Review

A review into the use of ceramics in microbial fuel cells

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HIGHLIGHTS

- Ceramics an inexpensive option for building microbial fuel cells (MFCs).
- Viable structural material, medium for proton exchange and electrode.
- Maintains healthy environment for electro-active bacteria.
- Benefits energy harvesting.
- Several examples of practical implementation using ceramic MFCs.

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ABSTRACT

Microbial fuel cells (MFCs) offer great promise as a technology that can produce electricity whilst at the same time treat wastewater. Although significant progress has been made in recent years, the requirement for cheaper materials has prevented the technology from wider, out-of-the-lab, implementation. Recently, researchers have started using ceramics with encouraging results, suggesting that this inexpensive material might be the solution for propelling MFC technology towards real world applications. 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. This review discusses progress to date using ceramics as (i) the structural material, (ii) the medium for ion exchange and (iii) the electrode for MFCs.

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1. Introduction

1.1. Historical use of ceramics

Ceramic materials have played an important role in shaping the cultures of ancient civilisations. Historically, distinct communities, thousands of miles apart developed ceramic products using the same basic methods; i.e. the excavation of earthy clay, mixing with water, crafting into shape, drying in the sun before finally baking in fire. The final product was a hard but brittle construct, described as 'earthenware' (Richerson et al., 2005). The earliest evidence of kiln-fired clay art and tools dates back 28,000 years (Vandiver et al., 1989) to the Czech Republic region. Perhaps one of the most stunning examples of ancient ceramic use, is the 5000 year-old Terracotta Army that was built to represent the armies of the first Emperor of China.

A ceramic discovery, which captures the imagination of both archaeologists and electrochemists is that of the Baghdad (or Parthian) battery; an ancient terracotta object believed to be about 2000 years old. This clay structure housing a copper cylinder isolated from an iron rod, resembles a modern day battery when filled with vinegar, or any other electrolyte solution. The Baghdad battery has all the necessary components of an electrochemical device although its purpose is not fully known. It is believed that it might have been used as a power source to electroplate gold or silver or disinfect water (Kraft, 2008).

1.2. Historical use of ceramics in electrochemical technologies

Ceramics are still used to this day for the electrochemical treatment of wastewater, particularly by transforming pollutants into non-toxic materials. This can be performed in a number of ways by using ceramic diaphragms, for example polluted river streams can be treated through electrocoagulation (Li et al., 2011) as well as ultrafiltration (Gringer et al., 2015). Ceramic membranes can be modified to achieve increased selectivity, for cation transfer, enabling treatment through effective electrodialysis (Linkov and Belyakov, 2001), whilst microporous ceramic diaphragms offer stability against oxidising agents, enabling their use in the electrodialytic removal of heavy metal cations (Dzyazko et al., 2007). Ceramic microfiltration membranes can be customised using an array of potential ingredients including alumina, mullite, cordierite, silica, spinel, zirconia and other oxides. These can influence the nature and magnitude of the interactions between the membrane surface and the solution, thus affecting the permeating fluxes of solvent and solute through the membrane pores. They can be used as basic water filters, as ultrafiltration units and for cleaning oily wastewaters (Abbasi et al., 2010).

An alternative use is through the electroosmotic flow, a phenomenon first reported in 1809 by F.F. Reuss who showed that water could be made to flow through a porous clay plug, by the application of an electric field (Reuss, 1809). When an electric field acts on an electrolyte solution, cations move to the cathode and anions move to the anode. Hence, a transfer of momentum between moving ions and surrounding solvent molecules takes place with the flow of liquid through the membrane, leading to an electro-osmotic transport. Electro-osmosis is an effective process of water treatment by removing water-soluble organics from clay-rich soil (Schultz, 1997). It is also an important feature of fuel cell applications, which is something that will be discussed later with respect to ceramic microbial fuel cells.

1.3. The use of ceramics in fuel cells

Ceramic membranes have been increasingly used in a broad range of industries including: biotechnological, pharmaceutical, dairy, food and beverage, as well as the chemical and petrochemical, microelectronics, metal finishing, and power generation (Sondhi et al., 2003); in the latter case, ceramics have been employed in high temperature fuel cells for many years.

