Current outlook towards feasibility and sustainability of ceramic membranes for scaling-up and practical applications of microbial fuel cells

Dipak A. Jadhav[a], Tasnim Eisa[a,b], Sung-gwan Park[a,b], Arvind K. Mungray[c], Evrim Celik Madenli[d], Abdul-Ghani Olabi[e, h], Mohammad Ali Abdelkareem [f,g,h**], Kyu-Jung Chae[a,b,*]

[a]Department of Environmental Engineering, College of Ocean Science and Engineering, Korea Maritime and Ocean University, 727 Taejong-ro, Yeongdo-gu, Busan 49112, Republic of Korea
[b]Interdisciplinary Major of Ocean Renewable Energy Engineering, Korea Maritime and Ocean University, 727 Taejong-ro, Yeongdo-gu, Busan 49112, Republic of Korea
[c]Department of Chemical Engineering, SV National Institute of Technology Surat, Gujarat 395007, India
[d]Department of Environmental Engineering, Suleyman Demirel University, Isparta, Turkey
[e]Mechanical Engineering and Design, Aston University, UK
[f]Department of Sustainable and Renewable Energy Engineering, University of Sharjah, PO Box 27272, Sharjah, United Arab Emirates
[g]Center of Advanced Materials Research, Research Institute of Science and Engineering, University of Sharjah, P.O. Box 27272, Sharjah, United Arab Emirates
[h]Chemical Engineering Department, Faculty of Engineering, Minia University, Minia, Egypt

*Corresponding author's Email: ckjdream@kmou.ac.kr (Prof. K. J. Chae)

**Co-corresponding author's Email: mabdulkareem@sharjah.ac.ae (M. A. Abdelkareem)

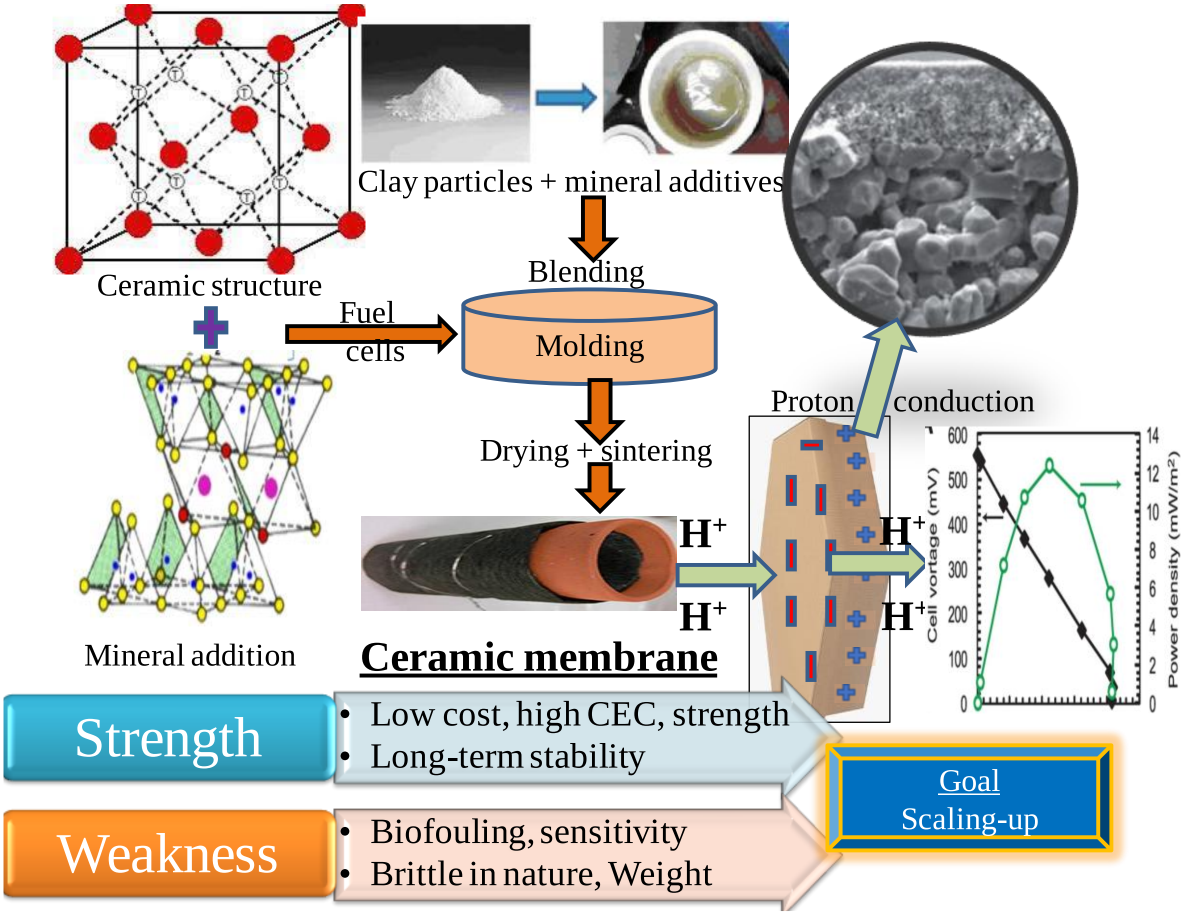
Abstract

Membrane cost, long-term stability, and sustainability are major concerns for the selection of membrane in microbial fuel cell (MFC) towards scaling-up applications. Recently, efforts have been taken for the improvement of the reactor architectural design and the exploration of ceramic membrane materials aiming to achieve techno-economical sustainability and efficiency. Since the last decade, ceramics have come forward as a low-cost separator, electrodes, and chassis material for MFC applications. Introduction of cation exchange minerals to ceramic membrane promotes the high proton transfer with improving the membrane characteristics. High cationic transfer, proton exchange rate, stability against thermo-chemical conditions, structural strength to withstand high hydraulic load, and long-term stability with easy biofouling mitigation support utilization of such membrane for scaling-up use. Successful field trials of Pee-power MFC, stacked urinal MFC, bioelectric toilet, and others showed the feasibility of ceramic membrane for practical applications. Present review emphasizedthe membrane characteristics, substantial effect of mineral additives, scaling-up applications, recent development, and perspectives towards practical utility of MFCs having ceramic membrane.

Keywords:

Ceramic membrane; Long-term stability; Membrane characteristics; Microbial fuel cells; Scaling-up applications; Techno-economic feasibility

Graphical abstract



Research highlights

- Ceramic membrane as a low-cost alternative to costly polymeric membranes in fuel cell
- Ceramic has wide scope as membrane, electrodes & chassis for industrial use of MFC
- Long-term stability, high CEC & performance makes ceramic suitable for scaling-up
- Cation mineral addition in membrane promotes proton transfer & membrane properties
- Successful scaling-up attempts are positive indicators towards commercialization of MFC

List of abbreviations

BES - Bioelectrochemical system,

BOD – Biological oxygen demand,

CE – Coulombic efficiency,

CEC - Cation exchange capacity,

COD – Chemical oxygen demand,

DC – Direct current,

LED – Light emission diode,

MFC – Microbial fuel cell,

MMT – Montmorillonite,

ORR – Oxygen reduction reaction,

SS – Stainless steel

1. Introduction

Current crisis of energy and water, as well as the issue of energy-intensive wastewater treatment, leads to finding out alternative means of renewable energy including bioenergy via bioelectrochemical technologies through water-energy nexus (Sayed et al., 2021). Advanced bioelectrochemical system (BES) employ bacteria for anaerobic oxidation of organic matter and capture energy stored in the wastewater (Kim et al., 2008). Microbial fuel cell (MFC) is one of the variations of BES where chemical energy of wastewater is trapped in electrical output through a series of electrochemical redox reactions with the help of microbial metabolism (Chae et al., 2009; Sabin et al., 2022). However, the performance of MFC is dependent on design aspects, electrode-membrane characteristics, operating conditions, substrate, and inoculum properties (Gunaseelan et al., 2021; Yang et al., 2016). The background genesis research into this novel innovative concept was introduced by Potter M.C. (1911) and further developed from lab-scale bench models towards scaling-up applications.

Over the past 110 years, most of the research on MFC has been executed at laboratory scale reactors and limited attempts towards scaling-up applications (Janicek et al., 2014). Moreover, scaling-up of MFC is restricted by several techno-economical, electrochemical, microbiological, engineering design, and other constraints (Jadhav et al., 2022). Most MFC variations involved anode and cathode electrodes, separated by membrane/separator along with a transformation in the design architecture. Additionally, each design architecture modification has its own specificity and applicability in favor of ease in operation and maintenance (Mathuriya et al., 2018). The major difference in these variations is with or without a physical separator between the anodic and cathodic chambers, and it affects overall wastewater treatment and energy harvesting in MFC. However, membraneless MFC encountered high resistance, substrate crossover, ion/oxygen diffusion, and low power output than MFC with membranes and hence less recommended for field use (Rudra et al., 2018).

Membrane being an important part of any BES and plays a crucial role in ion transfer from anodic to cathodic chamber (Jana et al., 2010). Membranes should hinder mass transfer between chambers; membrane performance depends on their physical and chemical properties as well as cation exchange capacity (CEC) (Yang et al., 2021). In MFC design, Nafion, Ultrex, and other polymeric membranes are mainly used due to their high conductivity and ion exchange capability, but they have a high cost (Logan, 2006). Generally, membrane accounts individually about 40-50% of the total cost required for MFC design (Aiken et al., 2019), and hence researchers are looking for alternatives to costly membranes such as porous membranes, separators, hybrid membranes, and more. Additionally, the chassis of anodic/cathodic chambers also need to be built using costly polymeric materials. Out of available low-cost alternatives, researchers are working on finding out suitable and economic separators for biological fuel cellthat can be replicated in practical use.

Recently, ceramic membrane/separator was found to be one of the economical and feasible solutions for scaling-up and long-term operation of MFC. It offers high structural strength, withstands hydraulic pressure, high stability in operation, ease of availability, low-cost of fabrication, etc., as compared to other polymeric membranes. Current publication database showed a rapid increase in research interest based on ceramic membrane applications in MFC within the scientific community since the past decade (Scopus, 2022) (**Fig. 1**). Apart from limited scaling-up attempts in this direction, more than 60% of such studies have been implemented ceramic membrane for up-scaling applications, and they showed feasibility for practical execution (Jadhav et al., 2021). Present review article discusses the applicability of ceramic separators in MFC and their characteristics affecting the performance. Also, it focuses on the suitability of ceramic membrane for up-scaling applications of MFC, which is attracting the attention of researchers as an exciting new discipline in the nexus of microbiology and electrochemistry.

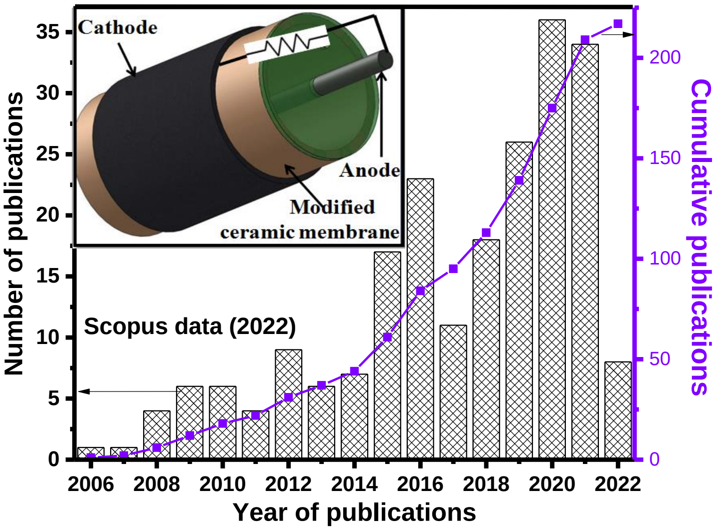
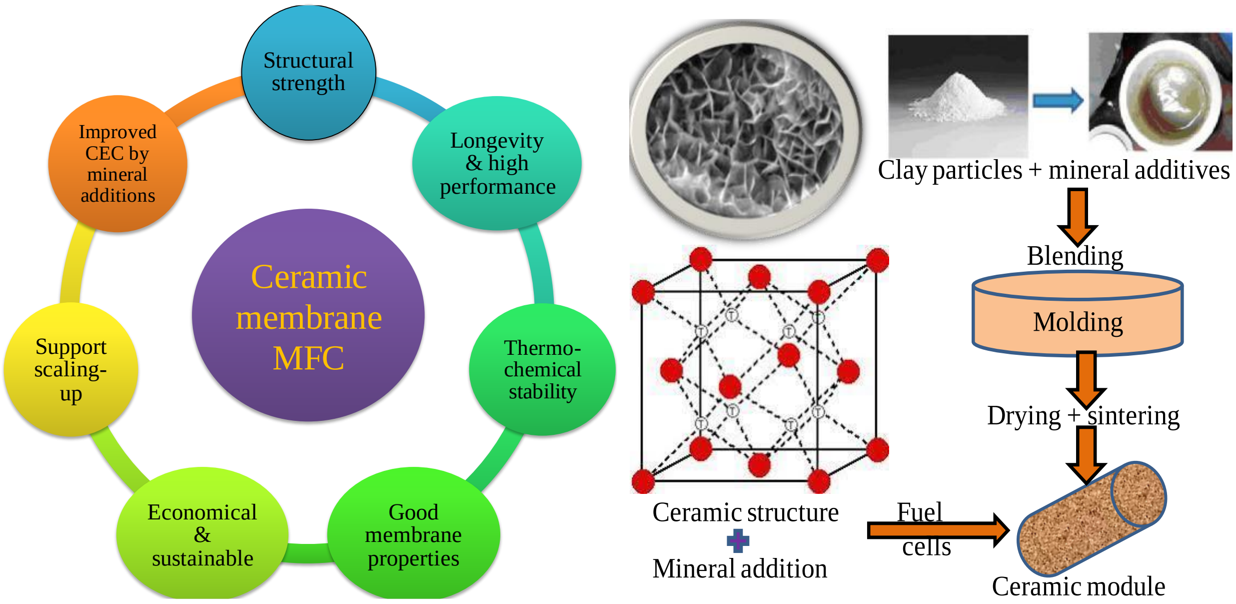


Figure 1: Number of publications on ceramic membrane MFC based on Scopus data with keyword search ‘microbial fuel cell’ and ‘ceramic’ (Scopus, 2022)

2. Applications of ceramic membranes

Ceramic membranes are generally adopted in the water treatment systems for filtration by eliminating the water impurities. Due to high mechanical strength and thermo-chemical stability, these materials are used over costly polymeric membranes (**Fig. 2**). Ceramic microfiltration membranes are commonly being adopted in the drinking water and wastewater treatment industries. Particularly in fuel cells, protonic ceramic and solid oxide fuel cells proposed use of ceramic membrane for ion conductions through membrane (Iwahara et al., 1983), and thus, it started being utilized in chemical fuel cells and later in biological fuel cells in the early 21st century. Such membranes offer several advantages, including separation of electrolytes physically, long life and durability, eco-friendly and ease-in-fabrication, can withstand variation in operational conditions and shock loads (**Fig. 2a**), and many more (Hakami et al., 2020).



