of binder employed, 10 wt % being the optimal value  
248 among the percentages studied. The higher the amount of PVC in the cathode layer,  
249 the lower the MFC performance. These results could be attributed to an excess of PVC  
250 in the cathode, which increases the rigidity of the electrode and in turn reduces the  
251 oxygen transfer throughout the conductive layer of the cathode. This would have a  
252 detrimental effect on the rate of the oxygen reduction reaction, limiting the overall  
253 MFC performance.

254 As previously commented, in the case of silicone and Ludox<sup>®</sup>, the optimum  
255 concentrations were selected in order to prepare a homogeneous cathode active layer.

256 For chitosan-based cathodes, 2.5 wt % was selected as the optimal percentage since

257 higher amounts of this binder significantly increased the volume of the final mixture in  
258 such a way that the total amount of active material could not be deposited on the  
259 carbon veil substratum. Amongst these three materials, the results confirm that  
260 silicone is the least suitable polymer that can be used as binder in ceramic MFCs in  
261 terms of maximum power. This finding may be due to the smooth, plastic and non-  
262 porous surface of the cathode, which hinders the diffusion of oxygen throughout the  
263 whole structure. In such a case, the oxygen reduction reaction only takes place over  
264 the external layer of the electrode. Moreover, the high ohmic losses brought about by  
265 this material are also observed on the polarisation curves obtained.

266 In the case of Ludox<sup>®</sup>-based cathodes, they offer moderate values of maximum power  
267 output of 422  $\mu\text{W}$  on average. However, ceramic MFCs working with cathodes  
268 containing 2.5 wt % of chitosan allow up to 510  $\mu\text{W}$  to be generated. These results may  
269 be caused by the spongy structure of these two types of cathode, which was similar to  
270 that observed for the PTFE<sup>®</sup>-based cathodes. The porous structure of these  
271 configurations facilitates better the oxygen reduction reaction, thus improving the  
272 MFC performance. Nevertheless, cathodes containing Ludox<sup>®</sup> show a more granulated  
273 and less rigid structure than chitosan-based cathodes, which could also cause them to  
274 detach from the cathode under certain conditions. These cathodes are therefore  
275 slightly less stable as reflected in the wide error bars.

276 ***[Insert Figure 2]***

277 Figure 3 summarises the maximum power output produced by the MFCs using  
278 cathodes based on the optimal amount of the respective binders tested. As can be  
279 seen, cathodes with 20 wt % of PTFE offer the best performance in terms of power  
280 output (846  $\mu\text{W}$ ). However, MFCs with 2.5 wt % of chitosan (8 times less than the

281 amount of binder needed for 20 wt % of PTFE) generated 510  $\mu$ W. It therefore seems  
282 that cathodes based on chitosan, allow ceramic MFCs to generate 60.3 % out of the  
283 power output achieved by PTFE-based devices.

284 ***[Insert Figure 3]***

285 Figure 4 includes individual polarisation curves for the anode and the cathode in the  
286 systems. Anode potential curves are similar in all systems regardless of the type of  
287 cathode set-up, since all of them were matured by following the same procedure.  
288 Therefore, the anode potential curve depicted in Figure 4 is the average trend for all  
289 the tests ( $\sigma$  of  $\pm 7$  %). However, the cathode potential curves show significant  
290 variations depending on the type of binder used, which directly affects the MFC  
291 performance.

292 Cathodes based on 20 wt % of PTFE exhibit the highest value of OCV (677 mV) followed  
293 by those prepared with 10 wt % of PVC, 60 wt % of Ludox<sup>®</sup> and 2.5 wt % of chitosan,  
294 respectively. The lowest values of voltage under open circuit conditions are achieved  
295 by cathodes containing 20 wt % of silicone. Independent of the values of current  
296 intensity, MFCs working with PTFE-based cathodes offer higher voltage values when  
297 compared with Ludox<sup>®</sup> and chitosan-based cathodes. Moreover, the voltage trends  
298 (voltage versus current intensity) are very stable in these cases, proving their suitability  
299 as cathode binders. Cathodes prepared with 10 wt % of PVC exhibit slightly higher  
300 ohmic losses due to the rigid structure of this polymer. Finally, the voltage responses  
301 of the cathodes based on silicone are notably lower, even reaching negative values.