The principles of fuel cell operation were first reported by Sir William Grove in 1839 (Minh and Takahashi, 1995) using hydrogen and oxygen as the reactants. Ceramics were first used in fuel cells in 1937 when a ceramic solid-oxide fuel cell (SOFC) was operated (Baur and Preis, 1937). SOFCs employ an all-solid construction comprising 3 ceramic layers; two electrodes, and an electrolyte (which is the medium for proton conduction) in the middle. Ceramic is the material of choice for SOFCs because it is tolerant to the high temperatures required for operation, and in addition it provides a useful electrode material, because both its porosity and permeability can be customised. As will be discussed later, these are attributes, which can also be beneficial for operation in ambient temperatures.

The next section will discuss the emergence of the use of ceramics in microbial fuel cells, which are a form of biorefinery utilising wastewater as a source of renewable energy.

2. Microbial fuel cells

2.1. Introduction to microbial fuel cells

In order to combat the challenge of climate change, renewable energy technologies need to be identified and optimised. Another immediate environmental challenge is pollution via the accumulation of anthropogenic waste. Bio-transformation systems can help tackle these issues, and microbial fuel cells (MFCs) are one such technology that can be particularly advantageous, due to the ability to utilise low grade waste that is too wet to burn. MFCs employ electro-active bacteria, which generate electricity by consuming organic pollutants, as part of their anaerobic metabolism. As will be discussed later, there are additional products and benefits that can be exploited through MFC operation.

For several decades there has been a focus on optimising MFC performance in terms of power production and organic load removal. These efforts have seen a fairly rapid improvement with power generation now several orders of magnitude greater than a few years ago (Li et al., 2011). However, a major consideration that has not received as much attention as possible, until recently, is the employment of inexpensive and sustainable materials for the construction of MFCs. This is imperative for scaling up, not only in terms of the cost benefit, but also because one of the major contributors to the accumulation of toxic waste comes in the form of old electronic components, plastics and batteries (Irimia-Vladu, 2014). Building sustainable energy devices from materials that may themselves contribute to the accumulation of waste build-up, would be a paradox.

Until recently most of the materials, components and configurations used for constructing MFCs originated from other fuel cell technologies such as proton exchange membrane fuel cells. These chemical fuel cells operate in distinctly different conditions to MFCs and environments which would be hazardous for the electro-active bacteria. In order for MFCs to progress from laboratory curiosities to real-life practical implementation, research must move away from using high maintenance chemicals (e.g. potassium permanganate and ferricyanide), expensive catalysts (e.g. platinum) and sub-optimal, costly components such as the polymeric ion exchange membrane (IEM).

Another obstacle that the MFC community has had to overcome, has been the reliance on artificial mediators. Up until the mid-2000s, chemicals such as neutral red, methylene blue and thionine were added into the anode chamber to enable the trans-

portation of electrons from within the bacterial cell to the anode surface (Allen et al., 1993; Ieropoulos et al., 2005). This was assumed to be a prerequisite for operation; however most of these chemicals are now obsolete, following the reports on species capable of naturally excreting shuttles (Habermann and Pommer, 1991) or direct conductance (Bond and Lovly, 2003).

For the same reason, the authors believe that the reliance on unsustainable materials for MFC operation will also soon be a thing of the past. Recent research has started focussing on scaling up MFCs, an advancement, which needs to take into account the cost and availability of materials. This is especially relevant to the research groups focussing on rolling out the technology for developing countries.

The cathode electrode can be limiting for MFC operation, which is why many groups still rely on platinum and other catalysts. However, there has been significant progress in recent years in developing materials comparable to platinum – in the short term – or even preferable to platinum in the long term (Cheng and Wu, 2013). The competitive advantage of these materials, compared to platinum, is the lower cost.

One other component that requires attention is the ion exchange membrane (IEM). MFCs use liquid feedstock in the anode, which in itself can carry charged ions such as protons, and so the IEM is not an essential requirement (Logan, 2008), provided that there is physical or electrochemical separation between the anode and cathode electrodes. One strategy is therefore simply to remove the membrane altogether from the design and

membrane-less MFCs have been described in the literature (Liu and Logan, 2004). Whilst this design reduces the cost of the reactor, it also has the disadvantage of oxygen diffusion towards the anode electrode and the requirement to keep the electrodes a certain distance apart. Furthermore, the chassis of membrane-less reactors still needs to be built from rigid materials and often these are plastic-based. An ideal scenario then, would be an inexpensive material that doubles as both the chassis and the medium for proton exchange. This would also enable electrodes to be in close proximity to each other whilst preventing a high flux of oxygen to the anode. A number of porous materials have been reported including microporous filtration membranes (Zuo et al., 2007), canvas (Zhuang et al., 2009), nylon infused membrane (Hernández-Fernández et al., 2015) and paper (Winfield et al., 2015). Furthermore, there have been some thorough investigations comparing a number of these low cost separators in terms of enhancing power generation and allowing field application (Kondaveeti et al., 2014). Perhaps the most exciting of the porous materials to be used in MFCs is ceramic.