(a) (b)

Figure 2: (a) Characteristic features and (b) fabrication of ceramic membrane used in MFC

The potential of ceramic chips for electrochemical sensors has also been reported for the detection of drug concentration in pharmaceutical formulations and the medical field (Takeda et al., 2020). It can be found effective in electrochemical reactors and fuel cells for transforming organic contaminants into useful products as well as for hydrogen separation (Guan, 1998; Jadhav and Chendake, 2019). Ceramic membranes are generally asymmetric in nature and covered with several layers in order to decrease the porosity. It can even mold in any particular shape, such as cylindrical, circular, pot shaped, tubular, and modular, so can be utilized in a wide variety of applications depending on the fabrication process (**Fig. 2b**). It can withstand high temperature during fabrication, high chemical fluctuations, extreme pH conditions, high hydraulic pressure and hence can be recommended for industrial applications. Also, cleaning such membranes is easy, and biofouling can be mitigated using normal chemical spray/cleaning.

2.1 Ceramic membranes for MFC

As stated earlier, typical MFCs consist of anodic and cathodic chambers separated by cation exchange membrane (polymeric/ceramic) (**Fig. 3a**). It provides a flexible platform for electrochemical redox reactions through adopting bacterial metabolism for degradation of organic matter present in wastewater and simultaneous electricity generation (Jadhav et al., 2015). Key driving forces for these electrochemical reactions are pH gradient profile, concentration gradient, and electromotive force via voltage difference, which are facilitated by effective functioning of membranes (Al-Sahari et al., 2022). Main purpose of the membrane is to allow proton ion conduction from anodic to cathodic chamber internally with electrostatic gradient (Santoro et al., 2017).

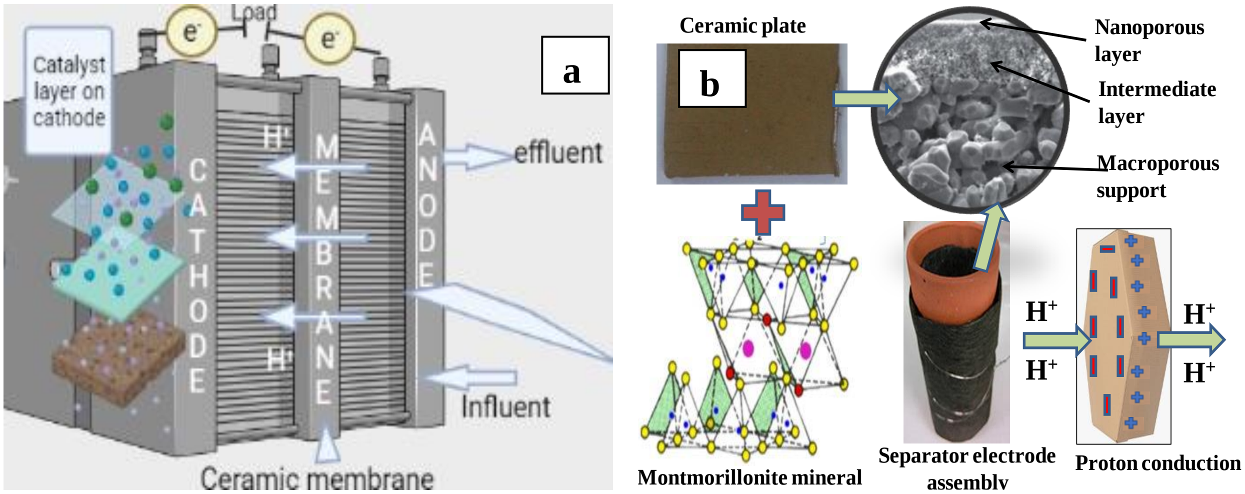


Figure 3: (a) Schematic diagram of MFC with ceramic membrane; (b) Structure and proton conduction in membrane

In practice, the ion transport mechanism through the membrane depends upon the crystalline structure of minerals present in it and electrolytes in contact (Carroll, 1959). The ionic transfer through ceramics is primarily governed by the clay composition and type of clay soil used for fabrication. Ion transport is driven by charge balance during chemical reactions between membrane surface and ions present in electrolyte solution (**Fig. 3b**). In case of ceramic membrane, clay consists of various oxides such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), aluminum sulfate ($Al_2(SO_4)_3$), aluminum silicate (Al_2SiO_5), and many more ionic groups (Banerjee et al., 2022). Negative excess charges available on mineral surface attract the cationic species from anolyte **(Fig. 3b)** in order to neutralize the charges (Shainberg and Levy, 2005). High anionic charges present due to the existence of free hydroxyl (-OH) ion, silicate, aluminate, etc., in these minerals allowed adhesion of loosely bound cations through intermolecular hopping of protons (Das et al., 2020). In case of MFC, the rate of proton transfer is influenced by bonding of cationic species to the mineral surface as well as the number of exchangeable cationic sites available for ion transfer (Carroll, 1959). Usually, demand for proton consumption for cathodic reduction reactions is on a higher side as compared to the supply of proton transfer through a ceramic membrane (Ghadge et al., 2014). Hence, CEC or charge density of membrane needs to improve with membrane modification, spiking of cation exchangers, and using different soil media for fabrication in order to achieve high performance with avoiding pH imbalance conditions. Apart from this, porous structure of membrane may cause substrate mass or oxygen crossover through the chamber, and hence modification in ceramics is desired for better output. The addition of cation exchangers or mineral fillers improves the microstructure of the membrane matrix and decreases the porosity, which is encountered in high energy output in MFC during wastewater treatment (Jain et al., 2020).

3 Influence of ceramic properties on performance of MFC

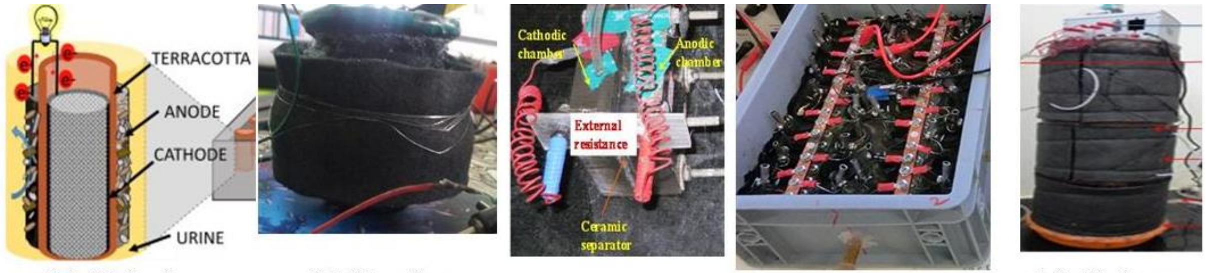
Ceramic membrane and its properties contribute strongly to the mass transport and internal resistance as well as limit the performance of MFC (Bagchi and Behera, 2022). Natural clay material derived from red soil used for making ceramic separators contained Na_2O - 3.95%, MgO - 0.654%, Al_2O_3 - 26.3%, SiO_2 - 57.5%, P_2O_5 - 1.13%, K_2O - 1.78%, SO_3 - 0.258%, CaO - 0.791%, Fe_2O_3 - 4.75%, Ti - 0.658% (Ghadge and Ghangrekar, 2015; Bose et al., 2018). Apart from chemical composition of clay, membrane characteristics such as wall thickness, size, and type of membrane, porosity, water holding capacity, design variations affect ion transfer through membrane along with overall performance and is of concern (Behera, 2012) (**Table 1**).

(a) Wall thickness

Thickness of the ceramic wall plays a significant role in proton conduction as well as maintaining the electrode spacing. Performance of cylindrical MFC decreased with an increase in ceramic wall thickness from 2.5 to 10 mm, reaching up to 2.1 mW at 2.5 mm thickness (Jimenez et al., 2017). The wall thickness affects membrane characteristics and resistance, oxygen reduction reaction, proton exchange as well as catholyte production rate in MFC. An increase in wall thickness from 3 to 8.5 mm resulted in a reduction in Coulombic recovery from 7.7 to 6.1%, and 3 mm thin membrane performed better in terms of mass and oxygen transfer over the thicker membrane in MFC (Behera and Ghangrekar, 2011). Wall thickness also supports for maintaining less electrode spacing and hence can contribute to higher proton flux and transport. MFC with unglazed ceramic separator with 9 mm thickness achieved Coulombic efficiency (CE) of 68% over that of 3 mm membrane (58%) due to smaller Ohmic and diffusion resistance and comparable with Nafion membrane (Khalili et al., 2017).

(b) Design characteristics

Several researchers have implemented different design variations of ceramic/earthen membrane such as tubular, cylindrical, plate-type, cup-shaped, chassis-type, and more to make a compact design of MFC for ease in operation (Pasternak et al., 2016). Due to flexibility in molding, ceramic membranes can be fabricated in various shapes depending upon applications in MFC, as shown in Figure 4. For small and portable applications, earthen pot and handy designs are preferred (Sharma et al., 2014), whereas plate or tubular (modular) structures are useful in the stacked/scalable architecture of fuel cells (Gajda et al., 2020). MFCs using the modified composition of the fine fire clay obtained higher power generation than the unmodified ceramics due to increase in water absorption capacity and ionic conductivity (Merino-Jimenez et al., 2019). Previously, Winfield et al. (2013) reported that the porous nature earthenware membrane having water absorption of 16.6% generated a higher energy recovery than the denser iron-rich terracotta (9.1% water absorption). During performance comparison of MFC with different membrane dimensions, ceramic cylinder with bigger membrane size (diameter 18 mm × height 18 mm; P- 40 μW) performed poor over smaller membrane size (diameter 30 mm × height 11.5 mm, P- 100 μW) (Tremouli et al., 2021). Such design characteristics determine the rate of proton conduction, and membrane shape varies according to the design of MFC.



(a) Tubular design (b) Earthen pot (c)Box design (d) MFC stack (e) Column design

(f) Clay plate (g) Pipe flow Single chambered Handy MFC

Figure 4: Various designs used in MFC with a ceramic membrane (adopted from Gajda et al., 2020; Jadhav and Ghangrekar, 2020; Ghadge and Ghangrekar, 2015a,b; Jadhav, 2017; Cheraghipoor et al., 2021; Jain et al.,2020; Sharma et al., 2015)

(c) Porosity

Porosity of the soil represents the hydraulic conductivity which depends upon the pore throat radii of clay materials. Being porous in nature, porosity, and pore size distribution affects the performance of ceramic membranes (Santoro et al., 2018). Earlier, Daud et al. (2018) reported that the comparative performance of ceramic membrane MFC with porosity of 13.80% (2.3 W/m^2) performed the highest compared to that of 11.00% (1.9 W/m^2) and 11.05% (2 W/m^2). While making optimization of internal structure, Salar-Garcia and Ieropoulos (2020) reported that pore size of clay membrane increases with increase in kilning temperature up to 1030 °C and decreases further. However, low bulk resistance with high current output was achieved in MFC having medium pore size distribution in membrane structure. However, ramp time has no significant effect on membrane characteristics and MFC performance. In contrast, high porosity can cause substrate crossover from anodic to cathodic chamber and may cease the availability of substrate for anodic oxidation as well as use of electrons for non-electrogenic reactions (You et al., 2019). Hence, different spacer pores play a main role in the proton transfer and controlling the porosity. Therefore, inclusion of filler mineral materials during the membrane fabrication process is a favorable strategy to maintain the optimum porous structure of membrane matrix.

(d) Membrane pretreatment

The proton conduction and membrane properties vary drastically when pretreated with alkali, acid, or neutral water solution. The oxygen diffusion coefficient was on the lower side with a decrease in pore space for alkali pretreated membrane (montmorillonite-20%) compared to Nafion membrane and hence resulted in higher power recovery (Das et al., 2020). The alkali-treated membrane in MFC demonstrated a 4-fold higher proton mass transfer coefficient and proton conductivity along with the least oxygen diffusion coefficient as compared to neutral water treated membrane. Similarly, addition of lime leads to change in pH of clay used for fabrication of membrane and thus improves the effective CEC due to ability of soil to develop negative charges, as reported by Mendonca et al. (2006).

