Journal of
Ceramic Science
and Technology

Review

An Overview of the Functional Ceramic and Composite Materials for Microbiological Fuel Cells

A.S. Galushko[1], A.G. Ivanova[2], M.S. Masalovich[2], O.A. Zagrebelnyy[2], G.G. Panova[1], I.Yu. Kruchinina[2, 3], O.A. Shilova[*2, 3]

[1]Agrophysical Research Institute, Grazhdanskiy pr., 14, Saint Petersburg, 195220, Russia
[2]Institute of Silicate Chemistry of Russian Academy of Sciences,
nab. Makarova, 2, St. Petersburg, 199034, Russia
[3]Saint Petersburg State Electrotechnical University "LETI",
ul. Prof. Popova, 5, St. Petersburg, 197376, Russia

Abstract

This review covers the contemporary state of a problem concerning the selection and usage of ceramic materials for fabricating the basic functional components (anode, cathode and membrane-separator) of microbiological fuel cells (MFCs). Electrogenesis on the surface of electrodes prepared from ceramic materials is analysed. The electrochemical and catalytic processes taking place on the surface of ceramic and composite electrode materials, functions and peculiarities of the membrane-separator structure and conductivity are evaluated in detail for the first time. The advantages and drawbacks of using ceramic materials for the fabrication of functional components of MFCs and the methods of their synthesis are analysed.

Keywords: Microbiological fuel cells, bioelectrogenesis, ceramic and composite anode materials, ceramic and composite cathode materials, ceramic and composite separating membrane

I. Introduction

Microbiological fuel cells are prospective bioelectrochemical devices able to facilitate and improve the quality of human life as they can utilize wastes, waste water, and different organic substrates by converting them into power and pure drinking water without significant expense. At present, commercially available microbiological fuel cells (MFCs) are not produced on a large scale because a number of problems obstructing their introduction in manufacture have not been resolved [1-3].

These problems include limited power generation, which is directly caused by low-efficiency electron transport from exogenous bacteria to the anode surface as well as by bacteria energy expenditure for maintaining their own metabolism; high cost of separators and catalytic electrode materials; the necessity of prolonged maintenance of the bacteria cells in active state; the necessity of protecting the electrodes from severe fouling, which reduces the efficiency of electron transport to the anode. To solve these difficult problems requiring an interdisciplinary approach, intensive R&D work has been conducted in the world scientific arena.

Diverse substances and materials are generally used as the functional elements for MFCs: carbon materials (carbon black, nanotubes, graphene, etc.), electroconductive poly-

mers and composite materials on the basis of polymers and metal oxides. In the present review, ceramic materials are considered in detail as the basic functional elements for MFCs. Ceramic materials are known to be conventionally used for the fabrication of electrode and electrolyte materials of solid oxide fuel cells (SOFCs) [3-6].

MFCs on the basis of carbon materials have so far been advanced furthest. At the same time, interest in ceramic materials as functional elements for the MFCs is growing [7,8]. In the paper [9], ceramics are shown as an excellent material for advancing MFCs. Ceramic-based separators are comparable with conventional ion exchange membranes and also considerably less expensive. Meanwhile the opportunities of ceramics for electrode material fabrication have not been highlighted enough.

In the present review, the ceramic materials with best prospects for use as anodes, cathodes or membrane-separators are shown within a broad scope. Moreover, the interacting processes of the ceramic materials and bacteria as well as the validity and feasibility of the choice of the ceramics for the fabrication of MFC are discussed.

To begin the review, the fundamentals of power generation by microorganisms is briefly discussed and the structure of a MFC described.