302 ***[Insert Figure 4]***

303 The performance of ceramic MFCs using cathodes based on different types of binders  
304 was also evaluated in terms of urine treatment capacity. For this purpose, the

305 evolution of the chemical oxygen demand (COD) in the anode chamber was measured.  
306 Figure 5 shows the COD removal trends. The best results were obtained with 2.5 wt %  
307 of chitosan (26 %), with a higher COD removal when compared with 20 wt % of PTFE®  
308 (23.5 %). In the case of Ludox® and PVC, both materials offer similar results, 15.7 %  
309 and 14.5 %. However, the cathodes based on silicone allow ceramic MFCs to remove  
310 only 10.3 % of COD. Organic load removal is related to the level of power output  
311 generated, although there are other factors involved. The composition of the binder  
312 could affect the COD removal in the MFCs, and therefore their urine treatment  
313 capacity. The final COD removal rates may be considered slightly low. These values can  
314 be explained by the short retention time in the systems (5.55 h) so that urine as  
315 feedstock cannot be completely treated. Despite the retention time, the values of COD  
316 removal in the MFCs based on 2.5 wt % of chitosan and 20 wt % of PTFE are notable.  
317 These results confirm that low cost ceramic MFCs are suitable for human urine  
318 treatment. However, urine does not only consist of organics. It mainly contains urea,  
319 which can be quickly hydrolysed to ammonia and CO<sub>2</sub>. To this respect, the inoculum of  
320 MFCs with mixed sludge cultures plays an important role, since they can oxidise  
321 ammonia as a part of their metabolism. This indirectly results in electron transfer  
322 through the symbiosis with other organisms in the mixture. During this process, a  
323 precipitate called struvite is formed (magnesium ammonium phosphate). Because of  
324 the urea hydrolysis, the pH in the anode tends to go alkaline quite quickly, and due to  
325 the electroosmotic drag through the ceramic separator, an alkaline solution is formed  
326 in the cathode, which contributes to the reduction of total nitrogen [32].

327

***[Insert Figure 5]***

328 The interest of researchers on chitosan applied to MFCs has risen in recent years. In  
329 2011, Liu *et al.* [33] prepared compatible carbon nanotube/chitosan based cathodes  
330 for MFCs. The mixture was electrodeposited onto carbon paper allowing MFCs to  
331 generate up to  $189 \text{ mW.m}^{-2}_{(\text{cathode})}$ , 2.3 times higher when compared with cathodes  
332 based on carbon cloth coated with platinum. These results demonstrate that the use of  
333 chitosan for the modification of biocathode surfaces favours the electron transfer  
334 between bacteria and electrode since chitosan boosts biofilm attachment. On the  
335 other hand, Krishnaraj *et al.* [34] performed the modification of both anode and  
336 cathode surfaces by using chitosan. In this case, chitosan was electrochemically  
337 deposited onto carbon felt modified with alginate and demonstrated that this material  
338 is suitable for biofilm growth. Furthermore, they also electrodeposited chitosan onto  
339 the cathode. Their results confirm that the combination of anode and cathode  
340 modified with chitosan in MFCs improves the coulombic efficiency of the system.  
341 These previous results support the promising use of chitosan as binder in MFCs and are  
342 in line with those obtained in this work.

343 Amongst the polymers tested, chitosan seems to be the most promising option since  
344 very low amounts of this binder allow ceramic MFCs to reach high values of power  
345 output and COD removal. On the other hand, this biopolymer is abundant in nature  
346 and has low cost in comparison with other binders. Furthermore, the preparation of  
347 cathodes based on PTFE requires a heat-pressing stage, which is not necessary for  
348 cathodes containing chitosan since they can be air dried whereas. All these factors  
349 make chitosan a potential material to replace fluorinated polymers such as PTFE as  
350 binder in ceramic MFCs. Ludox<sup>®</sup>-based cathodes also offer interesting results in terms  
351 of both power output and COD removal but the amount required of this binder is

352 significantly higher than in the case of chitosan and the stability of the cathode is  
353 slightly lower.

354

#### 355 **4. CONCLUSIONS**

356 In this work, four non-fluorinate polymers have been tested as alternative binders for  
357 PTFE in the cathode of ceramic MFCs fed with human urine. The results show that all  
358 the materials studied, except silicone, are suitable for bioenergy production and urine  
359 treatment in ceramic MFCs. Among them, Ludox<sup>®</sup> and chitosan prove to be the most  
360 sustainable materials as binders in comparison with PTFE. Both allow ceramic MFCs to  
361 reach similar values of power output, although chitosan based cathodes require a  
362 smaller amount of binder, only 2.5 wt % (24 times less than in the case of Ludox<sup>®</sup>-  
363 based cathodes). Ceramic MFCs containing cathodes prepared with 2.5 wt % of  
364 chitosan achieve 60.3 % out of the power output offered by the same device using 8 %  
365 less amount of PTFE in addition to being a sustainable material. Although further work  
366 is required to better understand the conductive mechanism of the chitosan, results  
367 confirm that chitosan could be a promising bio-alternative to PTFE, as a binder in  
368 ceramic MFC cathodes.