(e) Clay composition

Clay mineral composition and soil properties used for fabrication of membrane contribute to effective and efficient cationic ion transfer. Unglazed wall ceramic contains a high amount of silica oxide and calcium oxide over floor ceramic, along with higher porosity. Hence, it resulted in higher current recovery in MFC with ceramic wall (I - 1.58 A/m^2; R$_{int}$ - 91.7 Ω) as compared to floor ceramic MFC (I - 0.3 A/m^2; R$_{int}$ - 653 Ω) for the same wall thickness of 6 mm (Khalili et al., 2017). Similarly, You et al. (2019) tested brown, red, white, and spotty clay ceramic membrane in MFC. Brown ceramic has a dense matrix with lower porosity and larger pores in comparison to the red and white ceramics, and hence it can be suitable for long-term operation of MFC. In addition, composite spotty mixed ceramic is a novel means of improving the characteristics of ceramic matrix, as well as fine-tuning porosity/pore size distribution (You et al., 2019). Addition of certain mineral fillers (e.g., silica oxide) in the membrane structure resulted in improvement in performance of MFC. Effect of increasing the proportion of SiO_2

from 0 to 30% showed a reduction in melting point of ceramic composite and increase in power density from 0.48 to 6.9 W/m^3 in MFC having ceramic membrane made of Kalporgan's soil (Cheraghipoor et al., 2021; 2019). Barium-cerium-gadolinium oxides doped with 5% cobalt was found to be useful for reduction of pore space and decrease in absolute biofouling as in case of ceramic composite based yeast MFC (Frattini et al., 2020). Thus, presence of ionic species on membrane surface impacts on proton hopping mechanism and fastens the rate of proton transfer through ceramic membrane.

Table 1: Performance comparison of MFCs with different ceramic membrane (CM) conditions

MFC configuration	Operating conditions	Treatment efficiency	Power output	Major findings	Reference
Chitosan-montmorillonite nano-composite film coated on separator	Carbon cloth electrodes	COD- 88.5%; BOD- 87.28%	119.58 ± 19.16 mW/m^2; CE- 48.6%	Layer coating of polymer reduced the membrane resistance	Yousefi et al. (2018)
Activated carbon blended with natural clay	Carbon felt electrodes	COD- 81%	3.7 W/m^3	Activated carbon derived from coconut shell + clay can be cost effective solution	Neethu et al. (2019)
MFC with wall thickness	Carbon material	-	24.32 mW/m^2	Thinner membrane perform better than the thicker membrane	Behera & Ghangrekar (2011)
Algal MFC for dairy effluent treatment	Graphite felt	COD- 72%	0.38 W/m^3	Algal biocathode for biomass recovery	Mehrotra et al. (2021)
Alkali pretreated CM	Carbon felt	COD- 88%	83.5 mW/m^2	Alkali pretreated CM perform better than acid and neutral pretreatment	Das et al. (2020)
Constructed wetland CM- MFC	Carbon felt	COD- 86.2%	0.26 W/m^3	CW-MFC performed better than that without a ceramic separator	Khuman et al. (2020)
Stacked ceramic membrane MFC	carbon veil anodes; SS air cathode	-	10.6 W/m^3	Increase in conductivity of electrolyte enhances power output	Santoro et al. (2018)
CM-MFC and CEM-MFC	PBS catholyte	-	1.79 W/m^2	CM performed better than CEM in terms of ionic concentration	Daud et al. (2018)
Biotic and abiotic cathode in MFC	SS cathode	-	70.48 W/m^3	Thinner cathodic biofilm support ORR in cathodic side	Behera et al. (2010)
Earthen plate MFC	Graphite plates	COD -	145 mW/m^2	Ceramics as a low-cost option	Jana et al.

	48%	(2018)

4. Amelioration in the CEC of membrane

Application of ceramic membrane in MFC has been promoted in the last two decades and demonstrated its utility through different laboratory models to pilot-scale studies. CEC of a membrane can be expressed as the capability of clay to hold and exchange positively charged cations by means of electrostatic force. Thus, cation exchange rate through the ceramic membrane is controlled by exchangeable cations and available cationic sites. The main reason for the decrease of proton transfer through a ceramic membrane made by naturally available clay is the presence of inadequate exchangeable cations (Jain et al., 2020). However, alteration in the membrane through spiking of cation exchangers using a variety of soils, is desired in order to improve the CEC and ion flux through membrane structure (Ramirez-Nava et al., 2021). Earlier Pasternak et al. (2015; 2016) studied four different ceramic materials viz. pyrophyllite, earthenware, mullite, and alumina and achieved a power output of 6.93, 6.85, 4.98, and 2.6 W/m^3, respectively during urine treatment. With higher SiO_2 content in pyrophyllite and earthenware promoted cation transport through the ceramic membrane than other variations. Additionally, single chambered terracotta based biobattery is capable to harvest 1 mW power with CE of 21% (Ajayi and Weigele, 2012; Rago et al., 2018). On a similar basis, Ghadge et al. (2014) reported higher power output in earthen pot MFC fabricated with red soil than black soil. Availability of more cation exchange sites and exchangeable cations in red soil resulted in high proton exchange capacity in MFC with red soil over black soil.

On the other hand, membrane modified with certain mineral cation exchangers such as montmorillonite, bentonite, kaolinite, zirconia, goethite, vermiculite, etc., showed high power performance in MFC, and comparative performance evaluation is represented in Table 2. The first attempt of using a porcelain septum separator (with kaolin) and graphite electrodes for single chambered fuel cells was studied by Park and Zeikus (2003). This study supported a new outlook for using low-cost separators for fuel cells and promoted the use of sludge inoculum over *E. Coli* for rapid electron transfer. To boost the CEC of ceramic membrane, Ghadge and Ghangrekar (2015) studied the effect of blending membrane with minerals such as montmorillonite and kaolinite. Results suggested that spiking of cation exchanger promoted the proton exchange by decreasing the porosity with lowering oxygen mass transfer coefficient.

Membrane with montmorillonite-20% performed better than kaolinite-20% in MFC due to availability of higher exchangeable cationic site. Additionally, kaolinite-20% has a higher energy harvesting rate than montmorillonite-10% with similar specific conductivity and diffusion coefficients (Ghadge and Ghangrekar, 2015). Similar application of montmorillonite and kaolinite in membrane generated current of 0.43 and 0.37 mA, respectively, along with significant oxidation of organic matter in sediment BES (Midyurova et al., 2017). Mineral vermiculite was reported to have a high charge density and CEC than montmorillonite (Shainberg and Levy, 2005). Hence, montmorillonite and vermiculite blend (10% each) were found to be effective for promoting the CEC of ceramic membrane (Jain et al., 2020). In this study, proton transfer rate in ceramic membrane with vermiculite, montmorillonite (spray coated with Nafion solution) was 5.2×10^{-3} and 8.8×10^{-3} cm/s, comparatively higher than that with montmorillonite alone and control ceramic membrane. Also, nano-milling of minerals for 5 hr accelerated ion exchange capacity and water uptake in such MFCs. Such promising results promote the applicability of coating of polymer/nano-particles for ceramic membranes modified with cation exchangers for fuel cell use.

Comparative performance analyses conducted for MFCs with pure earthenware (GM) and montmorillonite from bentonite-Ca as a composite modified earthen membrane (GT) showed mixing of GT promotes trivalent (Al^{3+}, Fe^{3+}) and bivalent cations (Mg^{2+}) and hence, enhanced overall proton mobility (Sudarlin et al., 2020). Addition of bentonite in earthenware decreases the overall pore volume and hence promotes higher current generation while treating tempe liquid wastewater. Hydrous aluminum silicates rich fuller clay can be a promising strategy for improving the cationic transfer when mixed with ceramic separator. Recently, Gunaseelan et al. (2022) optimized the content of fuller clay from 10, 15, and 20% in clay separator, and results showed that high CEC of 43 meq/100 g and small pore size help to reduce the void spaces in membrane matrix as observed in case of 15% fuller clay content. However, an increase in the content further to 20% resulted in agglomeration followed by improper pores, surface roughness, formation of clusters, which has a negative impact on proton conductivity and ion transfer in ceramic biophotovoltaics MFC (Gunaseelan et al., 2022). On a similar trend, other minerals viz. smectite, goethite, vermiculite, mullite, illite, gibbsite, diaspore, alumina, mica, boehmite, zirconia, and many more possess high CEC due to the presence of high anionic charges present with existence of free hydroxyl ion, aluminate, silicate (Das et al., 2020; Ghadge, 2016). These mineral compositions and synergistic combinations can be tested further in MFC to widen the scope of improvement in terms of pollutant removal and resource recovery.

Dominance of high silica content can be a feasible option for improving the hydration properties and proton mobility through a ceramic membrane and tested with varying silica content from 0 to40% in MFC (Raychaudhuri et al., 2021). Such silica/alumina oxides form silicon-oxygen tetrahedron and aluminum octahedron structures and thus provide negatively charged centers, which can help to retain and exchange cations. The maximum power recovery of 791.72 mW/m^3 and organic matter removal of 76.2% was obtained in MFC with 30% silica modified membrane, comparatively higher than unmodified membrane (**Table 2**). Addition of such silica oxides transforms the micelle radius and size of the channel connection as well as helps to enhance the water uptake capacity of the membrane, which could facilitate a pathway for structural proton transport through the Grotthuss mechanism (Raychaudhuri et al., 2021). In another study, cylindrical MFCs with terracotta and mullite membranes showed an effective urine treatment and power generation of 40-80 µW and 20-40 µW, respectively (Tremouli et al., 2021). Application of bentonite and fly ash to transport ionic charge through intermolecular spaces in ceramic composite membrane was demonstrated in plant MFC by Sarma and Mohanty (2022). Increase in bentonite proportion in composite from 10 to 25% promoted the proton mass transfer coefficient from 6.2×10^{-5} to 8×10^{-5} cm/s with an increase in hydrophilicity and water absorption characteristics.

Red soil or mining mud contains huge amounts of iron oxides which can be useful for enhancing the micro-structural features, including pore size distribution in membranes (Jadhav et al., 2015). The amount of Fe_2O_3 used in the membrane resulted in upgradation of membrane properties via enriching the number of nano-pores in the structure and catalytic properties to degrade pollutants in ceramic based MFC. The increase of iron content from 1.06 to 5.75% achieved a 10-fold boost in power output from 31 µW to 0.28 mW (Salar-García et al., 2021). Energy generation from MFCs improved as the iron content increased, for high firing temperatures (1300 °C) due to the presence of Fe_2O_3 might help to develop an efficient anodic biofilm via extracellular electron transfer. Similarly, inclusion of 5% goethite recovered from mining mud in ceramic separator leads to a 36% lesser acetate transfer coefficient than Nafion membrane, along with higher Coulombic efficiency (CE) of 21.3% (Das et al., 2020). Cost-benefit analysis proposed by Das et al. (2020) showed such goethite modified membrane can be a potential candidate for field application.

For the long term operation, Daud et al. (2019) proposed zirconia ceramic filter over polymeric membrane in MFC in order to maintain the performance stability. Such filter showed a wide distribution of pore volume favored high water uptake and hence promoted proton transfer characteristics. For Kalporgan's soil ceramic membrane, zircon (zirconium orthosilicate) can be mineral filler to improve physical characteristics, including expansion of porosity and proton transfer behavior. Hence, 10% zircon addition in such membrane composition resulted in current density increment from 102.0 to 440.0 mA/m^2 with a decrease in internal resistance of MFC from 977.4 to 226.4 **Ω** along with 91% chemical oxygen demand (COD) removal (Cheraghipoor et al., 2022). Comparative statement between Anodisc 13 and Sterlitech 15 ceramic filtration membrane showed that Anodisc 13 facilitates high ion transfer with non-tortuous pore structure, small thickness (67 μm), larger pore size (0.1 μm) over Sterlitech 15 membrane (Yang et al., 2016). Further, application of Mfensi clay as an ionic exchange partition was demonstrated by Tamakloe et al. (2015; 2017) for dual chambered MFC with a power output of 118 mW/m^2. Similarly, functionalized tea-waste-ash-clay composite separator in MFC showed high proton transfer of 18.7×10^{-5} cm/s with net electricity generation of 1.8 W/m^3 (Vempaty and Mathuriya, 2022). In another approach, optimum mass of clay (70 g) at low preparation temperature (300° C) in manihot-clay starch composite membrane ensures better performance in terms of hydration stability and proton conductivity (Obasi et al., 2021). Such approaches proposed a means towards effective and efficient cation transfer through ceramic membrane modification during the fabrication process.

