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

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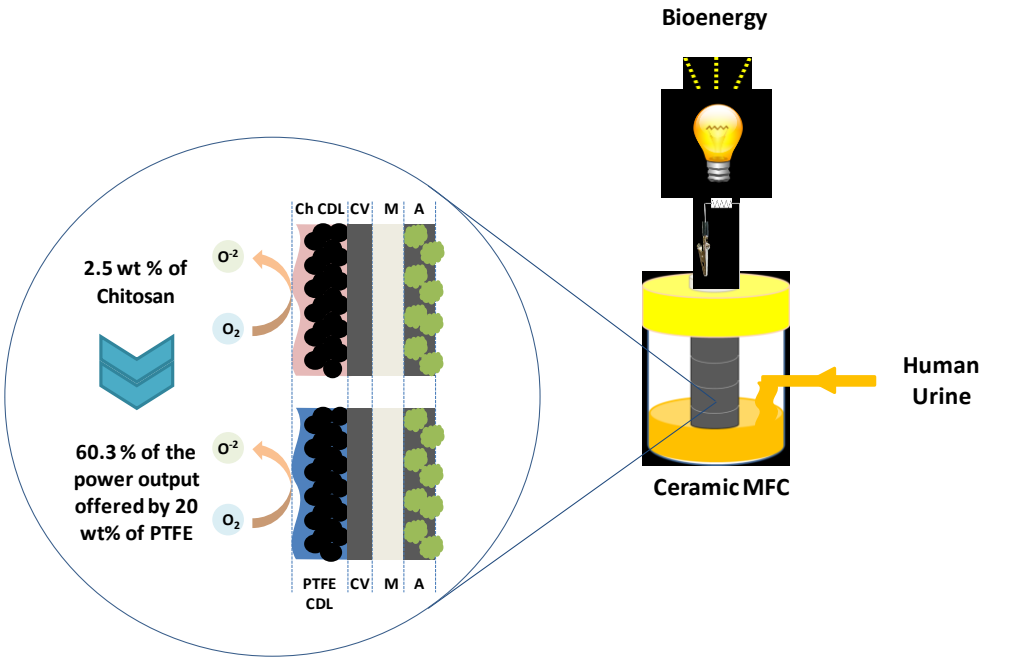
GRAPHICAL ABSTRACT



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

HIGHLIGHTS

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

- Chitosan-based cathodes allow MFCs to reach a maximum power of 510 µW.
- 60.3 % of the power output by PTFE obtained with 8 times less amount of chitosan.

ABSTRACT

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

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

1. INTRODUCTION

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

Fuel cell technology allows the chemical energy contained in a substrate to be directly transformed into electricity by using chemical reactions. A widespread use of this technology could help mitigate climate change since fuel cells generate clean energy with low CO_2 emissions. Although different fuel cells can vary significantly in operation, they essentially consist of the same main components: i) an anode, at which the substrate is oxidized while producing protons and electrons, ii) a cathode, at which protons and electrons are combined and iii) an electrolyte, for the selective transport of ions from the anode to the cathode [5, 6]. Fuel cells can be divided into two main categories, namely chemical fuel cells and biofuel cells, depending on the nature of the chemical reactions involved. Biofuel cells can be further categorised into enzymatic fuel cells, bioelectrochemical fuel cells and organelle fuel cells. Microbial Fuel Cells

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

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

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

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

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

In this work, four non-fluorinated and low cost polymers have been tested as alternative binders for cathode construction in ceramic MFCs fed with human urine. Several amounts (by weight) of polyvinyl chloride (PVC), Ludox® (colloidal silica), silicone and chitosan have been investigated to determine the best alternative to PTFE. Chitosan is the n-deacetylated derivative of chitin (acetylation degree < 0.35), one of the most abundant natural polysaccharides. It is generally found in crustacean shells from crabs, shrimp or insects. This bio-polymer is neither soluble in water nor in most of organic and alkali solvents. The chitosan structure is based on three different polar functional groups: i) hydroxyl (-OH); ii) primary amine ($-NH_2$); iii) ether (C-O-C). The most promising characteristic is the possibility of improving its mechanical and

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

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

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

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

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

2. MATERIALS AND METHODS

2.1. MFC configuration and operation mode

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

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

[Insert Figure 1]