369

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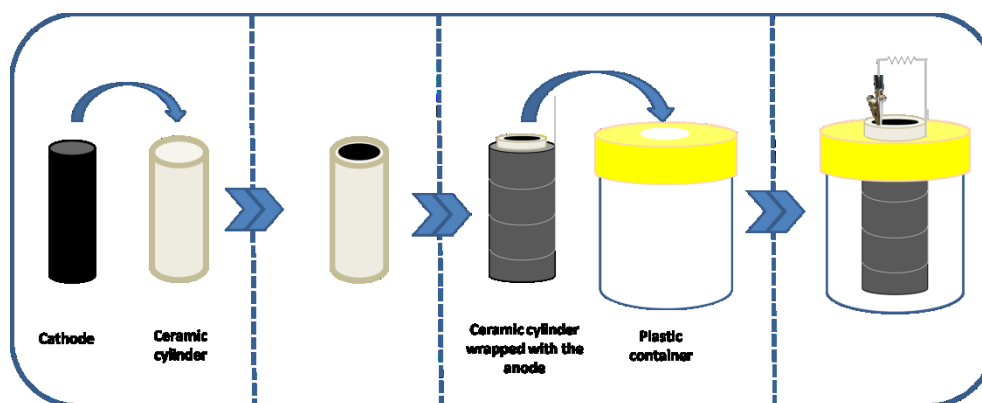
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#### FIGURES

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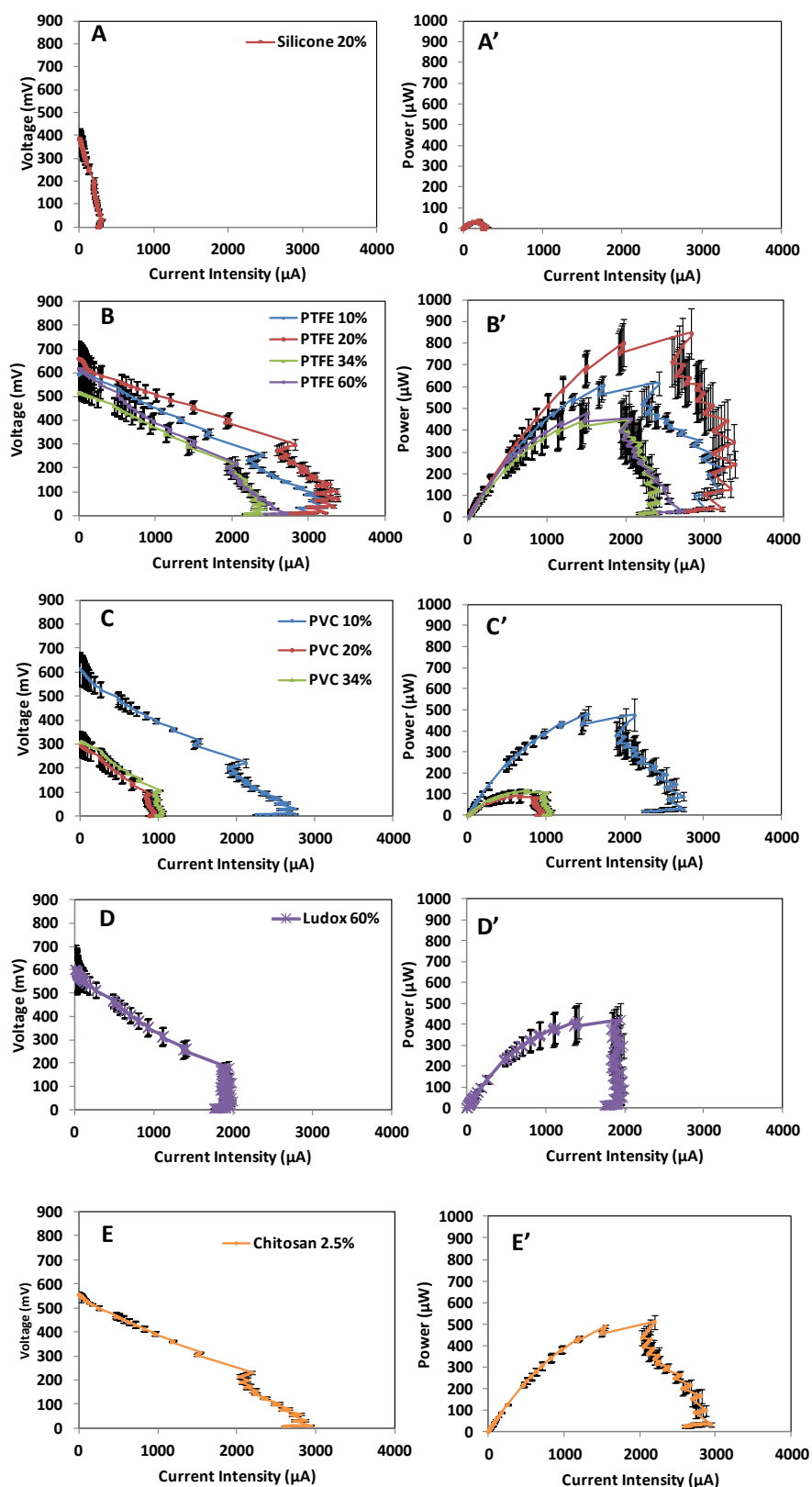
482 **Figure 1.** Main components and assembly process of MFCs.