Table 2 Comparative performance evaluation of MFC having ceramic membrane modified with mineral intrusion

Mineral addition	**MFC configuration**	**Electrodes**	**Ceramic membrane characteristics**				**Power generation (mW/m^2)**	**WWT (%)**	**Major findings**	**References**
			k_0, cm/sec	**k_H, cm/sec**	**D_H, cm^2/sec**	**t_+**				
Montmorillinite -10%	Dual chambered MFC, 50 mL capacity, Synthetic feed; Red clay + minerals	Carbon felt electrodes; Anode-21 cm^2; Cathode-15 cm^2	2.96×10^{-5}	4.18×10^{-6}	1.7×10^{-6}	0.62	5.28 W/m^3	75.2	20% MMT(M-20) mineral inclusion in clay yielded better conductivity of the separator & higher proton transfer	Ghadge and Ghangrekar, (2015)
Montmorillinite -15%			1.94×10^{-5}	6.56×10^{-6}	2.6×10^{-6}	0.79	6.87 W/m^3	78.5		
Montmorillinite -20%			1.09×10^{-5}	8.18×10^{-6}	3.3×10^{-6}	0.96	7.55 W/m^3	85.4		
Kaolinite -20%			2.1×10^{-5}	5.4×10^{-6}	2.2×10^{-6}	0.73	5.51 W/m^3	75.1		
Nafion			31×10^{-5}	0.26×10^{-3}	4.6×10^{-6}	0.97	--	-		
Control			4.3×10^{-5}	3.4×10^{-6}	1.1×10^{-6}	0.58	3.95 W/m^3	74.4		
Vermiculite - 20%	Single chamber cylindrical; air cathode MFC	Carbon felt electrodes; Anode-16 cm^2; Cathode-31 cm^2	6.9×10^{-5}	5.2×10^{-3}	2.1×10^{-3}	-	46.7 mW/m^3	72.5	Coat of conductive layer of Nafion solution enhances performance	Jain et al., (2020)
Vermiculite - 20% + 10% MMT			5.85×10^{-5}	1.38×10^{-3}	0.5×10^{-3}	-	49.6 mW/m^3	74.7		
MMT 20% + nafion binder			6.5×10^{-5}	8.8×10^{-3}	3.5×10^{-3}	-	84.3 mW/m^3	80.1		
MMT+ bentonite-Ca	Chemical catholyte	Graphite carbon	-	-	-	-	0.163 mW/cm^2	-	Decrease in pore volume by	Sudarlin et al. (2020)

		electrode							bentonite	
Silica (0%)	Dual chambered MFC; 800 mL,	SS mesh; Anode-150 cm^2; Cathode-115 cm^2	1.35×10^{-3}	2.24×10^{-5}	1.1×10^{-5}	-	0.49 W/m^3	64	Addition of silica in ceramic membrane improved the performance of MFC	Raychaudhuri et al. (2021)
Silica (10%)			1.1×10^{-3}	2.5×10^{-5}	1.2×10^{-5}	-	-	-		
Silica (20%)			1.0×10^{-3}	2.8×10^{-5}	1.4×10^{-5}	-	-	-		
Silica (30%)			0.7×10^{-3}	3.5×10^{-5}	1.7×10^{-5}	-	0.79 W/m^3	76		
Silica (40%)			0.7×10^{-3}	3.6×10^{-5}	1.8×10^{-5}	-	-	-		
Goethite 5% + clay	2 chamber MFC; 35 mL	Graphite felt ($8cm^2$)	1.95×10^{-5}	78.7×10^{-3}	-	0.73	112 mW/m^2	87.7	Low-cost goethite for scale-up	Das et al. (2020)
Iron oxide (5.75% vol.)	Air cathode MFC	C. veil anode, AC/PTFE on SS cathode	-	-	-	-	1.04 mW	Porosity-21%	Fe-O increases structural stability	Salar-García et al. (2021)
Fuller clay- 10%	2 chamber MFC (30 mL)	Carbon felt (16 cm^2)	2.1×10^{-5}	6.6×10^{-6}	2.7×10^{-6}	0.8	5.6 W/m^3	76%	MFC for chromium removal	Gunaseelan et al. (2022)
Fuller clay- 15%			1.1×10^{-5}	9.3×10^{-6}	3.2×10^{-6}	0.91	7.9 W/m^3	82%		
Fuller clay- 20%			1.9×10^{-5}	8.4×10^{-6}	2.9×10^{-6}	0.94	6.3 W/m^3	79%		
Zircon-10% KS	Pipe flow MFC	Carbon brush /cloth- anode/ cathode	-	-	P-27.8%	-	4.38 W/m^3	91.1%	Zircon as an additive for improving CEC	Cheraghipoor et al. (2022)
Zircon-10% LKS			-	-	P-49%	-	19 W/m^3	91.6%		

k_o - Oxygen mass transfer coefficient; k_H - Proton mass transfer coefficient; D_H - Proton diffusion coefficient; t_+ - Cation transport number; MMT- Montmorillonite; KS-Kalporgan's soil; LKS: Leached KS; SS- Stainless steel

Apart from natural fillers, Ahilan et al. (2018) proposed the use of montmorillonite and $H_3PMo_{12}O_{40}$ / SiO_2 / TiO_2 filler for polymer derived ceramic membrane in MFC. Such fillers tailored hydrophilicity of membrane matrix with high cation exchange numbers and low oxygen diffusion constant comparable with Nafion membrane (Ahilan et al., 2019; Ahilan, 2020). On a similar principle, MFC with 7 bi-layers of chitosan- montmorillonite nanocomposite film coated on a ceramic separator achieved a power density of 120 mW/m^2 with a decrease in solution resistance by accelerating the proton transfer (Yousefi et al., 2018). These studies expressed the feasibility and capability of polymer based clay nanocomposites incorporated ceramic membrane as a potential candidature owing to their improved proton conductivity as well as suitability towards practical applications of MFC.

Even coating the membrane surface with oil or varnish, followed by heating, is expected to be effective for long-term performance. Earlier, Sharma (2017) utilized *Brassica juncea* (mustard) oil to reduce the oxygen crossover through the surface of preheated ceramic separator in MFC. Reduction in the pore size (30-70 nm) due to oil smearing on membrane resulted in higher proton transfer and more redox current of 5.9 mA achieved during cyclic voltammetry analysis. Painting of commercial varnish can be a useful option for catalyzing the cationic ion transfer through pretreated membrane. Such painting or coating on both sides of the clay membrane resulted in power recovery of 1.8 W/m^3 over either side coating on the membrane surface (Kamraj et al., 2015). Limitation of insufficient exchangeable cationic sites in natural clayware membrane can be overcome through cation exchanger fillers inclusion, and thus, modified ceramic membrane can compete with polymeric membrane in terms of performance.

5. Secondary applications of ceramics in MFC

In conventional waste/water treatment systems, ceramics are used for filtration and filter media for microbial growth, as well as having numerous applications. Due to the wide diversity in characteristics and resistance to shock load conditions; ceramics can be used for various applications in fuel cells ranging from membrane (Jeong et al., 2008), electrode (Throne et al., 2011), chassis (Kumar et al., 2020) as well as membrane-electrode assembly (Li et al., 2011) for stacking-up of MFC units (Galushko et al., 2017; James, 2022). As per bibliometric analysis conducted by Khudzari et al. (2018) over the global research trends, ceramic membrane is one of the latest advancements in recent MFC studies. As stated earlier, ceramics have wide applications as a membrane/separator for biological fuel cells to achieve high Coulombic yield. Vermiculite and clay are famous for improving the water uptake as well as retention, and hence Liu et al. (2018) reported incorporation of such clay for enhancing the proton conductivity of polyvinyl alcohol-hydrogel based polymeric membrane in MFC. Such MFC with a modified membrane was capable of removing the toluene up to 99% along with power recovery of 25.14 mW/m^2. Ceramic membrane showed its feasibility for wide applications of MFC viz. plant MFC (Sophia and Sreeja, 2017), constructed wetland MFC, microbial carbon capture cells, algal MFC, scalable MFCs, and many more (**Table 1**). Apart from this, Ieropoulos and team (UK) reported application of MFC having ceramic membrane for operating different electronic appliances such as EcoBot robot, charging mobile phone battery, light emission diode (LED) bulbs, sensors, microcomputer, DC motor and many more (Walter et al., 2020; Santoro et al., 2017).

Electrode material derived from silicon oxycarbide (SiOC) using the polymer-derived ceramics route method was reported as a biocompatible anode for MFC and showed two-fold higher power density (211 mW/m^2) as compared to carbon felt electrode (e Silva et al., 2019). In bioelectrochemical reactor, ice-templated titanium-based ceramics electrode was capable of producing high current density with favoring the growth of *Geobacter sulfurreducens* biofilm (Massazza et al., 2015). Preliminary analysis on ceramic as an anode electrode showed that it produced higher energy recovery over control carbon anode in algal photo-MFC (Throne et al., 2011). Potential of the carbon coated ceramic Berl saddle as an anode electrode showed a significant energy harvesting rate of 0.13 W/m^2 (29.6 mA/L) along with good bacterial adhesion characteristics (Hidalgo et al., 2014). Such novel, innovative material fulfills the electrochemical requirement and serves as good packing material for bacteria growth and proliferation in MFC. Moreover, ceramic microbial interactions need to be studied in detail for better understanding of electron transfer mechanism.

Recently, Co/Ni-containing N-doped SiOC based porous ceramic catalysts have been found to be promising cathode material for promoting the oxygen reduction reaction (ORR) in MFC (e Silva et al., 2019; Ahilan, 2020). Nitrogen doping in ceramic catalysts showed durable performance with a positive influence on nitrogen functionalities. Significant enhancement in cathodic ORR reactions with introduction of MnO_2 and carbon fibers catalysts to the ceramic electrodes in

MFC having Trojan clay ceramic membrane was reported by Midyurova et al. (2015). Use of low-cost ceramic as a chassis or an anodic chamber outliner for stacking multiple modular MFCs was found effective during urine treatment and provides new directives for real on-site applications (Gajda et al., 2018). Such compact reactor design of stacked architecture achieved power of 245 mW from 560 units while simultaneously treating human urine. Earlier, Jadhav and Ghangrekar (2020) designed single chambered MFC using an earthen pot as an anodic chamber/separator to make it handier and more portable for biobattery applications. Earlier, Chatterjee and Ghangrekar (2014) proposed design of baked clayware separator electrode assembly for single chambered air cathode MFC. Performance of MFC was improved in such case to 4.38 W/m^3 and COD removal of 90% with activated carbon coating on both sides of membrane; however, electrolyte evaporation resulted in electrolyte loss over long term run. Thus, such numerous applications of ceramics present wide applicability of ceramics for electrodes, membrane, as well as chassis and future scope for development of MFC with complete ceramic materials (Ding et al., 2020). Even ceramic oxide membrane offers the advantage of large scale application to separate CO_2 from greenhouse gas mixture through physical adsorption and chemical reaction (Ramírez-Moreno et al., 2014). Ceramics has wide applicability in energy storage devices, electrochemical sensor use, and separation-filtration techniques (Meng et al., 2019).

6 Primary considerations for selection of ceramic membrane in scaling-up studies

6.1 Cost economics

Generally, cost-benefit analysis helps to understand the impact of scaling-up of technology and commercialization planning. Considering the economic analysis, the cost required for the fabrication of ceramic membranes is significantly lower compared to polymeric membranes such as Nafion and Ultrex membranes. Locally available clay soil can be used as a raw material for fabrication of such membranes with spiking of cation exchanger to improve the CEC. Pasternak et al. (2016) estimated the cost of 4.5 GBP/m^2 for pyrophyllite membrane while working with MFC for different ceramic membranes. Recently, Das et al. (2020) reported cost of fabrication of 1 m^2 of ceramic membrane blended with 5% goethite is around $ 607, which is fivefold less than Nafion membrane for MFC applications. Additionally, net power benefit recovery of 170 $/W was achieved in MFC with goethite blended ceramic membrane with high wastewater treatment efficiency. Even cost goes down (45 \$/m^2) with the use of activated carbon coconut shell powder mixed with clay and serves as a cost effective membrane solution for fuel cell applications (Neethu et al., 2019). Additionally, montmorillonite-clay membrane coated with nafion solution required cost of 1,500 \$/m^2, 10-fold lower than Nafion membrane in MFC (Jain et al., 2020). Similarly, fabrication cost of 0.43 €/m^2 was reported for tubular clay separator (1.55 mm thick) fabricated with slip-casting method with overall cost of 0.51 €/cell (Rodriguez et al., 2021). Majority of capital cost of MFC fabrication (around 40%) is contributed by costly polymeric membrane, and ceramic membrane can be an economical option for future commercialization of such bioelectrochemical systems. During the scaling-up attempt of bioelectric toilet MFC of 1.5 m^3 capacity, approximate cost of \$ 200 accounted for ceramic membrane modified with montmorillonite and proved to be sustainable technology with payback period of 10 years (Jadhav et al., 2021).

6.2 Long-term stability

Longevity of operational performance is of key constraint while taking into consideration practical applications of MFC (Gajda et al., 2020). It helps to understand the change in operating conditions, microbial metabolism kinetics, as well as characteristics of membrane and electrode behavior over the period of time. Over the 390 days of operation, the ceramic separator remained intact without any erosion or weathering (Ghadge et al., 2016). Even chemical cation species (Ca, Mg, Al, K) containing deposits during fouling were strongly bonded with ceramic separator acting as the barrier for oxygen diffusion, which resulted in a reduction in cathodic half cell potential (Ghadge and Ghangrekar, 2015). Previously, Cristani et al. (2019) also reported long-term stable operation of in-field floating MFC using vertical and horizontal configurations for remote monitoring. However, few studies reported issues such as membrane fouling over long-run (**Fig. 5**), as well as methanogenesis growth, which deteriorates the stability of MFC (Ghadge et al., 2016; Jadhav et al., 2021).

6.3 Membrane biofouling behavior

Over long-term operation, development of biofilm on membrane surface, as well as chemical deposition may result in biofouling and chemo-fouling of the membrane. It results in clogging of pores and reduction in proton transfer rate. Biofilm thickening and chemical deposition over the time period resulted in an increase in membrane resistance and decreased the overall performance of MFC (Ghadge et al., 2016). Over long-term operation, biofouling cause pH imbalance due to pH splitting as well as an increase in overall internal resistance of system (Ramirez-Nava et al., 2021), which deteriorates MFC performance index, as shown in **Figure 5**. Such membrane biofouling, i.e., unwanted growth of biofilm on membrane surface, can be mitigated with intermittent spraying of anti-fouling agents or providing alternative bio/chemical mitigation strategies (Jadhav et al., 2021). Thus, the cost of replacement of membrane can be reduced by adopting the proper biofouling mitigation strategies. Such an approach will be highly recommendable for the long run while taking into account complete use of ceramic as electrode-membrane materials and chassis for anodic chamber.

