CERAMIC STACKS FOR URINE ENERGY EXTRACTION

A. TREMOULI[1], J. GREENMAN[1] and I. IEROPOULOS[1,*]

[1] Bristol BioEnergy Centre, BRL, University of the West of England, T-Building, Frenchay Campus, Bristol BS16 1QY, UK

*Corresponding author: ioannis.ieropoulos@brl.ac.uk, tel: +44(0)117 32 86318

Keywords: MFC, stack, ceramic, urine

Abstract

Two ceramic stacks were developed aiming to produce energy when fed with neat undiluted urine. Each stack consisted of twelve identical MFCs which were arranged in cascades. Two types of ceramic were tested; terracotta (t-stack) and mullite (m-stack). In order to avoid a voltage reversal occurrence, different electrical configurations were examined. Despite the adverse conditions, the m-stack produced a maximum power of 0.8 mW whilst the t-stack produced a maximum power of 0.52 mW after 62.6 h of operation. Moreover, during the operation of both systems, the ceramic material was possibly blocked by the precipitation of struvite. The results suggest that parameters such as porosity, composition, geometry and size, in addition to environmental conditions (electrical connection, flow rate) are critical factors that need to be considered for stack improvement and use in practical applications.

1. Introduction

Microbial fuel cells (MFCs) are devices that convert biomass directly into electricity through the metabolic activity of microorganisms [1, 2]. In recent years, the interest for this technology has rapidly increased, since MFCs offer the advantage of simultaneous treatment of wastewater and energy generation in the form of electricity [3, 4]. Several MFC designs have been reported with optimised parameters for power production and wastewater treatment, when fed with different types of feedstock [5, 6].

In order to exploit the advantages offered by MFC technology the proposed configurations must be technically and economically sustainable. Although several bioreactor designs have been investigated under different operating conditions and both expensive and cheap materials have been tested with various substrates, the MFC technology is still in its infancy [2, 5]. The main obstacles that this technology has to overcome are the low energy generated when compared to more conventional mature technologies (chemical fuel cells, batteries, photovoltaics) as well as the high cost of some of the materials used [7, 8].

Stacking MFCs could enhance power production and wastewater treatment efficiency. However, issues are encountered when connecting multiple units together as this can be done in a number of different ways (series, parallel and series/parallel combined), it can result in losses via the conducting fluidic connections of interconnected units and it can affect the performance depending on whether the units are serially fed in a cascade or individually fed from the source [9]. Moreover, the material selection for the optimization of the MFC performance is of utmost importance. In order for MFCs to be practically implemented, research towards the effective use of inexpensive and sustainable materials for the construction of MFCs must be carried out. Recently, researchers have started using ceramics with encouraging results, suggesting that these inexpensive materials might be the solution for inciting MFCs to be practically implemented. There have even been reports of MFCs made from paper and other biodegradable materials, which in a way opens up new opportunities for low-cost, fixed-term MFC deployment [10]. Studies have demonstrated that ceramics can provide stability, improve power and treatment efficiencies, create a better environment for the electro-active bacteria and contribute towards resource recovery [6].

Urine is an abundant waste and it has already been reported that it can be used as a fuel in MFCs for generating electricity [11]. The daily production of human urine is calculated in the range 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 [11, 12].

The main objective of this study was the investigation of urine utilization in ceramic MFC stack/cascades. In order to accomplish this goal, two ceramic stacks were constructed and optimized in terms of power production.-MFCs within the stack were fed from a common tank with a dripping mechanism. Neat, urine was used as a feedstock while ceramic (terracotta and mullite) was used as (i) the structural material and (ii) the separator for ion exchange. To the best of the authors' knowledge this is the first time that stacks were constructed and optimized with the specific MFC design, selection and combination of materials while human urine was used as the feedstock.