---

* Corresponding author: olgashilova@bk.ru

II. Bacterial Electrogenesis, Microbial Fuel Cells and Compatibility with Ceramic Materials

The fundamental feature of microorganisms capable of performing the respiratory type of metabolism is vectorial electron transfer. That means that basically all of them are electroactive and have the capacity to generate an intercellular current, and under special circumstances may generate the current in the extracellular environment. The electrogenic property is used in the development and operation of microbial fuel cells (MFCs). Thus, an MFC is an electrochemical device that converts the chemical energy of organic compounds via metabolic action of the microorganisms to electrical energy. Microorganisms deliver electrons released during oxidation of organic matter to an anode. These electrons are utilized for reductive chemical or biochemical processes on a cathode [10, 11]. Anode and cathode compartments of a MFC are typically separated by a proton exchange membrane although that causes several operational problems [12–15]. The usage of other types of ion exchange membranes may also sustain or even improve the electrochemical performance and operation of bioelectrochemical systems of different types [16–18].

Microbiological electricity generation is a relatively new area of bioenergy production that has been developing rapidly within the last couple of decades [19], although the history of the electrical activity of microorganisms started more than 100 years ago [20]. The discovery of electrical properties of plants and animals led to understanding that the disintegration of organic compounds as the necessary source of energy by microorganisms was accompanied by the release of electrical energy [20]. Not much attention was paid to this field until the second half of the 20th century. At that time, the biology of electrical current generation was confined to studies of enzymes and extracellular electron transfer via mediators – redox-active compounds able to transfer electrons to the anode [21–24]. The reason for this was that normally intact cells of microorganisms were electrochemically inactive since the cell surface was covered by non-conductive structures and the release of internal electrons into the environment was occurring mostly by means of mediators that might penetrate into periplasm or cytoplasm and in reduced state transfer electrons on an anode into the extracellular environment [25, 26].

The interest in MFCs has sharply increased within the last 15–20 years owing to the discovery of new species of microorganisms capable of growing by intercellular organic compounds oxidation coupled to the electron transfer to external electrons acceptors, including water-insoluble ones [27]. It has been found that such microorganisms are able to transfer electrons onto extracellular solid compounds: iron(III) oxides, electron-conducting anodes [28–30]. The addition of electron shuttles mediating the electron transfer has not been required [12, 28–31]. Power density of the MFCs based on the latest discoveries has been increased by several orders of magnitude [11].

At present, it is considered that biological electricity could be generated by any biodegradable matter [11, 32]. In laboratory studies, glucose, acetate and lactate are traditionally used [32]. It has been assumed that only in some cases the complete degradation of the organic substrates occurs via reactions of the citric acid cycle. Indeed, complete oxidation of organic substrates by *Geobacter* spp. proceeds via the citric acid cycle and net ATP synthesis occurs exclusively through electron transport phosphorylation [12, 33]. The average redox potential of the oxidation steps in the citric acid cycle is around -247 mV. Another known pathway of acetate oxidation via CO dehydrogenase has a much lower average redox potential (-339 mV; all values are given for pH 7.0 [34]). This pathway might also be potentially beneficial for an MFC if electrons released from acetate oxidation were transferred to the anode via mediators or components of electron transport chain with a lower redox potential than $NAD(P)^+$ (Nicotinamide Adenine Dinucleotide (Phosphate)) [35]. Under anoxic conditions, species of the genus *Shewanella* normally degrade lactate to acetate incompletely [36]. Recently, it has been reported that the complete citric acid cycle could be switched on in the electrode potential-dependent mode in the cells of several strains of *Shewanella* spp. under MFC conditions [37, 38, 39].

Despite intensive investigations, mechanisms of electron transfer onto the anode are not fully understood. At present, two possibilities are considered for direct and indirect electron transfer onto the anode. Direct electron transfer (DIET) assumes direct contact of the terminal components of the electron – transport chain with the anode surface [40, 41]. That might occur via physical contact of the cell and anode surfaces. Another DIET hypothesis does not require surface contact but the electron transfer occurs via so-called nanowires – the type IV pili that are connected to the cell surface. In this case the distance between cells and the anode surface might be in the range from several "micrometers" up to few millimeters [42–48]. Both DIET cases require the presence of Mtr (metal reducing) respiratory complex that perform the delivery of electrons from cytoplasm to the external side of the outer membrane [39, 41, 49]. The problem of electron delivery via nanowires has not been completely elucidated to date either. In the last years, many studies with pro- and contra-arguments have been published on the subject [50, 51]. However, positive results are accumulating proving the pili hypothesis [52] for the case of *Geobacter* spp. and extended periplasm covered with outer membrane enriched with cytochromes for the *Shewanella* spp. case [51, 53, 54]. For example, it was shown that only pili consisting of short-chain monomers had the capacity to mediate the transfer of electrons via metallic-like conductivity that might be attributed to overlapping π-π orbitals of key aromatic amino acids [54, 55]. Electron transfer via conjugated double bonds was considered to facilitate the progress in the development of enzymatic fuel cells [56].