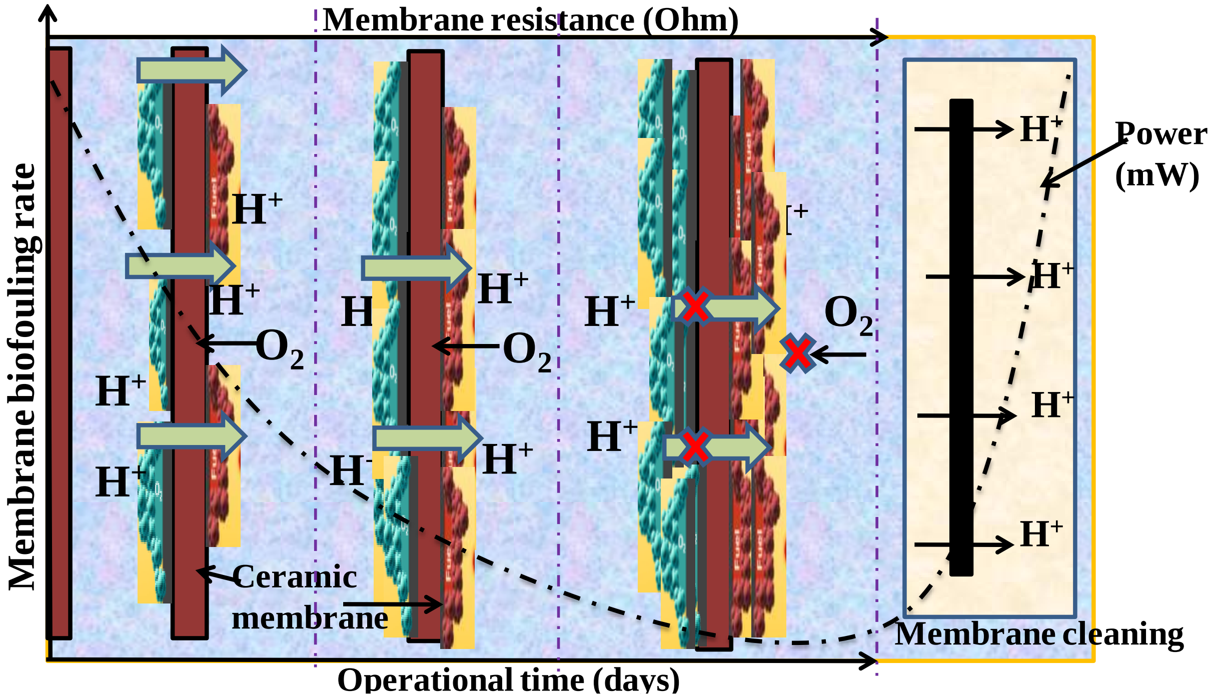


Figure 5: Membrane biofouling effect on the operation of MFC with ceramic membrane

6.4 Supporting characteristics

Suitable balancing of the water uptake and retention, ionic conductivity, structural strength, and porosity permits the design of ceramic based MFCs for on-site use (Cristani et al., 2020). Apart from physico-chemical stability, ceramic membranes are resistant to shock conditions developed due to change in fluid dynamic conditions. Top layer of ceramic membrane surface allows ion separation, and the bottom layer provides the mechanical strength to the structure; intermittent layers reduce the surface roughness (Zhu et al., 2021). Ceramic separators can withstand high hydrostatic pressure and against change in fluid dynamics as compared to polymeric membranes. Such ceramic partitions can sustain extreme acidity or alkalinity and bear high operating pressures (Ghadge, 2016).

7. Scaling-up attempts of MFCs with ceramic membrane

Recently, MFC has advanced towards scaling-up applications and has been tested during field trials for pollutant removal along with overcoming existing practical limitations (Das et al., 2018). Potential of ceramic membranes for such scalable designs have also been tested from 1 L to 1500 L capacity reactors with generating useful power output (**Fig. 6**). From the scaling-up perspective, electrode surface area plays a vital role in controlling redox reactions and microbial metabolism (Janicek et al., 2014). Anode to cathode electrode surface area of 3 is the best suited for pipe flow MFC with V-shaped earthen membrane and yielded volumetric power of 7.01 W/m^3 with COD removal of 45-48% during septage treatment (Thanh et al., 2015). The TiO_2 based photocathode in ceramic upflow MFC (2 L capacity) coupled with laterite filter reported more than 95% surfactant removal, 71% organic matter removal, and power generation of 0.73 W/m^3 within 12 hr short retention time (Sathe et al., 2020). Such integrated system used a ceramic separator modified with 20% montmorillonite and carbon felt electrodes for net energy recovery of 55.2 W.h/kg.COD.

To find out the best electrode material combination for electrochemical redox reactions, Ghangrekar and Ghadge (2013) compared the performance of 3.5 L MFCs with carbon felt, graphite plate, and flexible graphite electrode materials. Ceramic cylindrical MFC with carbon felt cathode and carbon cloth anode were found to be the best electrode pair and achieved maximum volumetric power density (1.05 W/m^3 at 30 Ω internal resistance) with lower overpotential losses. Ieropoulos and his team tested potential of MFC for human urine treatment using a stacked arrangement of electrodes (Walter et al., 2022). Field testing of Pee-power MFC having terracotta separators for urine treatment was successfully demonstrated for UWE Oxfam urinal system (with 288 MFCs) and Glastonbury Music Festival, England (432 MFCs) with stacking modular arrangement (Ieropoulos et al., 2016). COD reduction of about 90% was achieved with high hydraulic retention time (HRT: 2-3 weeks) in the first case and 70% for the second case with an HRT of 0.9 days. Power output was comparatively higher for Glastonbury MFCs (800 mW) and capable of illuminating the LED lamps during the music festival.

Tubular design of terracotta MFC showed practical applicability of MFC stack for charging mobile phone as well as catholyte generation during human urine treatment (Gajda et al., 2015; Ieropoulos et al., 2013). A simple design of algal MFC of 10 L size was fabricated using rock phosphate blended clayware as a separator and low-density polyethylene bags as a cathodic chamber (Khandelwal et al., 2020). Overall experimental set-up was capable of harvesting the net energy recovery, lipid, and algal productivity of 11.5318 kWh/m^3; 0.09 kg/m^3.d, and 0.307 kg/m^3.d, respectively, under normal outdoor environmental conditions (**Table 3**). Even MFC can be scaled in all 3 dimensions (length, width, and height) with no/minimum power density losses. Effect of increase in electrode height from 1 to 3 cm showed enhancement in power from 0.5 to 1.5 mW in self-stratifying scalable MFC fed with urine, mainly due to the control of diffusion losses (Walter et al., 2019). However, more detailed investigation is needed to consider the electrochemistry with an increase in size of the electrode and its effect on the electrochemical redox reaction rate. For simulation purpose, modeling study with the goal of finding out optimum anodic surface area to volume ratio was carried out for ceramic membrane MFC based on various electrochemical formulations (Ghadge et al., 2016). Experimental validation showed that maximum volume of 2.02 L can be supported in order to ensure enrichment of electrogenesis in anodic chamber of MFC with a catalyzed cathode while treating wastewater of 5 g.COD/L (Ghadge et al., 2016). In a similar study, an increase in anode surface area from 420 to 630 cm^2 achieved power increment from 4.71 to 5.92 mW in MFC of 1.6 L capacity. Similarly, current output improved from 8.71 to 24.31 mA with enlarging the anodic chamber size from 0.175 to 1.6 L in MFC with carbon felt anode and carbon ink as cathode catalyst (Ghadge, 2016).

As aforementioned, ceramic membrane can be a sustainable, low-cost alternative for fuel cell applications due to high structural strength, hydraulic stability, structural durability, and ease in fabrication. Innovative pilot scale design of 20 L integrated MFC-membrane bioreactor (MBR) system fabricated with polysiloxane derived ceramic membrane reported power recovery of 115 mW/m^2 with COD removal of 69% (Ahilan, 2020; Bhowmick, 2020). Recently, Das et al. (2020;

2021) expressed applicability of Cu-Zn/CuMnFe based cathode catalyst for proliferation of performance of 25 L cylindrical MFC having ceramic membrane modified with 20% montmorillonite. Such Cu-Zn catalyst accelerated the rate of cathodic reduction and generated power density 64-fold higher than non-catalyzed MFC (Das et al., 2020). Further, another study conducted by Das et al. (2021) using the same MFC with $Cu_{0.5}Mn_{0.5}Fe_2O_4$ showed anti-fouling characteristics for long-term stable operation. Such MFC with CuMnFe catalyst produced a power density of 7.74 mW/m^2 along with effective wastewater treatment in field scale MFC. Cost normalized power recovery of Cu-Zn/CuMnFe catalyst is more than Pt/C and hence warrants suitability for field application of MFC. These studies favoured the use of cathodic catalysts for overcoming the cathodic overpotential losses and long-term stable operation in field scale applications.

Table 3: Scaling-up attempts of MFCs with ceramic membrane

MFC size (L)	**MFC design**	**Power output(mW)**	**Major findings**	**References**
2	Upflow MFC with TiO_2 catalyst	0.73W/m^3 at HRT-12 h	Surfactant removal in MFC with photocathode	Sathe et al. (2020)
2	Pipe flow MFC for septage treatment	7.01 W/m^3; I – 17 mA	Anode/cathode ratio of 3 for better performance of MFC	Thanh et al., (2015)
3.5	Cylindrical MFCs with different electrode materials	1.05 W/m^3; 27.7 mW/m^2	Carbon felt served as better electrode material for MFC	Ghangrekar and Ghadge (2013)
10	*Chlorella* algal MFC with polyethylene cc	0.89 W/m^3	Algal MFC for biomass production and low-cost option	Khandelwal et al. (2020)
20	MFC-MBR system (Polysiloxane derived ceramic membrane)	115 mW/m^2; CE-3.4%; COD-69%	Polysiloxane based ceramics as PEM & ultrafiltration membrane in MFC-MBR	Ahilan (2020); Bhowmick (2020)
25	Cylindrical MFC (graphite felt)	7.5 mW/m^3	Suitability of Cu-Zn cathode catalyst for ORR	Das et al. (2020)
25	Cylindrical MFC (graphite felt)	7.74 mW/m^2	CuMnFe cathode catalyst with anti-fouling characteristics	Das et al. (2021)

26	3 MFCs in stack; single chambered cylindrical	17.85	3 g/L.d OLR found optimum for higher output	Ghadge and Ghangrekar (2015)
45	Dual Chambered MFC	17.63	4.5 g/L.d OLR for high output	Ghadge(2016)
100	S-shaped MFC (air & aqueous cathode)	36	Low R_{int}, power management system for power recovery	Jadhav (2017)
300	432 units in stack	800	On field demonstration of MFC for urine treatment	Ieropoulos et al., (2016)
720	Hexagonal MFC (air cathode assembly)	61	Illuminating toilets at night, human waste treatment	Das et al. (2020)
1500	Hexagonal MFC (49 units)	75	Field scale demonstration of bioelectric toilet system	Jadhav et al. (2021)

Earlier, Ghadge and Ghangrekar (2015) and Ghadge et al. (2016) attempted scaling-up application of ceramic membrane based MFC of 26 and 45 L capacity having single chambered and dual chambered design for the treatment of acetate based wastewater. Over long-term operation, 26 L MFC produced power of 17.85 mW and CE of 5.1%, whereas, for 45 L MFC power output was 17.63 mW along with COD removal of 69.5%. Such studies provided more insights into suitability of membrane for the field applications and positive direction towards commercialization of this technology.

Scaling-up application of bioelectric toilet MFCs of capacity 100 L, 720 L, and 1.5 m^3 was successfully demonstrated for human waste treatment and electricity generation (Jadhav, 2017; Das et al., 2020; Jadhav et al., 2021). Ceramic membrane modified with 20% montmorillonite was used as a separator between anodic chamber and air-cathode membrane assembly. Performance of bioelectric toilet MFC was 36, 61; 75 mW of power output and 174, 247, 239 mA of current recovery for 100 L, 720 L, and 1.5 m^3 reactor, respectively, along with organic matter removal of > 85% and simultaneous disinfection of treated effluent (Jadhav et al., 2020). Field application of bioelectric toilet MFC of 720 L capacity at National Thermal Power Corporation (NTPC), Noida, as well as 1500 L at Indian Institute of Technology (IIT) Kharagpur, India sites gave new strategic directives for addressing the scaling-up challenges (**Table 3**). Long term operation of more than 3 years, low-cost economics, and capability of illuminating the LED bulbs with stacking of units are key features of such design employed at the field scale. Such results demonstrated the applicability of ceramic separators to withstand scaling-up challenges and long term stability. Upscaling of ceramic membrane based MFC together with improvements in the current generation is shown in Figure 6.