2. Materials and methods

2.1. MFC stack configuration

Each MFC unit consisted of a single cylindrical ceramic chamber, whose internal volume was used as the anode chamber, and the external surface was used as the open-to-air cathode. A schematic cross section and a photo of the unit are shown in Figures 1a and 1b. Two circular 3D printed lids made from acrylo-nitrile butadiene styrene (ABS) material sealed the top and the bottom of the chamber. The influent port was coming from the top, but was directing the feedstock towards the bottom of the anodic chamber, for better fluid percolation. The effluent was coming from the top of the anodic chamber, with the use of a constant-level outlet tube. Carbon fibre veil material (PRF Composites, Dorset, UK) with a density of 20 g/ cm^2 and a total surface area of 64.8 cm^2 was folded and employed as the anode electrode. The cathode electrode (13.75 cm^2) was prepared by coating activated carbon (AC) (GBaldwin&Co) paste on polytetrafluoroethylene (PTFE) (60% wt. Sigma-Aldrich) treated carbon cloth and was tightly wrapped around the outside wall of the ceramic, with the AC side facing the ceramic material. The paste was prepared by mixing AC powder, PTFE solution and distilled water (80 g/140 mL), as previously described [12]. Stainless steel wire (0.5 mm, Scientific Wire Company) was threaded through the electrodes, which were connected with stainless steel crocodile clips acting as current collectors.

Two similar stacks were fabricated and each one consisted of twelve identical MFCs (Fig. 2). The units in the stack were arranged in cascades such that the effluent from the upstream MFC flowed as the influent into the downstream MFC unit. MFCs within the cascades were connected electrically together and a dripping mechanism was used for fluidic isolation and thus electrical insulation among units. Mullite ceramic material (Anderman ceramics Lt, Hartlebury Trading Estate, Hartlebury, UK) was used for the first stack (m-stack) and terracotta (Weston Mill Pottery, Sutton on Trend, UK) for the second stack (t-stack).

2.2. MFC enrichment and operation

The two stacks were operated under identical conditions in order to compare the performance of the two ceramic materials. The enrichment and adaptation of the electrochemically active bacteria in the MFCs was performed in batch mode, under a fixed external load of 2 kΩ for each cell. During inoculation, 50% of activated sewage sludge supplied from the Wessex Water Scientific Laboratory (Saltford, UK) and 50% of fresh urine was used as the feedstock. Urine was donated by healthy individuals aged between 18 and 70 years old, with a normal diet and no known medical conditions. Following the enrichment of the cells, the operation was shifted to continuous mode, using only fresh urine as the feed. The first unit placed at the top of each stack was being fed directly from the inlet reservoir using a peristaltic pump (205 U, Watson Marlow, Falmouth, UK). The 2kΩ external resistive loads were removed and a 1 kΩ load was connected to the each stack. Due to practical limitations such as urine availability, the MFC units operated at a slow flow rate 7.51 ml h^{-1} (HRT 0.8 h). The anodic liquid volume was 6 ml during batch operation. This volume gradually decreased to approximately 1 ml, as a result of struvite precipitation, probably due to the slow flow rate. The polarisation experiments were performed using a variable resistor (Centrad Boite A Decades De Resistances DR07). Data were produced by sweeping resistor values from 1MΩ to 0 Ω. The time interval between resistance changes was 3min. Two different electrical configurations were assessed. During the first electrical connection, the top four (1-4), the middle four (5-8) and the bottom four MFCs (9-12), where connected in parallel, and the three parallel groups were connected in series (3s4p). During the second electrical configuration MFCs 1, 2, 11, 12; 3, 4, 9, 10 and 5, 6, 7, 8, were connected in parallel, and the three parallel groups were then connected in series.

In an attempt to improve performance and recover power to at least the levels produced at the start of the experiment, a series of tests and parameter changes were performed such as: hydration of the cathode electrodes with deionized water, changing the electrical configuration, changing the flow rate, as well as replacing all the cathode electrodes with new identical ones. Moreover, the cells were opened up and the struvite, which had accumulated on the anode electrodes was removed. The final step was to examine if the ceramic material was blocked and for this the anode and cathode electrodes were replaced with new identical ones, but keeping the same ceramic chassis. All experiments were performed at room temperature 22 ± 2 ^{0}C.