MFCs are operated in less extreme environments than the SOFCs because the mesophilic bacteria thrive in much lower, ambient temperatures. However, the same properties making ceramics preferable for extreme conditions can theoretically make them an ideal material for MFCs. For example, the clay type, the porosity, the wall thickness and the density might all be optimised for a specific target application. In addition, the clay material could be adapted to encourage microbial colonisation.

Table 1
Comparison of ceramic type, MFC configuration and performance.

Ceramic type	Role	Structure	Thickness (mm)	Anode chamber volume	Cathode type	Temp (°C)	Operation time	Feedstock	Max power	Authors
Earthen	IEM	Pot	4	400 mL	Aerated	26–34	38 days	Synthetic (acetate)	26.8 mW/m^2	Behera et al. (2010a)
Earthen	IEM	Pot	4	400 mL	Air	None	70 days	Ricemill wastewater	0.53 W/m^2	Behera et al. (2010b)
Earthen	IEM	Cylinder	5	600 mL	Permanganate	24–26	Not given	Synthetic (sucrose)	480.18 mW/m^2	Jana et al. (2010)
Titanium oxide	Anode	Cylinder	N/A	None	Ferricyanide	None	17 days	Synthetic	1.4 μW/cm^2	Thorne et al. (2011)
Terracotta	IEM	Pot	None given	800 mL	Air	28	14 days	Hay extract	33.13 mW/m^2	Ajayi and Weigele (2012)
Terracotta	IEM	Single chamber	8	6 mL	Air	22 ± 2	6 weeks	Synthetic (TYE)	2.83 W/m^3	Winfield et al. (2013a)
Earthenware	IEM	Single chamber	8	6 mL	Air	22 ± 2	6 weeks	Synthetic (TYE)	3.66 W/m^3	Winfield et al. (2013a)
Earthenware	IEM	Single chamber	4	25 mL	Air	22 ± 2	8 months	Synthetic (TYE)	4.5 W/m^3	Winfield et al. (2013b)
Clayware	IEM	Cylinder	None given	1.3 L	NaClO	None	20 days	Synthetic (acetate)	6.57 W/m^3	Jadhav et al. (2014)
Red soil	IEM	Pot	5	550 mL	Aerated	33–37	22 days	Synthetic (acetate)	51.65 mW m^2	Ghadge et al. (2014)
Black soil	IEM	Pot	5	700 mL	Aerated	33–37	22 days	Synthetic (acetate)	31.2 mW m^2	Ghadge et al. (2014)
Berl saddles	Anode	Two chamber	N/A	100 mL	Ferricyanide	22 ± 2	None	Synthetic (glucose)	130 mW m^2	Hildago et al. (2014)
Clayware	IEM	Pot	4	450 mL	Air	30	75 days	Synthetic (acetate)	4.21 W/m^3	Chatterjee and Ghangrekar (2014)
Clayware	IEM	Pot	8	26 L	Air	None	14 months	Synthetic (sucrose)	0.74 W/m^3	Ghadge et al. (2015)
Geothite	Anode	Cylinder	5	350 mL	Air	27 ± 2	75 days	Synthetic (acetate)	17.1 W/m^3	Jadhav et al. (2015)
Montmorillonite	IEM	Two chamber	4	50 mL	Aerated	30 ± 2	2 months	Synthetic (acetate)	7.55 W/m^3	Ghadge et al. (2015)
Terracotta	IEM	Cylinder	3	200 mL	Air	22	14 days	Wastewater + acetate	286 mW/m^2	Gajda et al. (2015a)
Pyrophyllite	IEM	Cylinder	2	6.4 mL	Air	22	100 days	Urine	6.93 W/m^3	Pasternak et al. (2016)
Earthenware	IEM	Cylinder	3.5	11.4 mL	Air	22	100 days	Urine	6.85 W/m^3	Pasternak et al. (2016)
Mullite	IEM	Cylinder	4.0	Variable	Air	22	13 days	Urine	10 W/m^3	Walter et al. (2016)
Terracotta	IEM	Plates	2.5	Variable	Air	22	16 days	Urine	15 W/m^3	Walter et al. (2016)

Next the history of the use of ceramics in microbial fuel cells will be discussed, with firstly a focus on its dual use as a chassis and as the medium for proton exchange. It should be noted that throughout this review paper there will be made no attempt to systematically compare power densities from the cited papers, due to the differing conditions e.g. temperature, feedstock and pH, materials e.g. electrodes, wires and peripherals, and diverse microbial communities involved, as well as the various methods employed for normalising data. A range of these varying conditions can be observed in Table 1 in the next section. The important consideration is how ceramic compares to conventional membranes in each study (where applicable) with a focus on practical, scalable materials (i.e. air-breathing, non-platinum based cathodes).

