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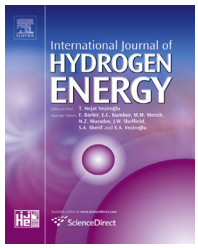

# Electricity and catholyte production from ceramic MFCs treating urine

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ABSTRACT

The use of ceramics as low cost membrane materials for Microbial Fuel Cells (MFCs) has gained increasing interest, due to improved performance levels in terms of power and catholyte production. The catholyte production in ceramic MFCs can be attributed to a combination of water or hydrogen peroxide formation from the oxygen reduction reaction in the cathode, water diffusion and electroosmotic drag through the ion exchange membrane. This study aims to evaluate, for the first time, the effect of ceramic wall/membrane thickness, in terms of power, as well as catholyte production from MFCs using urine as a feedstock. Cylindrical MFCs were assembled with fine fire clay of different thicknesses (2.5, 5 and 10 mm) as structural and membrane materials. The power generated increased when the membrane thickness decreased, reaching 2.1 ± 0.19 mW per single MFC (2.5 mm), which was 50% higher than that from the MFCs with the thickest membrane (10 mm). The amount of catholyte collected also decreased with the wall thickness, whereas the pH increased. Evidence shows that the catholyte composition varies with the wall thickness of the ceramic membrane. The possibility of producing different quality of catholyte from urine opens a new field of study in water reuse and resource recovery for practical implementation.



## Introduction

Microbial Fuel Cells (MFCs) present an attractive approach to renewable energy for electricity production from waste [1]. The research on electricity production from organic compounds has been investigated since the beginning of the 20th century [2]. Since then, the generation of voltage and current from several types of organic compounds including glucose, acetate and waste water, has been thoroughly investigated. However, the use of urine as a feedstock for MFCs offers a more recent approach, being reported for the first time in 2012 [3]. Urine is an abundant fuel with a daily production of 17.4 billion litres, based on a world population of 6.97 billion and considering that an adult produces an average of 2.5 L in a day [3]. In MFCs, the chemical energy in urine can be directly converted into electricity using microorganisms as biocatalysts. An MFC normally comprises two chambers, the anodic and the cathodic, that are separated by an ion exchange membrane, which can also act as support material, being sandwiched between the anode and cathode electrodes. The anodic chamber contains the microorganisms that break down the organic matter in urine into smaller molecules,

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whilst releasing electrons that travel through the wire to the cathode electrode, and protons that pass through the ion exchange membrane to the cathodic chamber. In the cathodic chamber, the oxygen reduction reaction (ORR) takes place by consuming oxygen from air to generate water or hydrogen peroxide, depending on the catalyst used. The ORR is one of the major limiting factors in fuel cells, especially in MFCs which operate at neutral pH and room temperature [4].

The efficiency of MFCs can also be limited by several other factors, such as microbial community on biofilm anode, internal resistance and many others [4]. The use of an electrochemically active catalyst on the cathode electrode, which can improve the ORR kinetics, and the use of membrane materials, with high ionic conductivity and low ohmic resistance, could improve the MFC power performance. An electrochemically efficient catalyst, such as Pt or Pt alloys, would promote the ORR through a $4e^-$ pathway, which in an alkaline medium would take place according to reaction (1):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, \quad E^o = 0.401\ V\ vs.\ SHE \tag{1}$$

This reaction can also take place in two steps, following a hydrogen peroxide formation and oxidation pathway:

$$O_2 + H_2O + 2e^- \rightarrow OOH^- + OH^-, \quad E^o = -0.065\ V\ vs.\ SHE \tag{2}$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-, \quad E^o = 0.867\ V\ vs.\ SHE \tag{3}$$