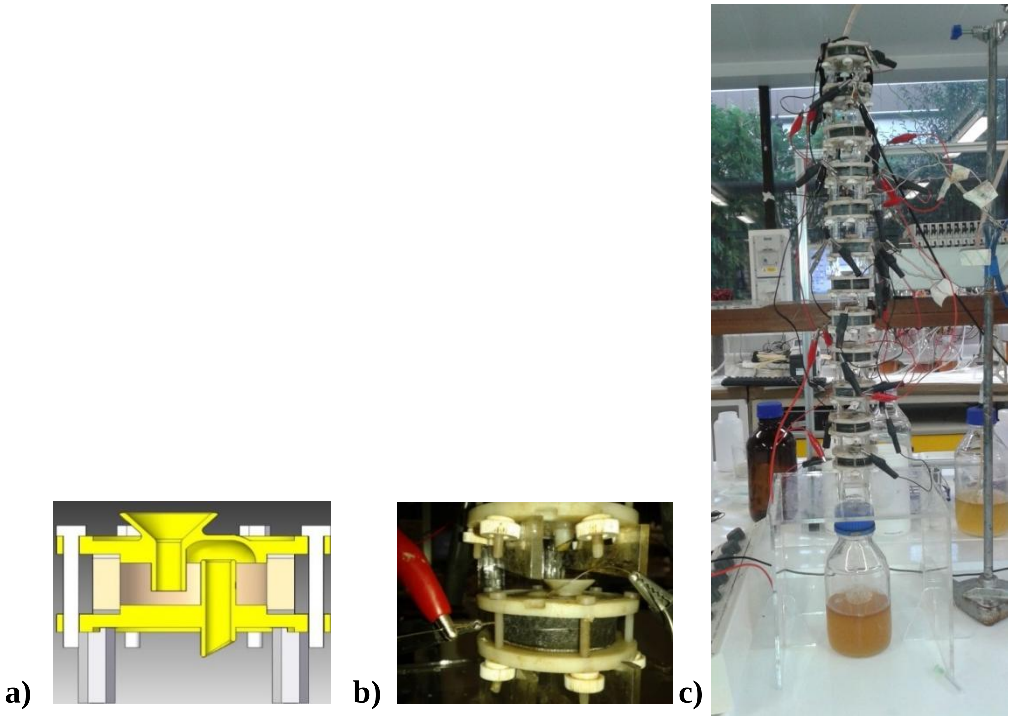

Figure 1. a) Schematic diagram of the cross section of the cell; b) photo of the cell; c) photo of the cascade stack

3. Results and Discussion

3.1 Effect of electrical configuration

The m-stack operated for ~ 3 days (79.8 h) under the first electrical connection while the t-stack for almost 4 days (~ 91.1 h). Figures 2 and 3 show the changes in the monitored voltage V of the quadruples and the stacks and the power output of the m-stack and t-stack, respectively. As can been seen in Figures 2 and 3 the voltage of the bottom four MFCs (m 9-12; t 9-12) in both stacks reversed in polarity and the effect was almost immediate. This result is attributed to substrate imbalance along the MFC cascade. This imbalance caused a disproportional variation in internal resistance among units, which further caused the reversal in polarity [9]. Despite the adverse conditions, the m-stack produced a maximum power of 0.8 mW whilst the t-stack produced a maximum power of 0.52 mW after 62.6 h of operation (Figures 4 and 5).