2.2. The use of ceramics in MFCs

2.2.1. Proton exchange and chassis

The first demonstration of the use of ceramic materials as part of the MFC was reported in 2003 (Park and Zeikus, 2003). This study incorporated a proton permeable porcelain separator positioned between graphite electrodes. Protons were able to pass through the microporous system utilising distinct metal catalysts at each electrode i.e. Mn^{2+} at the anode and Fe at the cathode. This original research was a relatively short study (20 days) employing non-sustainable mediators, but it demonstrated the potential of ceramics. A similar set up was described a few years later (Seo et al., 2009) using a porcelain membrane which operated stably for a longer period, albeit assisted by the use of a solar cell that was connected to their system.

In 2010, Behera et al. (2010a) employed a 400 mL, off-the-shelf ceramic pot with a clay make-up of 58–68% kaolinite, 15–26% illite, 5–9% smectite. This demonstrated a power output of 16.8 W/m^3 without employing any unsustainable cathodic mediators. Perhaps this study was the first to demonstrate that an inexpensive, ubiquitous material might be able to change the direction and accelerate the progress of MFC research.

Subsequent work from the same group employed ceramic MFCs to show that earthen pots could treat real (rice mill) wastewater whilst producing power comparable to an MFC with IEM (Behera et al., 2010b). This work was promising, however it did report higher power using non-sustainable chemicals, in this case potassium permanganate, as the catholyte. Clearly, a system cannot be realistically considered environmentally viable if even one of its components (e.g. chemical catholyte) is unsustainable. In 2012, an off-the-shelf terracotta flower pot purchased from a garden centre was employed and demonstrated that power could be produced from locally sourced materials including, ceramics, salt and hay as the feedstock (Ajayi and Weigele, 2012). This study demonstrated that all the materials necessary to produce power could be sourced locally in developing countries. Similarly, Chatterjee and Ghangrekar (2014a) used clay ware pots and quite rightly pointed out some of the challenges that come with using ceramics including the deposition of salts on the cathode and the loss of electrolyte through evaporation.

These reports used off-the-shelf artefacts that were not necessarily optimised in design. However another study investigated a different design and mode of operation, where ceramic cylinders were employed and operated in continuous flow (Jana et al., 2010). This design and mode of operation confirmed the findings made with the off-the-shelf pots that ceramic MFCs could be comparable to those with conventional ion exchange membranes (IEM). These early reports emphasised that ceramic could be used as the structural material and as the thoroughfare for proton movement but a vital factor to consider was the importance of wall thickness and/or porosity. This is an essential consideration

because the design, configuration and durability will be decided by the target application and environment.

The importance of ceramic thickness was investigated using off-the-shelf ceramic pots (Behera and Ghangrekar, 2011) where the MFCs with thinner walls outperformed those with thicker ones. This is perhaps not surprising because it is well known in the MFC field that the distance between electrodes (i.e. the path that the protons or charged ions travel) can directly affect the internal resistance (Liu et al., 2005). However, as will be discussed later, it is not only the thickness of the wall but the type of ceramic that can play a role.

The aforementioned studies demonstrated that ceramics could be a viable replacement to conventional ion exchange membranes but it can also provide the electro-active micro-organisms with a more favourable environment for metabolism (Winfield et al., 2013b), particularly when exposed to lower external resistances and therefore higher currents. A method for assessing both power capability and system stability in MFCs is the bi-directional polarisation sweep. MFCs are subjected to a gradual drop in external resistance down to low values before a second sweep immediately increases, step by step, the external resistance back up to open circuit conditions. This technique has demonstrated that MFCs with conventional IEMs behave in an unstable manner and cannot sustain the same level of power generation over the second sweep (Degrenne et al., 2013). For a number of years it has been suggested that the use of IEM membranes can result in pH drop at the biofilm level, a change that can inhibit metabolism and therefore the production of power (Torres et al., 2008).