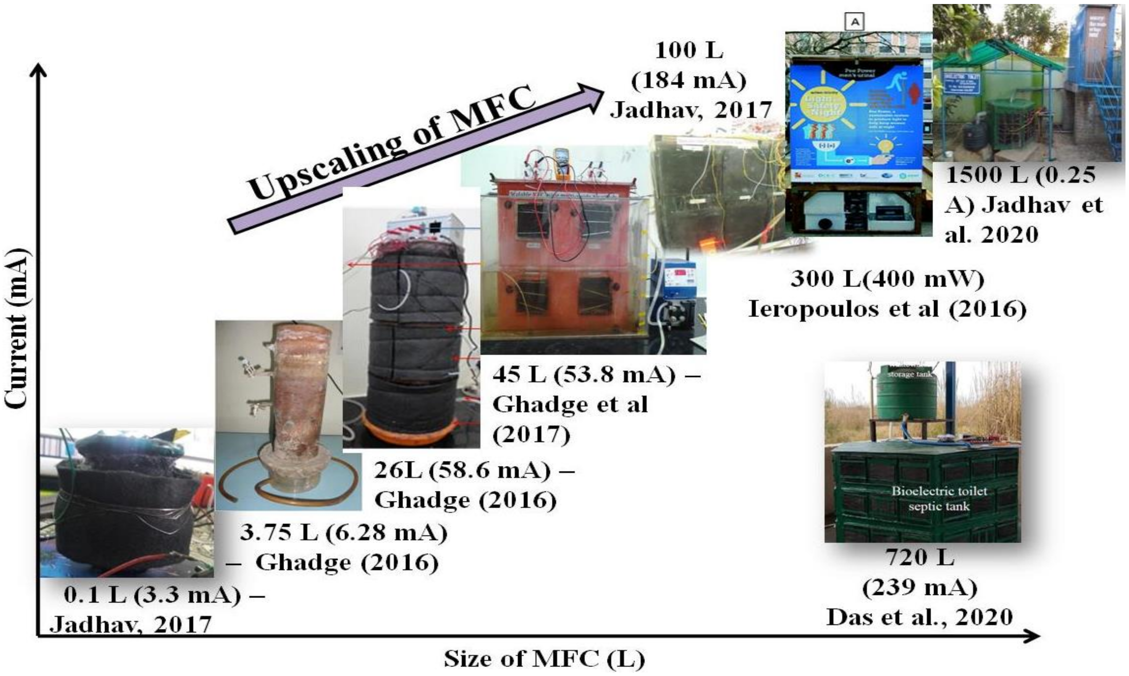


Figure 6: Development of lab-scale to scaling-up ceramic membrane based MFCs along with current generation

8. Perspectives and challenges

As stated earlier, the efforts in MFC technology application refer to the improvement in reactor design, optimization of operating conditions, and exploration of ceramic membrane aiming to reach techno-economical sustainability and efficiency. Being an interdisciplinary complex system, optimization of membrane performance and improving its characteristics are of concern and have developed significant interest among the MFC researchers in the past few years (Choudhury et al., 2017; Mercuri et al., 2016). Ceramic is chosen as a suitable material for membrane in fuel cell application because it is porous in nature and hence can reduce the restriction on the ionic exchange through a conventional membrane (Me and Bakar, 2020). Besides the aforementioned advantages, ceramics are also established as novel suitable materials for developing MFC from bench-top models to up-scaling applications because of their structural durability and plasticity (Behera et al., 2011). Successful scalable trials and demonstration of ceramic based MFC as Pee power MFC, bioelectric toilet MFC, MFC-MBR system (Bhowmick and Ghangrekar, 2018; Bhowmick, 2020), stacked modular MFC (Gajda et al., 2018), and many more are positive indicators for commercialization of such technology. Major key challenges of long-term stability and scalable applications of such membranes have been addressed in the last decade with the positive outcomes.

Techno-economical feasibility showed that ceramics can be an attractive alternative to polymeric membranes while considering the scaling-up aspects (Jadhav et al., 2021). Long term stable performance, ease in cleaning and maintenance, and higher mechanical strength are unique capabilities of membrane for providing sustainable solutions in fuel cells. Efforts should be taken to develop the MFC with complete ceramic material for anode, cathode, membrane, chassis as well as membrane-electrode assembly. These applications can be suitable for developing ceramic pipe MFC in order to transport waste inflow to wastewater treatment systems. Such pipe MFC would replace the existing polymeric pipelines along with generating electricity and simultaneous contaminant degradation.

During fabrication of ceramic membranes, fabrication process and clay composition are important concerns related to strength and ionic characterization. Due to the difference in basic raw materials, mineral composition, and manufacturing processes, the properties of low-cost ceramic membranes differ from those of commercial ceramic membranes based on pure oxides (Mestre et al., 2019). Hence, the composition of various mineral fillers and synergistic combinations can be tested for improving the membrane characteristics. Before moving ahead for practical applications, several researchers faced issues of membrane biofouling (chemical/biological) and electrolyte loss due to evaporation, as in the case of earthen pot MFC, which need to be taken care of in the near future (Chatterjee and Ghangrekar, 2014). The weight of ceramics is another challenge for upscaling applications. Ceramics are distinguished for high compressive strength but have lower impact strength characteristics. Those characteristics make ceramics become highly brittle and easily fracture when certain pressure is applied and has a possibility of damage during handling (Ahmad et al., 2019). Even though a lot of development has been carried out on ceramic modifications, there are still challenges of strength, stability, and sensitivity that need to be addressed before practical application.

Previously, Ghadge et al. (2016) proposed a modeling study to optimize the effective size of anodic chamber and anodic surface area based on various electrochemical approaches in order to promote the electrogenesis growth. Such more detailed modeling studies and optimization strategies need to be considered for achieving the higher power output from ceramic based MFC as well as simulating the ion transfer through ceramic membrane (Casula et al., 2021). Apart from ceramic as cation exchange membrane, it can be developed for anion exchange using certain mineral additives and would be a beneficial option for microbial desalination cells as well as other electrosynthesis applications (Martí-Calatayud et al., 2015). There is still ambitious scope for utilization of ceramic membrane for other variations of microbial electrochemical technologies such as microbial electrolysis cell for biohydrogen generation, microbial desalination cell for desalination, microbial electrosynthesis applications for resource recovery, and many more.

Moving from reality to practicability, researchers have demonstrated long-term operation of mL sized reactor to m^3 capacity system with generating the power sufficient for operating on-field electronic applications (Jadhav et al., 2022). High wastewater treatment, pollutant removal, and effective energy recovery showed scalable success of MFC technology having ceramic membrane. However, commercialization of this technology is still a pleasant dream, and ceramic industries should come forward in collaboration with scientific communities to tackle the practical challenges with necessary support. Such industrial participation can favor the utilization of ceramic microbial fuel cell for industrial wastewater treatment while focusing on a circular economy for sustainable development.

9. Conclusions

Considering the present research needs to make MFC a self-sustainable and economic solution, ceramic membrane is one of the promising candidates for the scaling-up applications of MFC. High proton exchange rate, structural strength, thermo-chemical stability, long-term stable operation, and low-cost promote the use of ceramics for stacking and scalable applications. With modification in ceramic characteristics by inclusion of cation minerals, ceramic membranes can compete with existing polymeric membranes in terms of proton transfer and membrane properties. Critical analyses of scalable studies showed that ceramic membrane can outperform for long-term stable operation with minimal maintenance, which can be potential hopes for commercialization of MFC technology to achieve the sustainable development goal. Such results encourage industries and ceramic companies to invest and collaborate with scientific researchers to achieve the commercialization of MFC in the near future.

Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2019R1A2C1006356), Brain Pool fellowship grant (2021H1D3A2A02044903), and “Cooperative Research Program for Agriculture Science and Technology Development (Project No. PJ016259022021)” Rural Development Administration, Republic of Korea.

Credit authorship contribution statement

D.A. Jadhav, T. Eisa & S.G. Park: Writing – original draft, visualization, investigation, conceptualization; K.J. Chae: Resources, writing original draft, conceptualization, visualization, editing, supervision; A.K. Mungray & A.G. Olabi: Writing - review & editing. All the authors played active roles in analyzing the literature review and finalizing the manuscript.

Conflict of Interest statement

All the authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Ahilan, V., Wilhelm, M., & Rezwan, K. (2018). Porous polymer derived ceramic (PDC)-montmorillonite-$H_3PMo_{12}O_{40}/SiO_2$ composite membranes for microbial fuel cell (MFC) application. *Ceramics International*, *44*(16), 19191-19199.
2. Ahilan, V., de Barros, C. C., Bhowmick, G. D., Ghangrekar, M. M., Murshed, M. M., Wilhelm, M., & Rezwan, K. (2019). Microbial fuel cell performance of graphitic carbon functionalized porous polysiloxane based ceramic membranes. *Bioelectrochemistry*, *129*, 259-269.

3. Ahilan, V. (2020). Porous polymer derived ceramic membranes for bioelectricity generation and wastewater treatment, Doctoral dissertation, Universität Bremen, Germany.
4. Aiken, D. C., Curtis, T. P., & Heidrich, E. S. (2019). Avenues to the financial viability of microbial electrolysis cells [MEC] for domestic wastewater treatment and hydrogen production. *International journal of hydrogen energy*, *44*(5), 2426-2434.
5. Ajayi, F. F., and Weigele, P. R. (2012). A terracotta bio-battery. *Bioresour. Technol.* 116, 86–91.
6. Al-Sahari, M., Al-Gheethi, A., Mohamed, R. M. S. R. M., Yashni, G., Vo, D. V. N., & Ismail, N. (2022). Microbial fuel cell systems; developments, designs, efficiencies, and trends: A comparative study between the conventional and innovative systems. *Chemosphere*, 134244.
7. Bagchi, S., & Behera, M. (2022). Effects of Pharmaceuticals on the Performance of Earthen Pot Microbial Fuel Cell. *Journal of Hazardous, Toxic, and Radioactive Waste, 26*(2), 04021057.
8. Banerjee, A., Calay, R.K., Eregno, F.E. (2022) Role and Important Properties of a Membrane with Its Recent Advancement in a Microbial Fuel Cell, Energies,15(2); 1-15.
9. Behera, M. (2012). Performance of microbial fuel cell under different operating conditions and employing earthenware as separator, Doctoral dissertation, IIT Kharagpur, India.
10. Behera, M., & Ghangrekar, M. M. (2011). Electricity generation in low-cost microbial fuel cell made up of earthenware of different thickness. *Water Science and Technology*, *64*(12), 2468-2473.
11. Behera, M., & Ghangrekar, M. M. (2011). Performance and economics of low-cost clay cylinder microbial fuel cell for wastewater treatment. In *World Renewable Energy Congress-Sweden; Linköping; Sweden*, No. 057, 1189-1196.
12. Behera, M., Jana, P. S., & Ghangrekar, M. M. (2010). Performance evaluation of low-cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode. *Bioresource technology*, *101*(4), 1183-1189.
13. Bhowmick, G. D. (2020). Development of bio-eletrochemical system assisted advanced hybrid treatment systems for aquacultural wastewater, Doctoral dissertation, IIT Kharagpur, India.

14. Bhowmick, G. D., & Ghangrekar, M. M. (2018). Integrated MFC-MBR system using low-cost, multifunctional ceramic membrane for efficient wastewater treatment and electricity recovery.
15. Bose, D., Yadav, D., Patel, R. K., Dhoundiyal, A., Gusain, L., & Tyagi, A. (2018). Biodiesel wastewater treatment and power generation using earthen membrane Microbial Fuel Cell. *Nature Environment and Pollution Technology,* 17(4), 1293-1297.
16. Carroll, D. (1959). Ion exchange in clays and other minerals. *Geological Society of America Bulletin*, *70*(6), 749-779.
17. Casula, E., Kim, B., Chesson, H., Di Lorenzo, M., & Mascia, M. (2021). Modelling the influence of soil properties on performance and bioremediation ability of a pile of soil microbial fuel cells. *Electrochimica Acta*, *368*, 137568.
18. Chatterjee, P., & Ghangrekar, M. M. (2014). Design of clayware separator-electrode assembly for treatment of wastewater in microbial fuel cells. *Applied biochemistry and biotechnology*, *173*(2), 378-390.
19. Cheraghipoor, M., Mohebbi-Kalhori, D., Noroozifar, M., & Maghsoodlou, M. T. (2019). Comparative study of bioelectricity generation in a microbial fuel cell using ceramic membranes made of ceramic powder, Kalporgan's soil, and acid leached Kalporgan's soil. *Energy*, *178*, 368-377.
20. Cheraghipoor, M., Mohebbi-Kalhori, D., Noroozifar, M., & Maghsoodlou, M. T. (2021). Production of greener energy in microbial fuel cell with ceramic separator fabricated using native soils: Effect of lattice and porous SiO_2. *Fuel*, *284*, 118938.
21. Cheraghipoor, M., Mohebbi-Kalhori, D., Noroozifar, M., Maghsoodlou M.T. (2022). Enhancing the efficiency of ceramic native soil membrane using Zircon in a continuous microbial fuel cell for wastewater treatment and sustainable energy, *Journal of Environmental Chemical Engineering*, (Accepted).
22. Cristiani, P., Gajda, I., Greenman, J., Pizza, F., Bonelli, P., & Ieropoulos, I. (2019). Long term feasibility study of in-field floating microbial fuel cells for monitoring anoxic wastewater and energy harvesting. *Frontiers in Energy Research*, *7*, 119.
23. Cristiani, P., Goglio, A., Marzorati, S., Fest-Santini, S., & Schievano, A. (2020). Biochar-terracotta conductive composites: new design for bioelectrochemical systems. *Frontiers in Energy Research*, 332.

24. Das, I., Das, S., & Ghangrekar, M. M. (2020). Application of bimetallic low-cost CuZn as oxygen reduction cathode catalyst in lab-scale and field-scale microbial fuel cell. *Chemical Physics Letters*, *751*, 137536.
25. Das, I., Das, S., Chakraborty, I., Bhowmick, G. D., Ghangrekar, M. M. (2018). Lab scale to field scale application of bioelectrochemical systems: a short review on current status and problems faced, *4th EU-ISMET conference*, UK.
26. Das, I., Das, S., Das, S., & Ghangrekar, M. M. (2021). Proficient sanitary wastewater treatment in laboratory and field-scale microbial fuel cell with anti-biofouling $Cu_{0.5}Mn_{0.5}Fe_2O_4$ as cathode catalyst. *Journal of the Electrochemical Society*, *168*(5), 054519.
27. Das, I., Das, S., Dixit, R., & Ghangrekar, M. M. (2020). Goethite supplemented natural clay ceramic as an alternative proton exchange membrane and its application in microbial fuel cell. *Ionics*, *26*(6), 3061-3072.
28. Das, I., Das, S., Sharma, S., & Ghangrekar, M. M. (2020). Ameliorated performance of a microbial fuel cell operated with an alkali pre-treated clayware ceramic membrane. *International Journal of Hydrogen Energy*, *45*(33), 16787-16798.
29. Das, I., Ghangrekar, M. M., Satyakam, R., Srivastava, P., Khan, S., & Pandey, H. N. (2020). On-site sanitary wastewater treatment system using 720-L stacked microbial fuel cell: case study. *Journal of Hazardous, Toxic, and Radioactive Waste*, *24*(3), 04020025.
30. Daud, S. M., Daud, W. R. W., Bakar, M. H. A., Kim, B. H., Somalu, M. R., Jahim, J. M., ... & Ghasemi, M. (2019). A comparison of long-term fouling performance by zirconia ceramic filter and cation exchange in microbial fuel cells. *International Biodeterioration & Biodegradation*, *136*, 63-70.
31. Daud, S. M., Daud, W. R. W., Kim, B. H., Somalu, M. R., Bakar, M. H. A., Muchtar, A., ... & Chang, I. S. (2018). Comparison of performance and ionic concentration gradient of two-chamber microbial fuel cell using ceramic membrane (CM) and cation exchange membrane (CEM) as separators. *Electrochimica Acta*, *259*, 365-376.
32. de Sá Mendonça, E., Rowell, D. L., Martins, A. G., & da Silva, A. P. (2006). Effect of pH on the development of acidic sites in clayey and sandy loam Oxisol from the Cerrado Region, Brazil. *Geoderma*, *132*(1-2), 131-142.