Indirect electrons transfer (iDIET) from microorganisms to the electrodes is performed by means of electron shuttling mediators. The mediators are reversibly redox active compounds that are added from outside or excreted by microorganisms themselves [25, 26]. These mediators are needed to make electron transfer to the anode possible in the case of non-exoelectrogenic microorganisms but also in the case of DIET microorganisms [57].

Natural microbial communities and pure cultures of microorganisms can generate electrical current as well [32, 58, 59]. The electrogenic property has been discovered within representatives of several classes of Proteobac-

teria, Firmicutes, Acidobacteria and others [11,32,60]. At present 69 species of microorganisms have been reported to be able to transfer electrons to the anode [59]. Unfortunately, up until now only representatives of Deltaproteobacteria and Gammaproteobacteria, namely species of genera *Geobacter* and *Shewanella*, respectively, have been investigated in detail for their capacity to generate electricity in MFCs. Surprisingly, not all known *Geobacter* spp. are equally efficient in current generation [61]. It is still unclear how microorganisms of various phylogenetic groups may generate electrical energy, for example, how Firmicutes can deliver electrons to anodes since they lack outer membranes [35,59,62,63].

The microbiological fate of electrons delivered to the cathode from the anode has also been attracting considerable attention since the graphite electrodes were discovered to serve as electron donors for bacteria [64]. Chemical reduction of molecular oxygen was for a long time the option for the cathode department of MFC. In recent years, the concept of microbially mediated reduction of various electron acceptors (including molecular oxygen reduction) via MFC cathodes has been developing [14,26,65–67]. In general, the same principles of the DIET and iDIET mechanisms of the electron transfer to the anode may be applied in the case of MFC cathodes [26,67]. However, this question is still under investigation and it is generally envisioned that phylogenetic diversity of electrotrophic microorganisms and mechanisms in microbioelectrochemical systems could be even broader than in the case of electrogenesis [26,59]. The microorganisms capable of using solid compounds as electron donors enlarge the group of electroactive microorganisms. However, not all of these microorganisms might be very efficient in the MFC since the prerequisite for MFC operation is a sufficiently high redox potential of the electron acceptors used by these microorganisms to allow current generation [67].

Since MFC operation strictly depends on the activity of living cells, the composition of electrolytes in the MFC compartments should be suitable to maintain the metabolic health of the microorganisms [68]. On the other hand, higher salinity of electrolyte is considered beneficial for current generation owing to the higher conductivity [69]. Considering both trends, it is clear that certain species of electroactive microorganisms would optimally operate only at a restricted range of salts concentration in the electrolyte. Thus, low NaCl content in the anode compartment of a MFC operated with acetate would be beneficial for current generation by *Geobacter*-like freshwater species [68]. Increase of NaCl content to the marine level would benefit the growth of the marine acetate-oxidizing species of *Desulfuromonas* spp. [70]. The latter microorganisms are metabolically similar to *Geobacter* and are adapted to live in brackish and marine sediments, subsurface brines [71–74]. A *Geobacter* strain tolerant to the higher NaCl content is also known [75]. Other compounds of electrolyte may also influence the performance of MFCs. Thus, phosphate and carbonate ions stimulate power production [76].

At present, short- and long-term application of MFCs may be preferred for industrial areas that do not require large currents and intensive reactors [19,77].