Under such bi-directional sweep conditions, the conventional IEM-based MFCs suffered a significant drop in power between the first and second polarisation sweeps (Winfield et al., 2013b). Furthermore, a power overshoot phenomenon was observed that often occurs during sub-optimal operation (Winfield et al., 2011) and in this case was attributed to a drop in pH at the higher current densities. In comparison, the MFCs with ceramic membranes showed no power overshoot and the maximum power points of the two curves were almost identical, indicating a stable environment for the microbes, over the experimental period.

The occurrence of pH-splitting is linked to the selectivity of ion exchange membranes for the dominant ionic species (which may not be protons) resulting in an accumulation of protons and hence an acidification of the anode (Harnisch and Schroeder, 2009). Ceramic membranes (and other porous ones for that matter) do not discriminate between ionic species and so protons are freer to migrate to the cathode (with hydroxide ions free to move from the cathode to the anode). This results in more stable conditions for the microorganisms, with the potential for producing higher power densities.

These studies demonstrate the suitability of ceramics, but another important consideration is assessing different types of ceramic and their role in MFCs. Recently, two ceramic types were compared; an iron-rich terracotta and a more porous earthenware (Winfield et al., 2013a). This study demonstrated that the earthenware, with a water absorption of 16.6%, over time produced a higher output than the denser terracotta (9.1% water absorption). The less dense material did demonstrate anolyte loss because the feedstock was not only consumed through operation, but also evaporated through the material. When the wall thicknesses of the same materials were compared, the MFCs with thinner walls (4 mm) outperformed MFCs with thicker walls (18 mm), which concurs with the work of Behera and Ghangrekar, 2011. However, when the different materials were compared against each other, the thickest earthenware MFC (18 mm) outperformed the narrowest terracotta (4 mm). A more comprehensive study recently compared four distinct ceramic types (mullite, earthenware, pyrophyllite and alumina) with the porous earthenware material

demonstrating a faster start-up and higher power output than the other clays (Pasternak et al., 2016). For a broad comparison between the different ceramic types used in MFCs, Table 1 lists a selection of some of the studies carried out to date. These reports demonstrate that whilst wall thickness is important, it is the ceramic material itself which dictates overall performance, and if robustness is a prerequisite then a thicker but more porous material might be beneficial.

Porosity is not the only parameter that can affect MFC performance, when considering different ceramic materials. Ghadge et al. (2014) reported that in two different starting soils (red and black), there are various factors in the composition that can affect performance, such as pH, conductivity, elemental make up and cation exchange capacity.

The factors aiding performance might also be incorporated into the material prior to kilning. For example, ceramic has been customised prior to the firing stage by adding cation exchangers such as montmorillonite and kaolinite (Ghadge and Ghangrekar, 2015a). Montmorillonite was reported as the better filler and improved performance both in terms of power output and coulombic efficiency. This was achieved because the presence of the exchanger improved cation transport ability and helped to reduce substrate crossover and oxygen diffusion.

To date, the cost of the proton exchange membrane has proven an obstacle to the progress of MFCs. Ceramic offers a cheaper solution such that off-the-shelf earthenware can be purchased for as little as £4.14 per meter squared compared to £79.17 per meter squared for conventional cation exchange membranes (Pasternak et al., 2016). This reduces the cost considerably and some researchers estimate that all the materials required to build a single MFC unit can be purchased for less than £1 (Ieropoulos et al., 2013; Behera et al., 2010).

Further work needs to be carried out to determine which clay type is preferable, particularly from the naturally occurring soils. Either way, the work to date has demonstrated that ceramic material is a viable alternative to conventional IEMs. The work discussed thus far has centred on using ceramics as the medium for proton exchange and as the structural material. In addition, ceramic might also be used to construct electrodes.

2.2.2. Ceramic electrodes in MFCs

It could be of great benefit to use ceramics as the material for the electrodes as well as for proton exchange. In this way the manufacturing process could be simplified, as the whole reactor could be constructed and kilned at the same time. A number of reports describe the coating of ceramics with a conductive material. For example, a porous ceramic anode was developed using titanium dioxide coated with a layer of fluorine-doped tin oxide (FTO) to make the material more conductive (Thorne et al., 2011). The algae-based photo-MFCs with the ceramic anodes proved to be 16 times more powerful than the best performing carbon-based electrode. Power curves displayed the overshoot phenomenon, which points to a system underperformance (Winfield et al., 2011); further work would therefore be essential to examine stability and longevity.