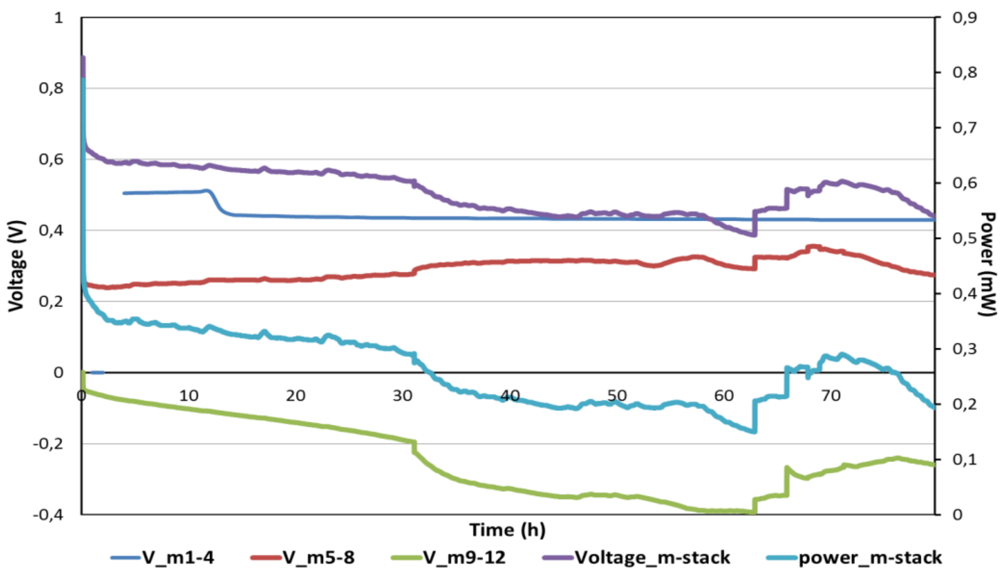

Figure 2. Voltage behaviour of the quadruplets of the m-stack versus time. Right axis: Power behaviour of the stack during time

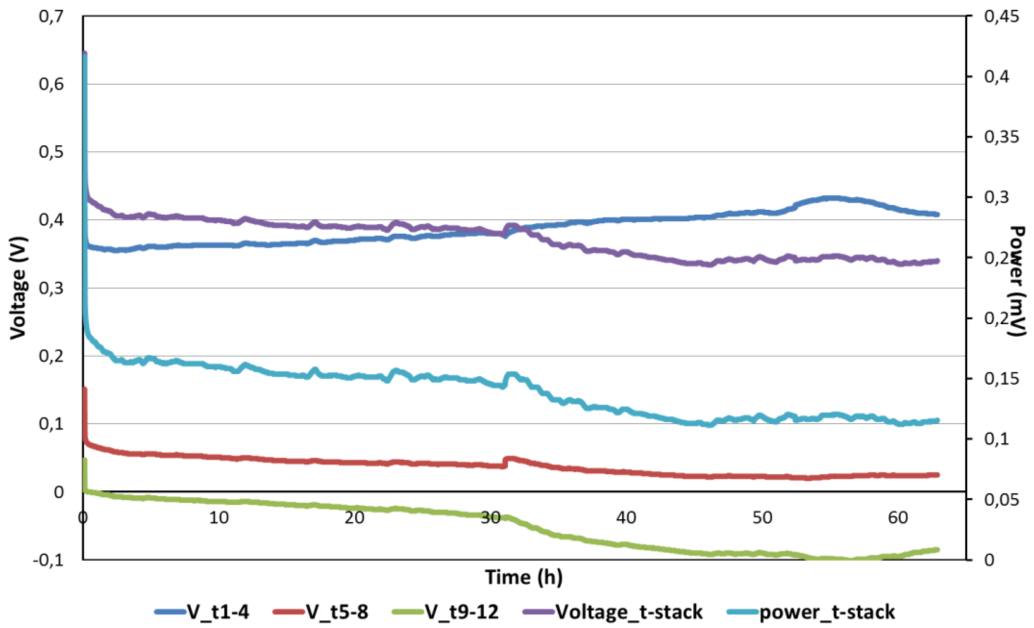

Figure 3. Voltage behaviour of the quadruplets and the t-stack versus time. Right axis: Power behaviour of the stack during time

As can be seen without exception, all MFCs showed a power overshoot behaviour, which is a sign of biofilm immaturity or suboptimal system performance; given the length of time this experiment has been running for, it was evident that there were intrinsic factors negatively affecting the performance.