However, when using non-noble metal catalysts, the reduction of hydrogen peroxide in alkaline media usually follows a $2e^-$ pathway and hydrogen peroxide degradation. Therefore, the ORR could involve either the 2 or $4e^-$ pathway depending on the catalyst used. However, the majority of the highly effective catalyst materials are unaffordable for a commercially viable technology. In terms of catalysts for the ORR, there has been an extensive line of work for low cost cathode electrodes for MFCs, which has given rise to activated carbon based materials since it offers performance stability at lower cost [10,11]. In an effort to find low-cost effective materials to reduce the manufacturing cost of MFCs, ceramics have been reported as a good candidate for successfully substituting expensive commercially available ion-exchange membranes [5–8]. The interest in using ceramic as low cost membrane materials for MFCs is receiving increasing attention also because of the improved performance in terms of power and catholyte production [9]. However, the optimisation of such materials, including composition, porosity and wall thickness, needs to be studied further. Recent studies demonstrated simultaneous electricity generation from MFCs and catholyte accumulation in the cathode compartment without the need for external power [12]. This accumulation of catholyte, in the initially empty cathode chamber, was attributed to the combination of the following factors: (i) the water produced as a result of the ORR in the cathode electrode; (ii) the passive water diffusion across the membrane; and (iii) when the MFC was under load, the electroosmotic drag of water molecules together with the cations that migrate from the anode to the cathode [13]. The catholyte generation, in this case, has several advantages including the self-hydration of the ionic exchange membrane, the hydration of the cathode electrode, and the possibility to extract such solution for other applications, such as fertiliser enrichment. Although the hydration of the membrane and the catalyst layer benefits the ion transfer and the electrode kinetics [13,14], water accumulation at the cathode side might also lead to an increase in membrane resistance and consequent decrease in fuel cell performance [15]. Therefore, a rigorous analysis of the effect of the catholyte accumulation in the MFC power output should be performed.

In this study, the effect of wall thickness of fine fire clay (FFC) ceramic membranes for MFCs treating urine was evaluated, in terms of power generation and catholyte accumulation. For this purpose cylindrical MFCs were assembled with ceramics of three different thicknesses (2.5, 5 and 10 mm), as structural and membrane materials. The catholyte produced from the MFCs was analysed in terms of volume, pH and mineral composition. The correlation between the catholyte produced, its composition and the effect of the membrane thickness was evaluated for both catholyte production and power output.

## Methods

### MFC assembly

Cylindrical ceramic MFCs were assembled using fine fire clay cylinders (ROCA, Spain) with three different wall thicknesses 2.5, 5 and 10 mm as membranes. The ceramics were tested in triplicates and control MFCs of each thickness, were left at open circuit throughout the whole experiment. All the cylinders had 84 mm height and an external diameter of 48 mm. The anode electrode was constructed from 90 × 27 $cm^2$ untreated carbon veil with a density of 30 $g/m^2$ (PRF Composites, Dorset, UK), which was folded and wrapped around the external surface of the ceramic cylinder. Stainless steel wire (0.5 mm, Scientific Wire Company) was threaded through the electrodes and used as a current collector. Once the anode electrode was wrapped around the ceramic membrane, the cylindrical MFC was housed in a separate acrylic cylinder, forming the anode chamber, with a top and bottom acrylic lids, bolted together, as shown in Fig. 1. The internal volume of the anode chamber for each MFC was 200 mL. The inlet was introduced from the bottom and the outlet discharged from the top of the container to optimise the distribution of fresh urine through the anodic chamber. The cathode electrode consisted of a gas diffusion electrode with carbon veil as the support material and a microporous layer (MPL), which was prepared with a mixture of activated carbon (GBaldwin&Co, 80 g/140 mL solution), polytetrafluoroethylene (PTFE) (60% wt. Sigma–Aldrich) and distilled water, as previously described [16]. The cathode electrodes were cut with a surface area of 65 $cm^2$ and placed inside the ceramic cylinders. A stainless steel crocodile clip was connected to the cathode electrodes as a current collector and acrylic rings were placed inside the ceramic cylinder to improve contact between the cathode electrode and the ceramic membrane.

The images of the ceramic structure were captured using a Philips XL30 scanning electron microscope (SEM). Energy

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