More recently, Bowen and Thomas (2015) fabricated a porous electrically conductive MAX-phase ceramic (Ti$_2$ AlC) which demonstrated high surface area and strength. This novel material has the potential for use in MFCs and further work will assess its suitability in terms of operation in the presence of electro-active bacteria. Functional examples were also reported, for example stainless steel anodes modified by adding goethite from iron-ore mining mud (Jadhav et al., 2015). This adaptation improved performance because the Fe ions in the mud facilitated more efficient electron transfer from the bacterial cells. Ferric iron has been used successfully to improve the oxygen reduction reaction at the cathode as well and so an interesting line of work would be to incorporate the same material into the cathode.

Non-conductive ceramic can also be transformed into a viable electrode material. Berl saddles are small ceramic scaffolds used as a support for bacterial growth in bioreactors (Hidalgo et al., 2014). By applying a thin conductive carbon coating over the ceramic saddles, may result in effective anode electrodes for improved power generation. Potassium ferricyanide was used as the catholyte and as discussed in Section 2.1, this is not a sustainable option; therefore it would have been of interest to see how the material fared with oxygen cathodes.

Titanium has also been adopted to transform ceramic based anodes in order to optimise biofilm colonisation and conductivity (Massazza et al., 2015). This was performed using the monoculture *Geobacter sulfurreducens*. It would be interesting to investigate this material's behaviour when mixed cultures and complex feedstocks are used.

The work discussed thus far has focussed on the material, however a number of studies have used ceramic MFCs with a focus on improving reactor design and optimising operational parameters, which will be discussed next.

2.2.3. Optimising ceramic MFCs

As discussed in Section 2.2.2 ceramic material has been demonstrated as a suitable replacement to the more commonly used component materials in terms of power, treatment efficiency and longevity. A number of studies has also looked at trying to improve performance by changing the operating environment, for example by investigating the reactor configuration. In previous studies using cylindrical MFCs, but with conventional membranes, researchers have shown that positioning the cathode internally with an external anode can improve performance. For example, an upflow MFC was developed using proton exchange membranes that incorporated internal cathodes in order to improve the volume to surface area ratio, with scale-up in mind (He et al., 2006). Another example was a 'U-tube' MFC, developed using a glass fibre separator and which demonstrated that this setup could degrade petroleum hydrocarbons (Wang et al., 2012).

Applying this reverse electrode positioning to ceramic cylinders, aquarium 'fish caves' were adapted by placing the cathode
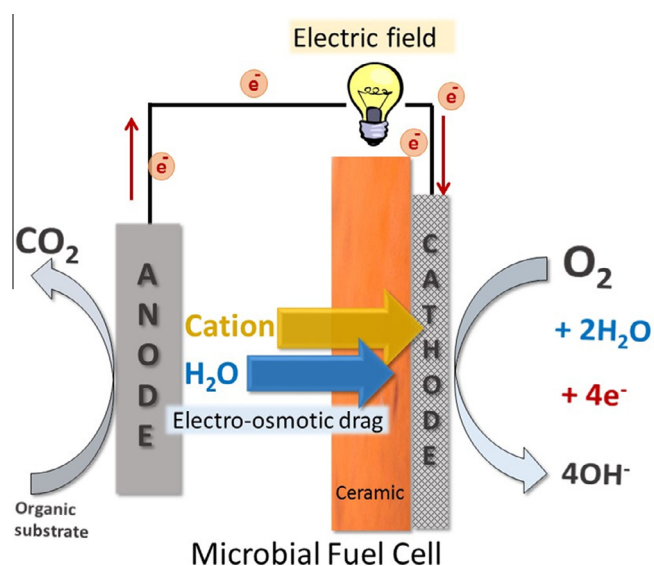

Fig. 1. Schematic highlighting the mechanism of electro-osmotic drag in ceramic microbial fuel cells.

inside the cylinder with the anode wrapped around the outside (Gajda et al., 2015a,b,c).

The internal cathode not only improved power generation but the closed ceramic chamber proved ideal for collecting useful catholyte, which was essential in elucidating the mechanism of proton transfer in ceramic MFCs. As discussed in Section 1.2, electro-osmotic flow occurs in ceramic systems when an electric field is applied. In MFCs, protons are released upon oxidation in the anodic half-cell and move concertedly in the applied electric field at the ceramic–water interface by dragging bulk water. Therefore, proton-selective properties of the material and its configuration in MFCs give the opportunity to extract cations from the anolyte to the cathode, producing liquid catholyte (Gajda et al., 2014) as a result of electro-osmosis (Kim et al., 2009; Gajda et al., 2015d). The electro-osmotic transport of water through the membrane varies with the total charge transfer according to the external load resistance (system power performance) (Kim et al., 2009; Gajda et al., 2014).