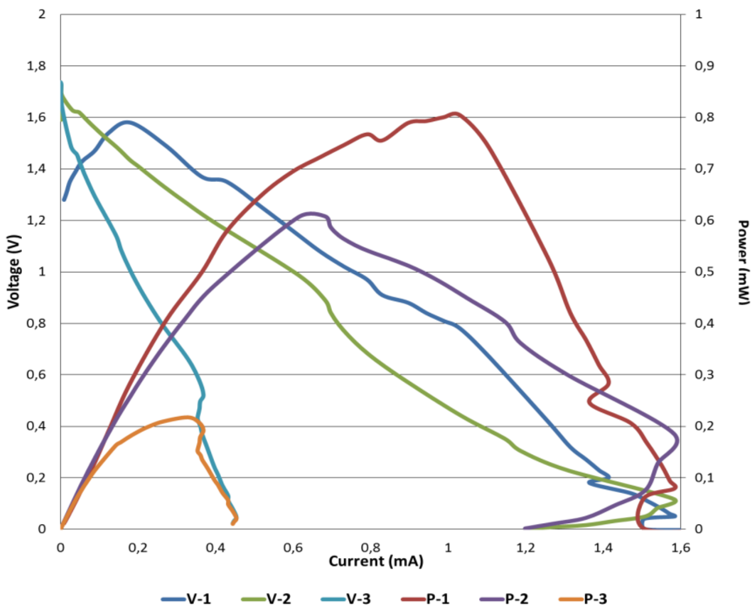

Figure 4. Power and polarisation curves for the m-stack.

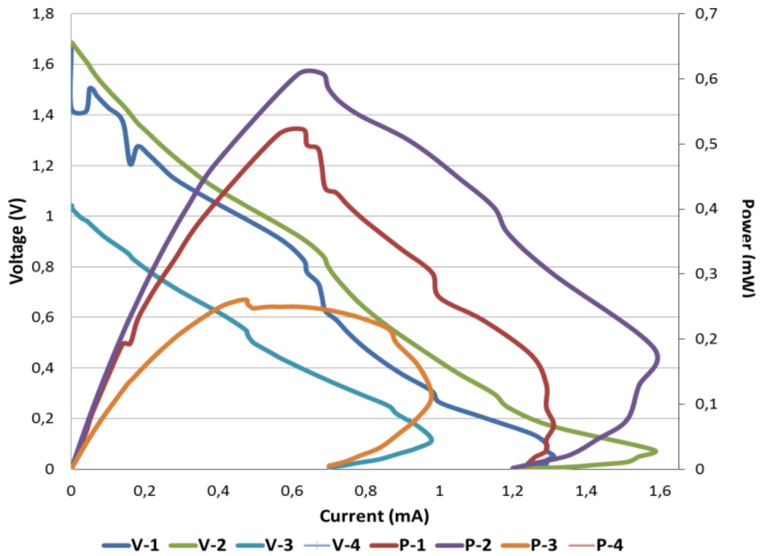

Figure 5. Power and polarisation curves for the t-stack.

In order to overcome this barrier, the electrical configuration was changed to compensate for the sequential treatment in the cascade that would inevitably starve the bottom MFCs. Specifically, MFCs 1, 2, 11, 12; 3, 4, 9, 10 and 5, 6, 7, 8, were connected in parallel, respectively. The external load applied to each stack was 1 kΩ.

The stacks operated for ~ 373.9 h under this electrical configuration. Figures 6 and 7 show the changes in the monitored voltage V of the quadruples and the stacks and the power output of the m-stack and t-stack, respectively. Under this electrical configuration the parallel group formed by MFCs 5, 6, 7, 8 reversed in polarity. The maximum power obtained immediately after the new electrical configuration (t = 0 h) was 0.61 mW for both stacks whereas after 373 h of continuous operation it decreased to 0.26 mW and 0.22 mW for the t-stack and the m-stack, respectively (Figures 4 and 5).