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

2.2. Binder selection

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

- PTFE (60 wt % dispersed in water) for MFC cathode construction was tested at concentrations of 10, 20, 34 and 60 wt %.
- A two-component commercial silicone rubber PlatSil 73 (Mouldlife, UK) was used as binder in the MFC cathodes at 20 wt %. Component A and component B were mixed in equal proportion.
- PVC powder was first dissolved in tetrahydrofuran. The final amounts of PVC in the activated layer of the cathodes were 10, 20 and 34 wt %. It was not possible to test higher percentages of PVC due to the high viscosity of the resulting final mixtures, which prevented handling and folding to the cylindrical shape of the MFCs.
- Commercial colloidal silica dioxide Ludox®TM-50 (50 wt % suspended in water) was provided by Sigma-Aldrich (UK). This material was only tested at 60 wt % since it was the minimum amount of Ludox® to obtain a suitable consistency of paste to be used as conductive layer.
- Chitosan, a biopolymer made out of crab shells, was dissolved in a water solution of acetic acid 3 v/v. The amount selected to prepare the cathodes was 2.5 wt % due to the high viscosity of the final mixtures of chitosan/activated carbon at higher percentages.

2.3. Analytical method

Power output vs time was monitored by a 16-channel ADC-24 Picolog recorder data logger (Pico Technology Ltd, Cambridgeshire, UK). An automatic resistorstat tool was used to perform polarisation tests by varying the external resistance load from 999999 to 0 Ω (including open circuit voltage) [31]. The urine treated (anode chamber) was 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®, 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® (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®-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®, 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®-based cathodes, they offer moderate values of maximum power
267 output of 422 µW on average. However, ceramic MFCs working with cathodes
268 containing 2.5 wt % of chitosan allow up to 510 µW 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®-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® 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 µW). 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 μW. 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 (σ of ± 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® 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® 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

evolution of the chemical oxygen demand (COD) in the anode chamber was measured. Figure 5 shows the COD removal trends. The best results were obtained with 2.5 wt % of chitosan (26 %), with a higher COD removal when compared with 20 wt % of PTFE® (23.5 %). In the case of Ludox® and PVC, both materials offer similar results, 15.7 % and 14.5 %. However, the cathodes based on silicone allow ceramic MFCs to remove only 10.3 % of COD. Organic load removal is related to the level of power output generated, although there are other factors involved. The composition of the binder could affect the COD removal in the MFCs, and therefore their urine treatment capacity. The final COD removal rates may be considered slightly low. These values can be explained by the short retention time in the systems (5.55 h) so that urine as feedstock cannot be completely treated. Despite the retention time, the values of COD removal in the MFCs based on 2.5 wt % of chitosan and 20 wt % of PTFE are notable. These results confirm that low cost ceramic MFCs are suitable for human urine treatment. However, urine does not only consist of organics. It mainly contains urea, which can be quickly hydrolysed to ammonia and CO_2. To this respect, the inoculum of MFCs with mixed sludge cultures plays an important role, since they can oxidise ammonia as a part of their metabolism. This indirectly results in electron transfer through the symbiosis with other organisms in the mixture. During this process, a precipitate called struvite is formed (magnesium ammonium phosphate). Because of the urea hydrolysis, the pH in the anode tends to go alkaline quite quickly, and due to the electroosmotic drag through the ceramic separator, an alkaline solution is formed in the cathode, which contributes to the reduction of total nitrogen [32].

[Insert Figure 5]