An example of this electro-osmotic mechanism is highlighted in Fig. 1 where the movement of the cation will drag with it molecules of water. The specific cation species will vary depending on the anolyte, and the electro-osmotic drag coefficient of the water molecule will be dependent on the cation species i.e. a sodium ion will drag more water molecules to the cathode than a proton. This process suggests that it follows the peroxide pathway of the oxygen reduction reaction (ORR), possibly explaining why the catholyte in ceramic MFCs is highly alkaline. Furthermore, in ceramic based systems electro-osmotic drag enables the efficient extraction of cations and mineralisation (Gajda et al., 2015a,c). In this way ceramic MFCs can be self-sustainable electrolysers, which might be used in the future, for electrochemical wastewater treatment, elemental recycling and as net electricity producers.

In addition, the produced catholyte could also be utilised as a valuable commodity. Recent studies have used sodium hypochlorite, which is a form of bleach, and added it to the cathode chamber of ceramic MFCs (Jadhav et al., 2014a; Ghadge et al., 2015). This bleach aided performance but could be construed as non-sustainable because its addition was a prerequisite. As detailed earlier however, bleach-like substances can be produced de novo in the cathode chamber as the by-product of electro-osmotic drag (Gajda et al., 2015a,c) and could be used for a number of useful purposes, including as flocculants/coagulants (Gajda et al., 2015b).

The cathode is a key element in MFCs particularly in terms of its composition, as has been previously discussed (Wei et al., 2011). Ceramic MFCs have been improved by incorporating ionic liquids into the ceramic and the cathode in some studies (Ortiz-Martínez et al., 2016). With ceramic cylinder MFCs, other aspects have to be taken into consideration – such as the mechanical strength of the material and the physical contact of the electrode to the inside wall of the cylinder. These parameters are now being investigated; for example Santoro et al., 2015a fabricated a cathode material using carbon materials and microporous layer (MPL). They found that a carbon mesh with MPL was most cost effective and efficient for optimising contact with the ceramic surface. Another issue often reported is the fouling of the cathode, and low cost fouling-resistant cathodes have been developed using ceramic MFCs that can help prolong the life of the MFC which is imperative for long term practical applications (Chatterjee and Ghangrekar, 2014b).

As detailed in the introduction, ceramic has been used in a number of treatment and electrochemical processes, and new studies are showing that it can be incorporated in multistage treatment processes for improving efficiency. Ghosh Ray and Ghangrekar (2015) developed a two-stage system using ceramic vessels, where a fermentation stage using fungal species improved performance in the downstream MFC both in terms of power and COD removal. Other researchers have shown that algae, in a pre-treatment stage, can improve fuel quality (Walter et al., 2015a) and Rajesh et al. (2015) demonstrated that a particular acid produced from marine algae helps control methanogenesis, which in turn improves power output in downstream ceramic MFCs. These examples reported on cascading set-ups and therefore for scale-up to be realised, MFCs will most likely need to be configured into stacks, which will be discussed next.

2.2.4. Stacking ceramic MFCs

As discussed in Section 2.2.1 ceramic material can provide a stable environment for the bacterial contingent; additionally its properties can also be utilised, making it suitable for more efficient energy harvesting. This was demonstrated using stacks of ceramic MFCs connected in parallel compared to conventional IEM MFCs (Walter et al., 2014). The ceramic stack displayed a capacitive-like behaviour when subjected to intermittent loading, i.e. switching between open circuit and closed circuit conditions. This resulted in significantly higher power bursts than when operated under continuous load, and it confirmed that ceramic membrane MFCs can provide a more efficient platform for operating energy harvesting and power management systems.

For scaling up MFCs, stacks need to be employed consisting of a number of units connected together electrically. Many studies were conducted using MFCs with conventional membranes, which demonstrated that series–parallel might be the optimal electrical configuration (Ieropoulos et al., 2008). Recently there have been a number of studies employing ceramic MFC stacks. For example a multi-electrode MFC system represented a scaled-up ceramic system using 3 anodes in a large 26L chamber (Ghadge and Ghangrekar, 2015b), which demonstrated that litre-scale ceramic MFCs can operate on a long term basis (14 months). Previous work has demonstrated that a plurality of smaller units improves power density (Ieropoulos et al., 2008) and so the large chamber might be optimised using a more efficient configuration.