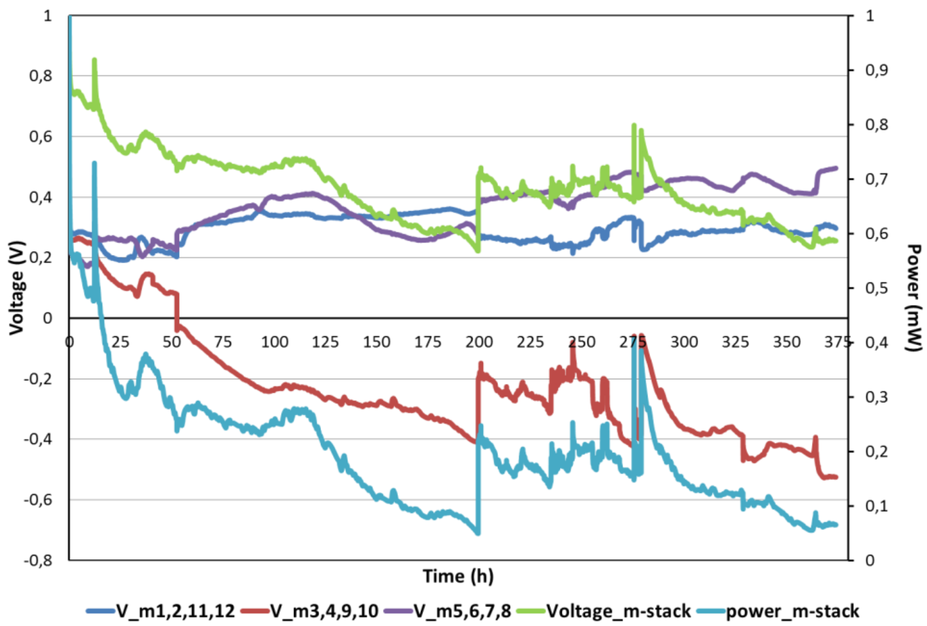

Figure 6. Voltage behaviour of the quadruplets and the m-stack versus time. Right axis: Power behaviour of the m-stack during time

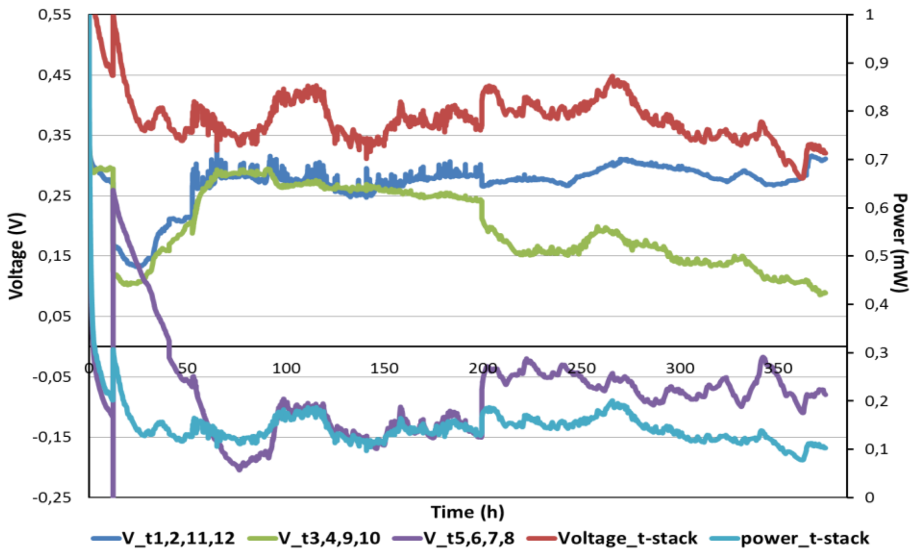

Figure 7. Voltage behaviour of the quadruplets and the terracotta stack versus time. Right axis: Power behaviour of the t-stack during time

3.2 Identification of the factors that caused the power decrease

After approximately 19 days (453.1 h) of continuous operation, the voltage and the power output of both stacks gradually decreased. In order to identify the factors that caused this decrease and to enhance the performance of the stacks, a series of relevant targeted experiments were conducted.