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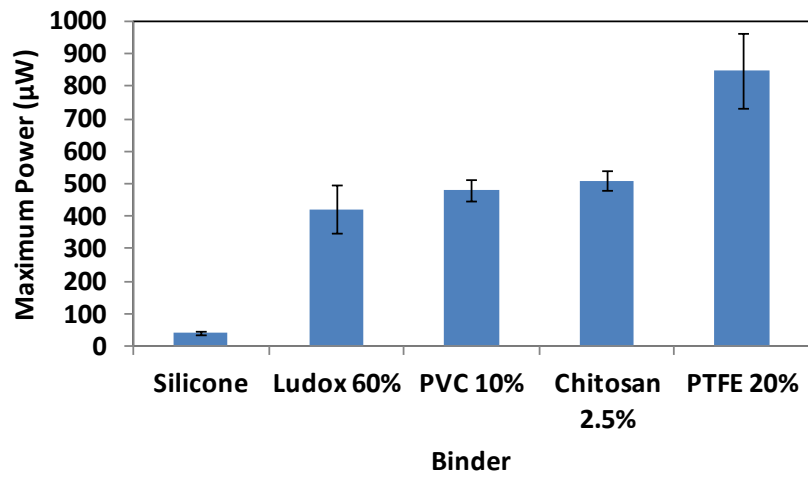
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488 **Figure 2.** Polarisation (A, B, C, D and E) and power curves (A', B', C', D' and E') for the

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ceramic MFCs working with cathodes based on different binders.

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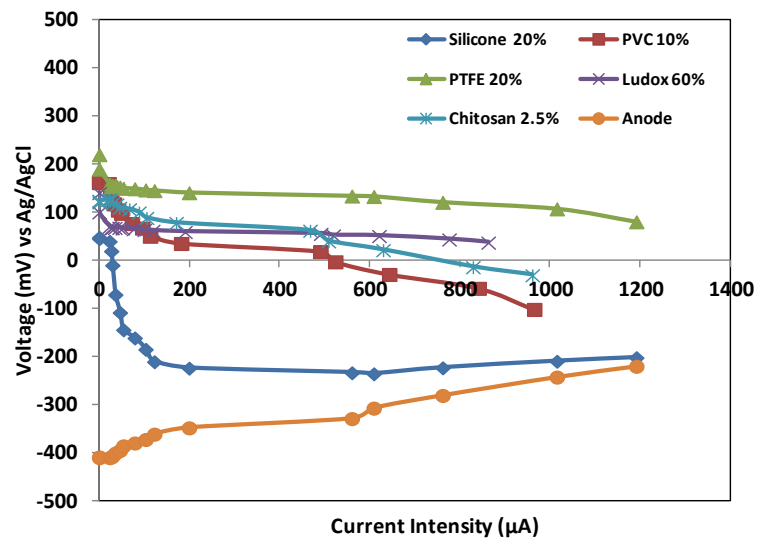
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492 **Figure 3.** Maximum power output by ceramic MFCs using optimal amounts of binders.

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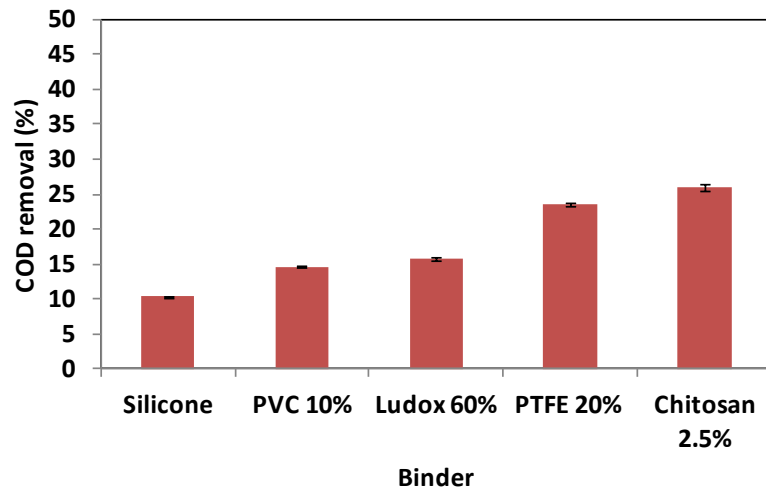
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**Figure 4.** Anode and cathode polarisation curves.



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**Figure 5.** COD removal by ceramic MFCs using optimal amounts of binders.

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