33. Ding, H., Wu, W., Jiang, C., Ding, Y., Bian, W., Hu, B., ... & Ding, D. (2020). Self-sustainable protonic ceramic electrochemical cells using a triple conducting electrode for hydrogen and power production. *Nature communications*, *11*(1), 1-11.
34. e Silva, T. C. D. A., Bhowmick, G. D., Ghangrekar, M. M., Wilhelm, M., & Rezwan, K. (2019). SiOC-based polymer derived-ceramic porous anodes for microbial fuel cells. *Biochemical Engineering Journal*, *148*, 29-36.
35. e Silva, T. C. D. A., Mooste, M., Kibena-Põldsepp, E., Matisen, L., Merisalu, M., Kook, M., ... & Rezwan, K. (2019). Polymer-derived Co/Ni–SiOC (N) ceramic electrocatalysts for oxygen reduction reaction in fuel cells. *Catalysis Science & Technology*, *9*(3), 854-866.
36. Frattini, D., Accardo, G., & Kwon, Y. (2020). Perovskite ceramic membrane separator with improved biofouling resistance for yeast-based microbial fuel cells. *Journal of Membrane Science*, *599*, 117843.
37. Gajda, I., Obata, O., Salar-Garcia, M. J., Greenman, J., & Ieropoulos, I. A. (2020). Long-term bio-power of ceramic microbial fuel cells in individual and stacked configurations. *Bioelectrochemistry*, *133*, 107459.
38. Gajda, I., Stinchcombe, A., Greenman, J., Melhuish, C., & Ieropoulos, I. (2015). Ceramic MFCs with internal cathode producing sufficient power for practical applications. *International Journal of Hydrogen Energy*, *40*(42), 14627-14631.
39. Gajda, I., Stinchcombe, A., Merino-Jimenez, I., Pasternak, G., Sanchez-Herranz, D., Greenman, J., & Ieropoulos, I. A. (2018). Miniaturized ceramic-based microbial fuel cell for efficient power generation from urine and stack development. *Frontiers in energy research*, 6, 84.
40. Galushko, A. S., Panova, G. G., Ivanova, A. G., Masalovich, M. S., Zagrebelnyy, O. A., Kruchinina, I. Y., & Shilova, O. A. (2017). An overview of the functional ceramic and composite materials for microbiological fuel cells. *Journal of Ceramic Science and Technology*, *8*(4), 433-454.
41. Ghadge, A. N., & Ghangrekar, M. M. (2015a). Development of low-cost ceramic separator using mineral cation exchanger to enhance performance of microbial fuel cells. *Electrochimica Acta*, *166*, 320-328.

42. Ghadge, A. N., & Ghangrekar, M. M. (2015b). Performance of low-cost scalable air–cathode microbial fuel cell made from clayware separator using multiple electrodes. *Bioresource technology*, *182*, 373-377.
43. Ghadge, A. N., (2016). Scaling-up of microbial fuel cells for wastewater treatment and development of ceramic separator using mineral cation exchanger (Doctoral dissertation, IIT, Kharagpur).
44. Ghadge, A. N., Ghangrekar, M. M., & Scott, K. (2016a). Maximum anode chamber volume and minimum anode area for supporting electrogenesis in microbial fuel cells treating wastewater. *Journal of Renewable and Sustainable Energy*, *8*(4), 044302.
45. Ghadge, A. N., Jadhav, D. A., & Ghangrekar, M. M. (2016b). Wastewater treatment in pilot-scale microbial fuel cell using multielectrode assembly with ceramic separator suitable for field applications. *Environmental Progress & Sustainable Energy*, *35*(6), 1809-1817.
46. Ghadge, A. N., Sreemannarayana, M., Duteanu, N., & Ghangrekar, M. M. (2014a). Influence of ceramic separator's characteristics on microbial fuel cell performance. *Journal of Electrochemical Science and Engineering*, *4*(4), 315-326.
47. Ghadge, A.N., Ghangrekar, M. M., Pandit, S., Das, D. (2014b). Performance of air cathode earthen pot microbial fuel cell for simultaneous wastewater treatment with bioelectricity generation. *International Journal of Environmental Technology and Management*, 17(2), 143-153.
48. Ghangrekar M.M., Ghadge A.N., (2013). Scaling-up of Microbial Fuel Cell Using Clay Membrane Separator and Non-catalyzed Electrode Materials, Advances in industrial biotechnology, *I K International Publishing House*, New Delhi, India, 45-57.
49. Guan, J. (1998). Development of mixed-conducting ceramic membranes for hydrogen separation (No. ANL/ET/CP-95197). Argonne National Lab., IL (US).
50. Gunaseelan, K., Jadhav, D. A., Gajalakshmi, S., & Pant, D. (2021). Blending of microbial inocula: An effective strategy for performance enhancement of clayware Biophotovoltaics microbial fuel cells. *Bioresource Technology*, *323*, 124564.
51. Gunaseelan, K., Jadhav, D.A, Pant, D., Gajalakshmi, S. (2022). Effectiveness of biophotovoltaics system modified with fuller-clay composite separators for chromium removal, *Electrochemica Acta* (Accepted).

52. Hakami, M. W., Alkhudhiri, A., Al-Batty, S., Zacharof, M. P., Maddy, J., & Hilal, N. (2020). Ceramic microfiltration membranes in wastewater treatment: Filtration behavior, fouling and prevention. *Membranes*, *10*(9), 248.
53. Hidalgo, D., Tommasi, T., Cauda, V., Porro, S., Chiodoni, A., Bejtka, K., & Ruggeri, B. (2014). Streamlining of commercial Berl saddles: a new material to improve the performance of microbial fuel cells. *Energy*, *71*, 615-623.
54. Ieropoulos, I. A., Ledezma, P., Stinchcombe, A., Papaharalabos, G., Melhuish, C., & Greenman, J. (2013). Waste to real energy: the first MFC powered mobile phone. *Physical Chemistry Chemical Physics*, *15*(37), 15312-15316.
55. Ieropoulos, I. A., Stinchcombe, A., Gajda, I., Forbes, S., Merino-Jimenez, I., Pasternak, G., Sanchez-Herranz, D. & Greenman, J. (2016). Pee power urinal–microbial fuel cell technology field trials in the context of sanitation. *Environmental Science: Water Research & Technology*, *2*(2), 336-343.
56. Iwahara, H., Uchida, H., & Tanaka, S. (1983). High temperature type proton conductor based on $SrCeO_3$ and its application to solid electrolyte fuel cells. *Solid State Ionics*, *9*, 1021-1025.
57. Jadhav D.A. (2017). Performance enhancement of microbial fuel cells through electrode modifications along with development of bioelectric toilet, Doctoral dissertation, IIT Kharagpur, India.
58. Jadhav D.A., Pandit S., Gajalakshmi S., Shah M. (Eds.) (2022). Scaling-up of microbial electrochemical system: From reality to practicability, First edition, Elsevier Publications, Cham.
59. Jadhav DA, Ghadge AN, Ghangrekar MM (2015) Enhancing the power generation in microbial fuel cells with effective utilization of goethite recovered from mining mud as anodic catalyst. *Bioresource Technology*, 191, 110–116.
60. Jadhav, D. A., & Chendake, A. D. (2019). Advance microbial fuel cell for waste to energy recovery: Need of future era for sustainable development. *International Journal of Alternative Fuels and Energy*, *3*(1), 22-24.
61. Jadhav, D. A., & Ghangrekar, M. M. (2020). Optimising the proportion of pure and mixed culture in inoculum to enhance the performance of microbial fuel cells. *International Journal of Environmental Technology and Management*, *23*(1), 50-67.

62. Jadhav, D. A., Das, I., Ghangrekar, M. M., & Pant, D. (2020). Moving towards practical applications of microbial fuel cells for sanitation and resource recovery. *Journal of Water Process Engineering*, *38*, 101566.
63. Jadhav, D. A., Deshpande, P. A., & Ghangrekar, M. M. (2017). Enhancing the performance of single-chambered microbial fuel cell using manganese/palladium and zirconium/palladium composite cathode catalysts. *Bioresource technology*, *238*, 568-574.
64. Jadhav, D. A., Mungray, A. K., Arkatkar, A., & Kumar, S. S. (2021a). Recent advancement in scaling-up applications of microbial fuel cells: from reality to practicability. *Sustainable Energy Technologies and Assessments*, *45*, 101226.
65. Jadhav, D. A., Pandit, S., Sonawane, J. M., Gupta, P. K., Prasad, R., & Chendake, A. D. (2021b). Effect of membrane biofouling on the performance of microbial electrochemical cells and mitigation strategies. *Bioresource Technology Reports*, *15*, 100822.
66. Jadhav, D. A., Park, S. G., Pandit, S., Yang, E., Abdelkareem, M. A., Jang, J. K., & Chae, K. J. (2022). Scalability of microbial electrochemical technologies: Applications and challenges. *Bioresource Technology*, *345*, 126498.
67. Jain, S., Tiwari, A. K., & Mungray, A. K. (2020). Modification of clayware ceramic membrane for enhancing the performance of microbial fuel cell. *Environmental Progress & Sustainable Energy*, *39*(6), e13427.
68. James, A. (2022). Ceramic-microbial fuel cell (C-MFC) for waste water treatment: A mini review. *Environmental Research*, 112963.
69. Jana, P. S., Behera, M., & Ghangrekar, M. M. (2010). Performance comparison of up-flow microbial fuel cells fabricated using proton exchange membrane and earthen cylinder. *International Journal of Hydrogen Energy*, *35*(11), 5681-5686.
70. Jana, P. S., Ghangrekar, M. M., & Leech, D. (2018). Comparison of performance of an earthen plate and Nafion as membrane separators in dual chamber microbial fuel cells. *Environmental Engineering & Management Journal*, 17(2).
71. Janicek, A., Fan, Y., & Liu, H. (2014). Design of microbial fuel cells for practical application: a review and analysis of scale-up studies. *Biofuels*, *5*(1), 79-92.
72. Jeong, C. M., Choi, J. D. R., Ahn, Y., & Chang, H. N. (2008). Removal of volatile fatty acids (VFA) by microbial fuel cell with aluminum electrode and microbial community

identification with 16S rRNA sequence. *Korean Journal of Chemical Engineering*, *25*(3), 535-541.

73. Jimenez, I. M., Greenman, J., & Ieropoulos, I. (2017). Electricity and catholyte production from ceramic MFCs treating urine. *International journal of hydrogen energy*, *42*(3), 1791-1799.
74. Kamaraj, S. K., Rivera, A. E., Murugesan, S., García-Mena, J., Maya, O., Frausto-Reyes, C., ... & Caballero-Briones, F. (2019). Electricity generation from Nopal biogas effluent using a surface modified clay cup (cantarito) microbial fuel cell. *Heliyon*, *5*(4), e01506.s
75. Khalili, H. B., Mohebbi-Kalhori, D., & Afarani, M. S. (2017). Microbial fuel cell (MFC) using commercially available unglazed ceramic wares: Low-cost ceramic separators suitable for scale-up. *International Journal of Hydrogen Energy*, *42*(12), 8233-8241.
76. Khandelwal, A., Chhabra, M., & Yadav, P. (2020). Performance evaluation of algae assisted microbial fuel cell under outdoor conditions. *Bioresource Technology*, *310*, 123418.
77. Khudzari, J. M., Kurian, J., Tartakovsky, B., & Raghavan, G. V. (2018). Bibliometric analysis of global research trends on microbial fuel cells using Scopus database. *Biochemical engineering journal*, *136*, 51-60.
78. Khuman, C. N., Bhowmick, G. D., Ghangrekar, M. M., & Mitra, A. (2020). Effect of using a ceramic separator on the performance of hydroponic constructed wetland-microbial fuel cell. *Journal of Hazardous, Toxic, and Radioactive Waste*, *24*(3), 04020005.
79. Kumar, K., Manangath, S. P., Manju, P., & Gajalakshmi, S. (2020). Resource recovery from paddy field using plant microbial fuel cell. *Process Biochemistry*, *99*, 270-281.
80. Li, W. W., Sheng, G. P., Liu, X. W., & Yu, H. Q. (2011). Recent advances in the separators for microbial fuel cells. *Bioresource technology*, *102*(1), 244-252.
81. Liu, S. H., Chang, C. M., & Lin, C. W. (2018). Modifying proton exchange membrane in a microbial fuel cell by adding clay mineral to improve electricity generation without reducing removal of toluene. *Biochemical Engineering Journal*, *134*, 101-107.
82. Logan, B. E. (2008). Microbial fuel cells. John Wiley & Sons, DC, USA.
83. Logan, B. E. (2010). Scaling up microbial fuel cells and other bioelectrochemical systems. *Applied microbiology and biotechnology*, *85*(6), 1665-1671.