Initially the cathode electrodes of the t-stack were hydrated with deionized water. Following the first hydration of the cathodes, an increase of 37.5 % of the cell voltage of the t-stack (V_{cell}=0.33 V) was observed. However, the voltage of the t-stack gradually decreased (within 60 h) to its previous values. When the second hydration occurred, a similar increase of 43.5% of cell voltage was observed. The cell voltage dropped again to its previous levels after 60 h of continuous operation, despite a third cathode hydration, 18.3 h after the second hydration. Thus, dehydration of cathodes was possibly one of the contributing factors to the decreasing performance of stacks.

Since the level of voltage was not completely recovered to its initial value after the hydration of the cathodes, more tests were performed in order to identify the reasons that contributed to the detriment of the stack's performance. The electrical configuration was shifted to the optimum electrical connection of the cells (all in parallel) and 100 Ω load was applied to each stack. In order to examine if the activity of the biofilm was negatively affected by the operational conditions of the voltage reversal, a second enrichment and adaptation of electrochemically active bacteria in the cells was performed in batch mode. During the second inoculation, 50% of anolyte from a separate stack, running under identical conditions, was added mixed with 50% fresh urine, used as feed, but no performance improvement was observed.

The possibility that the activated layer of the cathode electrode coating was degrading (fouling) over time was also examined. In order to assess this, the cathode electrodes were replaced by new identical ones, approximately 2 weeks after the start of the parallel configuration. Once again, no improvement in performance was observed. The replacement of the cathode electrodes was followed by hydration with deionized water, which improved performance by 22%. However, approximately 16 hours after this, the voltage returned to its previous levels before replacing the cathodes.

As already mentioned, the greatest challenge was fuel availability, which resulted in having to run the MFCs at very low – and possibly suboptimal – flow rates (7.51 ml h^{-1}). This was certainly a contributing factor both to the detriment of performance, but also to the deposition of struvite inside the anode chamber (see Figure 8). In order to examine this, and check whether struvite was blocking the biofilm and preventing fuel from percolating through, the cells were opened and the struvite, which was deposited on the anode electrodes was removed, after approximately 1 month (756.1 h) from the start of the parallel configuration, however there was no significant improvement recorded following this step.

Figure 8. Photo of the anode chamber after 756.1 h of cell operation

The final step of the investigation was to examine if the ceramic material was gradually blocked during time. In order to examine this parameter, the anode and cathode electrodes were replaced by fresh identical ones, whilst keeping the same ceramic materials as the membrane. The cells were inoculated and matured exactly in the same way as before, i.e. in batch mode, under a fixed external load of 2 kΩ for each cell. During inoculation, 50% of activated sewage sludge and 50% of fresh urine was used as feed. These attempts proved unsuccessful, indicating the distinct possibility that the ceramic material itself was blocked by the precipitation of struvite. This was probably due to the sub-optimally low flow rate, which would have promoted slow growing organisms and - as proven - a significant accumulation of struvite. This may not have been the case if the material porosity was different or the material itself was of a different composition.