The theoretical and constructive sides of the MFC concept are currently developing. One of the directions in the creation of more effective MFCs is the application of new materials in the construction of MFC elements. Such prospective materials include ceramic-containing candidates. The benefit of using ceramic materials is that they are not toxic for aerobic and anaerobic microorganisms and are used in wastewater treatment reactors as supporting [78,79] or filtering [80] materials. Furthermore, application of ceramics in the design of MFC electrodes is beneficial for MFC operation [81].

III. Electrochemistry of Interaction between Bacteria and Ceramic (Composite) Anode Materials

The anode material is known to contribute significantly to the high efficiency of an MFC as it provides the interaction between the bacterial layer and the anode surface, which in turn determines the amount of power produced.

As a rule, diverse carbon allotropic modifications (graphite, graphene, carbon black, nanotubes, etc.) are used as anode materials [82–90]. The popularity of carbon materials can be attributed to the low cost, large surface area and high conductivity, biological inertness, chemical stability and catalytic activity. Nevertheless, the carbon material is not universal as its electrical activity that influences the electron transport from the bacterial cell to the anode is low [2].

Thus, at present, an active search for the anode material corresponding to the listed criteria is being conducted. The analysis of numerous publications shows that the significant research interest is focused on the synthesis and research of ceramic powders, films, coatings and composites based on them as parts of a MFC [9].

In general, the tested ceramic anode material may be divided into three main groups, which are discussed in the following subsections.

(1) Ceramic catalytic conductive material for the MFC anode

The authors [91] obtained porous ceramics on the basis of titanium oxide based on a template synthesis. Then they covered the ceramics with the conductive ceramic film consisting of fluorine-doped tin oxide (FTO) by means of chemical vapour deposition. The resistance range of the ceramic material reached 10–15 Ω. Then a *Chlorella vulgaris* biofilm was grown on the fabricated anode of the experimental MFC. Finally, the power density of the experimental MFC with the ceramic anode was 16 times higher than that of the standard MFC with a carbon anode. The substantial enhancement of the performance of the experimental MFC is probably caused by the effective biofilm growth on the ceramic anode surface [91].

The authors [92] described the anode made of the porous conductive ceramics $M_{n+1}AX_n$, where n=1-3, M–transition metal, A-a 3^d or 4th subgroup element of Mendeleev periodic table, X–carbon or nitrogen. Thus, the anode material Ti_2AlC synthesized with a template method possesses a total porosity of 60–70 %, high conductivity up to $\sim 3 \cdot 10^4$ S/cm and is peculiar owing to its strength and resistance to corrosion. These are the main characteristics of the material demonstrating the advantages of such a MFC anode. The authors had the intention

to test the ceramic anode in the presence of electroactive bacteria and expected positive results in the future. Lately, considerable attention has been paid to the ceramic materials based on transition metal carbides and nitrides, which have the reputation of the materials with chemical stability, rigidity and high conductivity (Table 1). Moreover, the carbides possess high catalytic activity.

Table 1: The electrical conductivity of some metal carbides [93] and metal nitrides [94].

Carbides	Bulk resistivity, $\mu\Omega\cdot$cm	Nitrides	Bulk resistivity, $\mu\Omega\cdot$cm
TiC	52,5	TiN	27
ZrC	50	ZrN	24
HfC	45	HfN	27
VC	76	VN	65
TaC	24	NbN	60
Cr_3C_2	75	CrN	640
Mo_2C	71		
W_2C	75.5		
WC	19.2		

In the research paper [95, 96], tungsten carbide was reported to demonstrate high catalytic activity towards a number of organic compounds such as formic acid, formaldehyde, acetic aldehyde, propylaldehyde, acetylene and ethylene. This indiciates the possibility of using tungsten carbide as a MFC anode material to catalyse the decomposition of the microbial waste.