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

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

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

4. CONCLUSIONS

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

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FIGURES

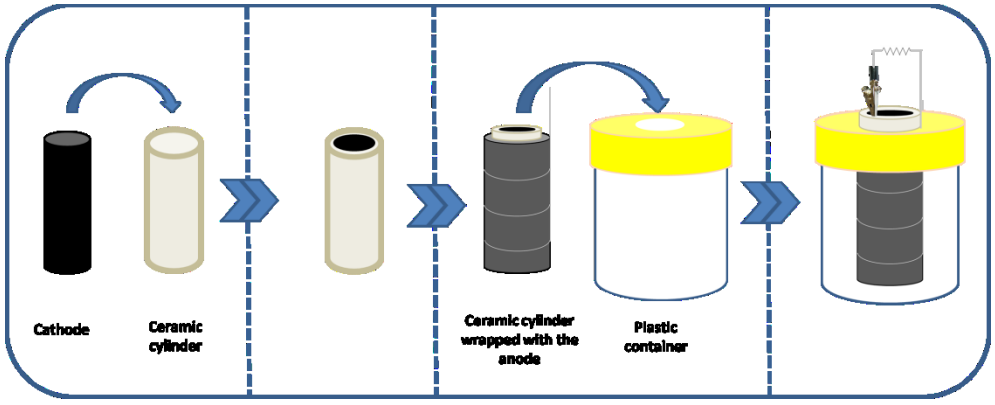
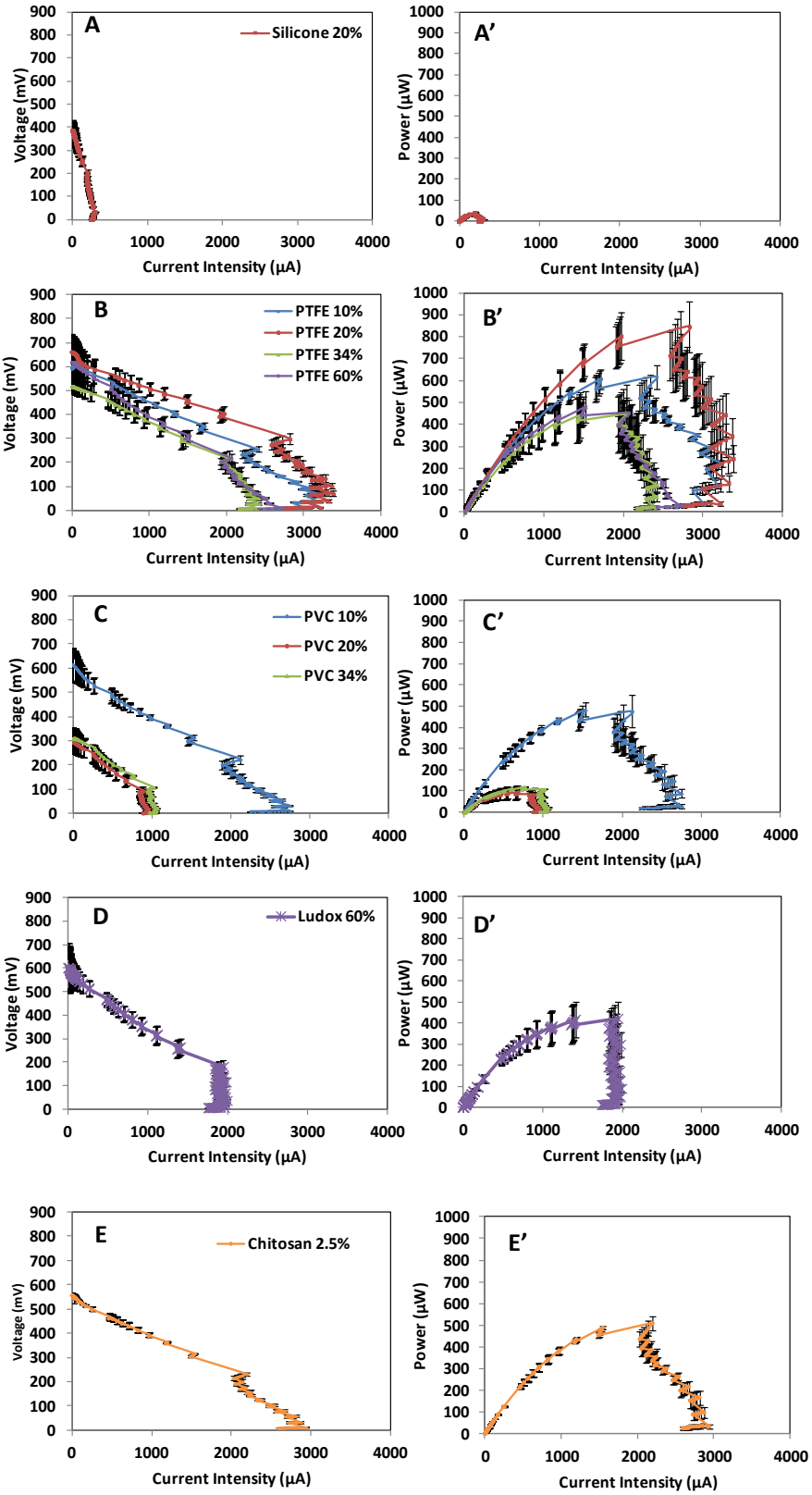


Figure 1. Main components and assembly process of MFCs.