Although the performance did not improve, following the various attempts of recovery, it is worth noting that through these experiments (final step in particular) it was shown that the ceramic material can actually block, just like any other filter/porous material). This is usually if the movement of particles through the material is not continuous or is occurring at a suboptimum rate of transfer. The MFC operation is based on charged movement of electrons and ions, which if continuous and at optimum rates, then the movement across the membrane will also be continuous with minimum or no 'stuck' molecules. Further work will investigate more thoroughly this parameter and study how power output can directly affect (or not) the blockage of the ceramic separator. In addition, the study of factors contributing to the stable performance of the stacks and improving system performance will also be investigated. In particular, the role of ceramic material parameters (porosity, composition, geometry and size) on stack performance, in addition to different operating conditions (electrical connection, flow rate) are critical parameters being considered for stack improvement and use in practical applications.

Conclusions

A newly designed, ceramic MFC unit was operated as a part two twelve cell cascade stacks using urine as a feedstock. The best performance occurred during the first electrical connection which produced a maximum power of 0.8 mW after 62.6 h of continuous operation. However, the voltage and the power output of m-stack and t-stack gradually decreased. In an attempt to improve performance a series of targeted tests were performed. These experiments indicated that during continuous operation mullite and terracotta were blocked by the struvite precipitation, which was the result of flow rate and electrode conformation.

Acknowledgments

The work has been funded by the Bill & Melinda Gates Foundation, grant no. OPP1094890. The Authors would like to thank Mr. Andrew Stinchcombe for his invaluable technical support.

References

1. Bennetto, H.P.: Electricity generation by microorganisms. Biotechnol. Educ. 1, 163 - 168 (1990)
2. Pant, D., Bogaert, G., Diels, L., Vanbroekhoven, K.: A review of the substrates used in microbial fuel cells (MFCs) for sustainableenergy production. Bioresour. Technol. 101, 1533 – 1543 (2010)
3. Habermann, W., Pommer, E.H.: Biological fuel cells with sulphide storage capacity. Appl. Microbiol. Biot. 35, 128–133 (1991)
4. Lu, N., Zhou, S., Zhuang, L., Zhang, J., Ni, J.: Electricity generation from starch processing wastewater using microbial fuel cell technology. Biochem. Eng. J. 43, 246 – 251(2009)
5. Pandey, P., Shinde, V.N., Deopurkar, R.L., Kale, S.P, Patil, S.A., Pant, D.: Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery. Appl. Energy 168, 706–723 (2016)
6. Winfield, J., Gajda, I., Greenman, J., Ieropoulos, I.: A review into the use of ceramics in microbial fuel cells. Bioresour. Technol.215, 296 – 303 (2016)
7. Santoro, C., Arbizzani, C., Erable, B., Ieropoulos, I.: Microbial fuel cells: From fundamentals to applications. A review. J. Power Sources 356, 225-244 (2017)
8. Min, B., Angelidaki, I.: Innovative microbial fuel cell for electricity production from anaerobic reactors. J. Power Sources 180, 641–647 (2008)
9. Greenman, J., Ieropoulos, I., Melhuish, C.: Microbial fuel cells: Scalability and their use in robotics. In: Eliaz, N., Applications of Electrochemistry and Nanotechnology in Biology and Medicine I. Springer, pp. 239-290. ISBN 978-1-4614-0346-3 Available from: http://eprints.uwe.ac.uk/22251 (2011)
10. Winfield, J., Chambers L.D., Rossiter, J., John Greenman, J., Ieropoulos, I.: Towards disposable microbial fuel cells: Natural rubber glove membranes. Int. J. Hydrogen Energy 39, 21803-21810 (2014)
11. Ieropoulos, I., Greenman, J., Melhuish, C.: Urine utilisation by microbial fuel cells; energy fuel for the future. Phys. Chem. Chem. Phys. 14, 94 – 988 (2012)
12. Merino Jimenez, I., Greenman, J., Ieropoulos, I.: Electricity and catholyte production from ceramic MFCs treating urine. Int. J. Hydrogen Energy 42, 1791-1799 (2017)

13. Gajda, I., Greenman, J., Melhuish, C., Ieropoulos, I.: Simultaneous electricity generation and microbially-assisted electrosynthesis in ceramic MFCs. Bioelectrochemistry 104, 58-64 (2015)