Using the smaller sized stacks of cylindrical MFCs with internal anodes, an exciting demonstration of practical implementation was demonstrated where, via energy harvesting, a mobile phone was charged using urine as the feedstock (Ieropoulos et al., 2013). Following on from this, a multi-electrode system incorporating small scale MFCs with internal cathode configuration demonstrated improved efficiency in charging mobile phones (Gates Foundation, 2014). Ongoing work has continued to improve efficiency through the development of innovative designs. For example, novel ceramic-based stacks have been developed using membrane-less systems. Utilising multiple modules, each consisting of stacks of closely packed terracotta plates, the efficient utilisation of urine was demonstrated in the setup whereby the insulation between cathode and anode was driven by the self-stratification of the urine (Walter et al., 2015b).

The combination of ceramic MFCs and urine as fuel has helped push MFC technology closer to deployment in real life applications. For example, prototype urinals have now been trialled on a University campus and at Glastonbury music festival (Ieropoulos et al., 2016). In both cases (field trials), energy generated by the "Pee Power" system was sufficient to operate motion sensors, light LED modules and perform efficient urine treatment. Over 400 inexpensive ceramic MFCs were used in the festival urinal and the success of these trials demonstrates that the deployment of ceramics in MFCs can help push the technology towards real world applications. The use of ceramics in microbial fuel cells is still relatively new and despite the progress made, there still are some challenges to be overcome, as will be discussed next.

3. Challenges and future work

In a relatively short space of time the use of ceramics in MFCs has helped lower the cost while improving performance to the extent that successful field trials have been reported. There still are numerous challenges and questions to be answered through more studies.

One of the problems accompanying the use of ceramic material as separators is the loss of anolyte through evaporation (Ajayi and Weigele, 2012; Winfield et al., 2013a; Chatterjee and Ghangrekar, 2014a). One method of avoiding this is the application of a hydrophobic gas diffusion layer which at least limits the evaporative losses. Synthetic plastics have been employed (Ajayi and Weigele, 2012) but other methods, such as selective glazing could also be used. The hydrophobic layers could be strategically incorporated into designs, forcing the liquid to evaporate from particular points in the fuel cell, therefore aiding the mixing process and managing the accumulation of salts. This could be introduced in the kilning process, by patterning the ceramic with a glazing agent, which would be an interesting line of work incorporating artistic design for optimised reactor configuration.

For the cylindrical ceramic MFC design with internal cathodes, a focus should be on the effect that the build-up of catholyte has on long term performance. It would be interesting to investigate whether this catholyte can be harvested and how best can the operation be customised in order to produce both a desired product along with stable and reliable power output.

Other factors that need consideration are whether or not it would be possible to produce MFCs made up entirely of ceramic material, consisting of ceramic electrodes, separator and chassis. It would be of further interest to see whether these systems could be constructed without any form of metallic wire. Ceramic MFCs have been shown to remove problem elements from wastewater e.g. ammonium (Jadhav et al., 2014b) and future work could look at customising the system to remove specific, target contaminants. This could be carried out using the internal cathode chamber and utilising the cathode potential for removing unwanted pollutants, for example heavy metals.

One of the key considerations in the use of ceramic is how the material performs in the long-term. Reports to date suggest it is more stable over time than conventional membranes but further work is needed to examine whether there might be a decline in performance, perhaps due to biofouling, clogging of pores or contamination. Nevertheless, reports so far are promising, suggesting that it may be a viable long-term option. This would be particularly beneficial for operation in scenarios where minimal hands-on maintenance was available, for example in remote areas, wastewater treatment and in emergency disaster areas.

There are challenges to overcome, but it is the authors' contention that ceramics will one day be the material of choice for MFCs rather than the IEMs. It is envisaged that the use of ceramic as the core MFC structure can only help bring closer an economically viable system scale-up.

4. Conclusions

Ceramic is an ideal material for advancing microbial fuel cells. Research to date has shown that not only is the material comparable with conventional ion exchange membranes, it is also considerably less expensive. It can provide a natural, stable environment for the bacteria, while also enabling a more efficient system for energy harvesting. It is envisaged that in the near future totally ceramic MFC systems may be constructed through low-cost bespoke manufacturing, for a wide range of target applications. Such systems could be fine-tuned in terms of their porosity, chemical make-up and thickness for optimal efficiency in the chosen environment.

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