487

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

489 ceramic MFCs working with cathodes based on different binders.

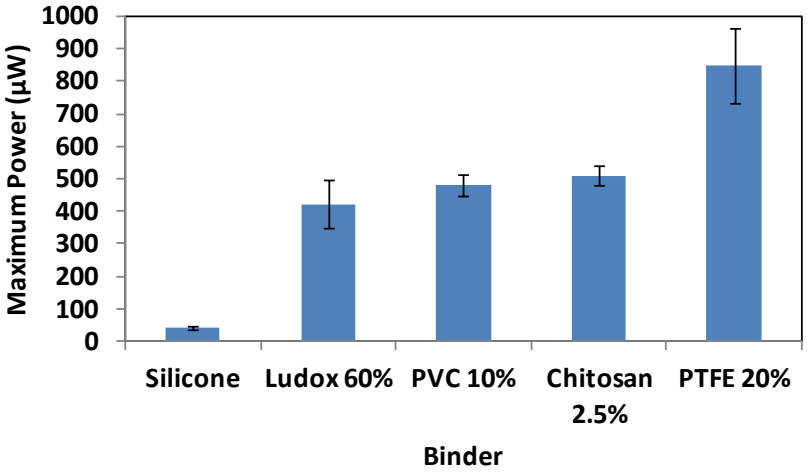


Figure 3. Maximum power output by ceramic MFCs using optimal amounts of binders.

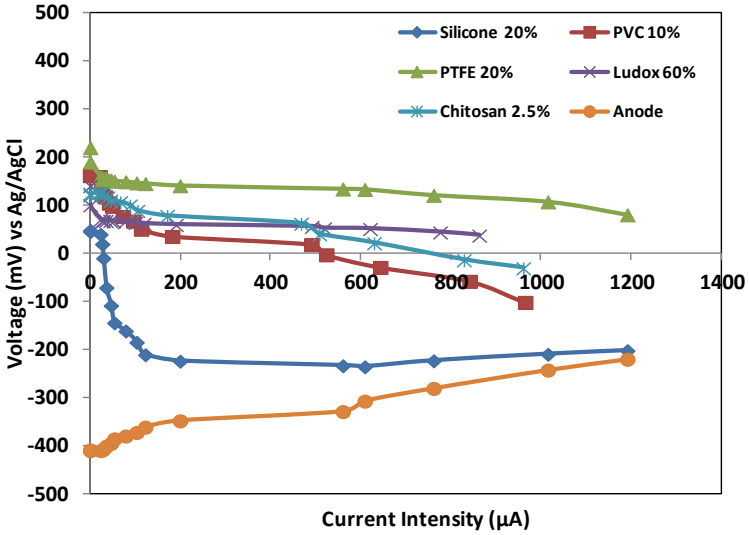
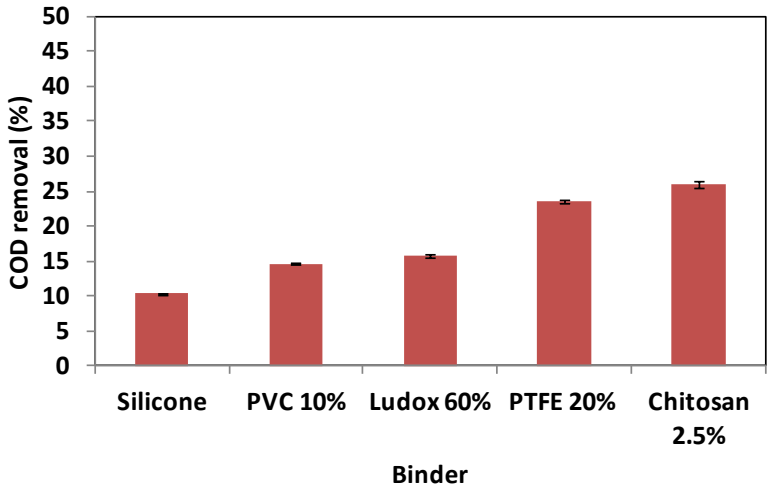


Figure 4. Anode and cathode polarisation curves.



498

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

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