84. Martí-Calatayud, M. C., García-Gabaldón, M., Pérez-Herranz, V., Sales, S., & Mestre, S. (2015). Ceramic anion-exchange membranes based on microporous supports infiltrated with hydrated zirconium dioxide. *RSC Advances*, *5*(57), 46348-46358.
85. Massazza, D., Parra, R., Busalmen, J. P., & Romeo, H. E. (2015). New ceramic electrodes allow reaching the target current density in bioelectrochemical systems. *Energy & Environmental Science*, *8*(9), 2707-2712.
86. Mathuriya, A. S., Jadhav, D. A., & Ghangrekar, M. M. (2018). Architectural adaptations of microbial fuel cells. *Applied microbiology and biotechnology*, *102*(22), 9419-9432.
87. Me, M. H., & Bakar, M. A. (2020). Tubular ceramic performance as separator for microbial fuel cell: A review. *International Journal of Hydrogen Energy*, *45*(42), 22340-22348.
88. Meng, Y., Gao, J., Zhao, Z., Amoroso, J., Tong, J., & Brinkman, K. S. (2019). recent progress in low-temperature proton-conducting ceramics. *Journal of Materials Science*, *54*(13), 9291-9312.
89. Merino-Jimenez, I., Gonzalez-Juarez, F., Greenman, J., & Ieropoulos, I. (2019). Effect of the ceramic membrane properties on the microbial fuel cell power output and catholyte generation. *Journal of power sources*, *429*, 30-37.
90. Mestre, S., Gozalbo, A., Lorente-Ayza, M. M., & Sánchez, E. (2019). Low-cost ceramic membranes: A research opportunity for industrial application. *Journal of the European Ceramic Society*, *39*(12), 3392-3407.
91. Midyurova, B., Yemendzhiev, H., Tanev, P., & Nenov, V. (2015). Application of ceramic materials to the microbial fuel cell design. *Journal of Chemical Technology & Metallurgy*, 50(4).
92. Neethu, B., Bhowmick, G. D., & Ghangrekar, M. M. (2019). A novel proton exchange membrane developed from clay and activated carbon derived from coconut shell for application in microbial fuel cell. *Biochemical Engineering Journal*, *148*, 170-177.
93. Obasi, L. A., Onukwuli, O. D., & Okoye, C. C. (2021). Performance of microbial fuel cell operating with clay-manihot starch composite proton exchange membrane using RSM. *Current Research in Green and Sustainable Chemistry*, *4*, 100117.
94. Park, D. H., & Zeikus, J. G. (2003). Improved fuel cell and electrode designs for producing electricity from microbial degradation. *Biotechnology and bioengineering*, *81*(3), 348-355.

95. Pasternak, G., Greenman, J., & Ieropoulos, I. (2016). Comprehensive study on ceramic membranes for low-cost microbial fuel cells. *ChemSusChem*, *9*(1), 88.
96. Potter, M.C.: Electrical effects accompanying the decomposition of organic compounds, *P. R. Soc.*, 84, 260 – 276, (1911).
97. Rago, L., Zecchin, S., Marzorati, S., Goglio, A., Cavalca, L., Cristiani, P., et al. (2018). A study of microbial communities on terracotta separator and on biocathode of air breathing microbial fuel cells. *Bioelectrochemistry* 120, 18–26.
98. Ramírez-Moreno, M. J., Romero-Ibarra, I. C., Ortiz-Landeros, J., & Pfeiffer, H. (2014). Alkaline and alkaline-earth ceramic oxides for CO_2 capture, separation and subsequent catalytic chemical conversion. *CO_2 Sequestration and Valorization. InTech*, 403-441.
99. Ramirez-Nava, J., Martínez-Castrejón, M., García-Mesino, R. L., López-Díaz, J. A., Talavera - Mendoza, O., Sarmiento-Villagrana, A. …& Hernández-Flores, G. (2021). The implications of membranes used as separators in microbial fuel cells. *Membranes*, *11*(10), 738.
100. Raychaudhuri, A., Sahoo, R. N., & Behera, M. (2021). Application of clayware ceramic separator modified with silica in microbial fuel cell for bioelectricity generation during rice mill wastewater treatment. *Water Science and Technology*, 84 (1): 66–76.
101. Rodríguez, J., Mais, L., Campana, R., Piroddi, L., Mascia, M., Gurauskis, J., ... & Palmas, S. (2021). Comprehensive characterization of a cost-effective microbial fuel cell with Pt-free catalyst cathode and slip-casted ceramic membrane. *International Journal of Hydrogen Energy*, *46*(51), 26205-26223.
102. Rudra, R., Kumar, V., Nandy, A., & Kundu, P. P. (2018). Performances of separator and membraneless microbial fuel cell. In *Microbial Fuel Cell*, Springer, Cham, 125-140..
103. Sabin, J. M., Leverenz, H., & Bischel, H. N. (2022). Microbial fuel cell treatment energy-offset for fertilizer production from human urine. *Chemosphere*, 133594.
104. Salar-García, M. J., & Ieropoulos, I. (2020). Optimisation of the internal structure of ceramic membranes for electricity production in urine-fed microbial fuel cells. *Journal of Power Sources*, *451*, 227741.
105. Salar-García, M. J., Walter, X. A., Gurauskis, J., de Ramón Fernández, A., & Ieropoulos, I. (2021). Effect of iron oxide content and microstructural porosity on the performance of ceramic membranes as microbial fuel cell separators. *Electrochimica acta*, *367*, 137385.

106. Santoro, C., Arbizzani, C., Erable, B., & Ieropoulos, I. (2017). Microbial fuel cells: From fundamentals to applications. A review. *Journal of power sources, 356*, 225-244.

107. Santoro, C., Flores-Cadengo, C., Soavi, F., Kodali, M., Merino-Jimenez, I., Gajda, I., ... & Atanassov, P. (2018). Ceramic Microbial Fuel Cells Stack: power generation in standard and supercapacitive mode. *Scientific Reports*, *8*(1), 1-12.

108. Sarma, P. J., & Mohanty, K. (2022). A novel three-chamber modular PMFC with bentonite/flyash based clay membrane and oxygen reducing biocathode for long term sustainable bioelectricity generation. *Bioelectrochemistry*, *144*, 107996.

109. Sathe, S. M., Bhowmick, G. D., Dubey, B. K., & Ghangrekar, M. M. (2020). Surfactant removal from wastewater using photo-cathode microbial fuel cell and laterite-based hybrid treatment system. *Bioprocess and Biosystems Engineering, 43*(11), 2075-2084.

110. Scopus data (2022) https://www.scopus.com/ (Accessed on March 20, 2022)

111. Shainberg, I., Levy, G.J. (2005), Encyclopedia of Soils in the Environment, *Reference Module in Earth Systems and Environmental Sciences*, 27-34.

112. Sharma, I. (2017). Rapid Electrogenic Activity Determination of Anodic Inoculum and Customized Microbial Fuel Cell Treating Selected Household Organic Waste, Doctoral dissertation, IIT Kharagpur, India.

113. Sharma, I., Ghangrekar, M. M., Biswal, R. C., & Biswas, K. (2015). Bioelectrogenesis detection of inoculums using electrochromic tungsten oxide and performance evaluation in microbial fuel cells. *Journal of The Electrochemical Society*, *163*(3), F183.

114. Sophia, A. C., & Sreeja, S. (2017). Green energy generation from plant microbial fuel cells (PMFC) using compost and a novel clay separator. *Sustainable Energy Technologies and Assessments*, *21*, 59-66.

115. Sudarlin, S., Afrianto, A. W., Khoerunnisa, M., Rahmadhani, D. W., & Nugroho, A. (2020) Utilization of Montmorillonite-Modified Earthenware from Bentonite-Ca as a Microbial Fuel Cell (MFC) Membrane Based on Tempe Liquid Waste as a Substrate. *Jurnal Kimia Sains dan Aplikasi*, *23*(6), 222-227.

116. Takeda, Y., Kanai, M., Hatano, A., Yoshimi, Y., & Kida, M. (2020). A “single-use” ceramic-based electrochemical sensor chip using molecularly imprinted carbon paste electrode. *Sensors*, *20*(20), 5847.

117. Tamakloe, R. Y., Donkor, M. K. E., & Singh, K. (2017). Fabrication and study of power-output of multi-chamber microbial fuel cells (mfcs) with clay as ion exchange partition, *European Scientific Journal, 13*(30), 1857.

118. Tamakloe, R. Y., Opoku-Donkor, T., Donkor, M. K. E., & Agamasu, H. (2015). Comparative study of double-chamber microbial fuel cells (DC-MFCs) using Mfensi clay as ion-exchange-partition: effect of electrodes. *African Journal of Science, Technology, Innovation and Development*, *7*(3), 207-210.

119. Thanh, C. N. D., & Nitisoravut, R. (2015). Earthen membrane microbial fuel cell in septage treatment. *Energy Procedia, 79,* 296-300.

120. Thorne, R., Hu, H., Schneider, K., Bombelli, P., Fisher, A., Peter, L. M., ... & Cameron, P. J. (2011). Porous ceramic anode materials for photo-microbial fuel cells. *Journal of Materials Chemistry, 21*(44), 18055-18060.

121. Tremouli, A., Greenman, J., & Ieropoulos, I. (2021). Effect of simple interventions on the performance of a miniature MFC fed with fresh urine. *international journal of hydrogen energy*, *46*(67), 33594-33600.

122. Vempaty, A., & Mathuriya, A. S. (2022). Strategic development and performance evaluation of functionalized tea waste ash-clay composite as low-cost, high-performance separator in microbial fuel cell. *Environmental Technology,* 1-33.

123. Walter, X. A., Greenman, J., & Ieropoulos, I. A. (2020). Microbial fuel cells directly powering a microcomputer. *Journal of Power Sources*, *446*, 227328.

124. Walter, X. A., Madrid, E., Gajda, I., Greenman, J., & Ieropoulos, I. (2022). Microbial fuel cell scale-up options: Performance evaluation of membrane (c-MFC) and membrane-less (s-MFC) systems under different feeding regimes. *Journal of Power Sources*, *520,* 230875.

125. Walter, X. A., Santoro, C., Greenman, J., & Ieropoulos, I. A. (2019). Scalability of self-stratifying microbial fuel cell: Towards height miniaturisation. *Bioelectrochemistry*, *127,* 68-75.

126. Winfield, J., Gajda, I., Greenman, J., & Ieropoulos, I. (2016). A review into the use of ceramics in microbial fuel cells. *Bioresource technology*, *215*, 296-303.

127. Winfield, J., Greenman, J., Huson, D., Ieropoulos, I., (2013). Comparing terracotta and earthenware for multiple functionalities in microbial fuel cells. Bioprocess Biosyst. Eng. 36 (12), 1913–1921.

128. Yang, E., Chae, K. J., & Kim, I. S. (2016). Assessment of different ceramic filtration membranes as a separator in microbial fuel cells. *Desalination and Water Treatment*, *57*(58), 28077-28085.

129. You, J., Wallis, L., Radisavljevic, N., Pasternak, G., Sglavo, V. M., Hanczyc, M. M., Greenman, J., Ieropoulos, I. (2019). A comprehensive study of custom-made ceramic separators for microbial fuel cells: towards "living" bricks. *Energies*, *12*(21), 4071.

130. Yousefi, V., Mohebbi-Kalhori, D., & Samimi, A. (2017). Ceramic-based microbial fuel cells (MFCs): A review. *International Journal of Hydrogen Energy*, *42*(3), 1672-1690.

131. Yousefi, V., Mohebbi-Kalhori, D., & Samimi, A. (2018). Application of layer-by-layer assembled chitosan/montmorillonite nanocomposite as oxygen barrier film over the ceramic separator of the microbial fuel cell. *Electrochimica Acta*, *283*, 234-247.

132. Zhu, W., Liu, Y., Guan, K., Peng, C., & Wu, J. (2021). Design and optimization of ceramic membrane structure: From the perspective of flux matching between support and membrane. *Ceramics International*, *47*(9), 12357-12365.

133. Kim, I. S., Chae, K. J., Choi, M. J., & Verstraete, W. (2008). Microbial fuel cells: recent advances, bacterial communities and application beyond electricity generation. *Environmental Engineering Research*, *13*(2), 51-65.

134. Chae, K. J., Choi, M. J., Lee, J. W., Kim, K. Y., & Kim, I. S. (2009). Effect of different substrates on the performance, bacterial diversity, and bacterial viability in microbial fuel cells. *Bioresource technology*, *100*(14), 3518-3525.

135. Sayed, E. T., Abdelkareem, M. A., Bahaa, A., Eisa, T., Alawadhi, H., Al-Asheh, S., ... & Olabi, A. G. (2021). Synthesis and performance evaluation of various metal chalcogenides as active anodes for direct urea fuel cells. *Renewable and Sustainable Energy Reviews*, *150*, 111470.

136. Yang, W., Li, J., Fu, Q., Zhang, L., Wei, Z., Liao, Q., & Zhu, X. (2021). Minimizing mass transfer losses in microbial fuel cells: Theories, progresses and prospectives. *Renewable and Sustainable Energy Reviews*, *136*, 110460.

137. Choudhury, P., Uday, U. S. P., Mahata, N., Tiwari, O. N., Ray, R. N., Bandyopadhyay, T. K., & Bhunia, B. (2017). Performance improvement of microbial fuel cells for waste water treatment along with value addition: a review on past achievements and recent perspectives. *Renewable and Sustainable Energy Reviews*, *79*, 372-389.

138. Mercuri, E. G. F., Kumata, A. Y. J., Amaral, E. B., & Vitule, J. R. S. (2016). Energy by Microbial Fuel Cells: Scientometric global synthesis and challenges. *Renewable and Sustainable Energy Reviews*, *65*, 832-840.

139. Ahmad, F. N., Sazali, N., Shalbi, S., Ngadiman, N. H. A., & Othman, M. H. D. (2019). Oxygen separation process using ceramic-based membrane: a review. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, *62*(1), 1-9.

140. Midyurova, B., Bonev, B., & Nenov, V. (2017). Characterisation and performance of sediment bioelectrochemical system with ceramic separator. *Oxidation Communications*, *40* (4), 1376-1383.