The anode material Mo_2C obtained with a chemical method at the temperature of 900 °C; in argon medium was shown to demonstrate high catalytic activity [97]. The maximum power density of the MFC with *Klebsiella pneumoniae* as a biocatalyst reached 2.39 W·m^{-3}, which was significantly higher than the specific power of the MFC with the anode material of carbon felt – 0.61 W·m^{-3}. Moreover, the analysis of cyclic voltammograms (CVAs) of the test electrochemical system fabricated from the Mo_2C coated electrode, electrolyte with the substrate (glucose) and the biocatalyst – *Klebsiella pneumoniae* revealed two anodic peaks. These peaks may indicate oxidation of microbial fermentation products like formiates and lactates. At the same time, the CVAs of a similar electrochemical system but with an unmodified electrode did not have these oxidation peaks. Therefore, it is molybdenum(II) carbide that catalyses the oxidation process of microbial fermentation waste. Besides, it had been previously revealed [98] that Mo_2C encouraged the direct electron transfer from the biofilm to the electrode. Thus, the Mo_2C anode coated with *Klebsiella pneumoniae* catalyses two processes of the direct oxidation of microbial fermentation products and the direct electron transfer from the bacteria to the electrode.

The electrochemical performance of an experimental MFC with the anode fabricated from the ceramic powder Ni_3Mo_3C was studied in the other paper by the same authors. The ceramic powder was obtained by means of chemical synthesis with the use of the biocatalyst *Klebsiella pneumoniae* (Fig. 1) [99]. It can be seen from Fig. 1 that the MFC maximum power is 2.230 W·m^{-3} (0.250 W·m^{-2}), which is significantly higher than the MFC power with the carbon felt anode – 0.070 W·m^{-2}.
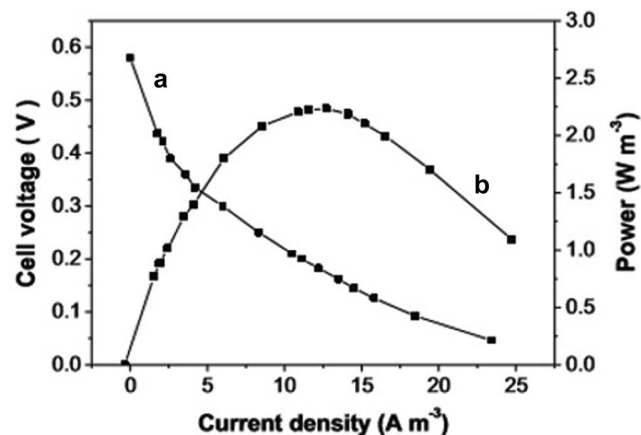

Fig. 1: Polarization (a) and volumetric power output (b) curves of the cube MFC with Ni_3Mo_3C (catalyst load 3.0 mg·cm^{-2}) (after [99]).

It is worth mentioning that the anode ceramic material based on Ni/β-Mo_2C catalyses three processes in a test MFC: 1) oxidation of fermentation products; 2) electron transfer from the biofilm to the electrode; 3) electron transfer from the electron carrier (2,6-di-rubs-butyl-p-quinone produced by *Klebsiella pneumoniae*) to the anode (Fig. 2) [100].

The search for the literature referring to metal nitrides as a MFC anode material has not returned any results. Nevertheless, this catalytic material is effectively applied for electrode modification in a low-temperature polymer electrolyte membrane fuel cell (PEMFC) and performs high catalytic activity. The evidence points out its potential application as a MFC anode modifier [94].

Therefore, the ceramic materials possessing catalytic activity and intrinsic conductivity are a suitable prospect for application as anodes in MFCs. And the more so as the overwhelming part of these materials has not been tested yet in experimental MFCs with diverse species of bacteria.

(2) Ceramic catalytic material being a part of a composite

A great number of research papers are devoted to composite anode materials for MFCs [81, 101–107].

The composite materials may be divided in relative groups as follows:
a) the composites of transition or non-transition metal oxides with carbon (carbon black, nanotubes, graphene, graphene oxide, doped carbon, etc.);
b) the composites of transition or non-transition metal oxides with conducting polymers (polypyrrole, polyaniline, polythiophene);
c) the composites of transition or non-transition metal oxides with conducting polymers, carbon and its derivatives, and transition metal nanoparticles;
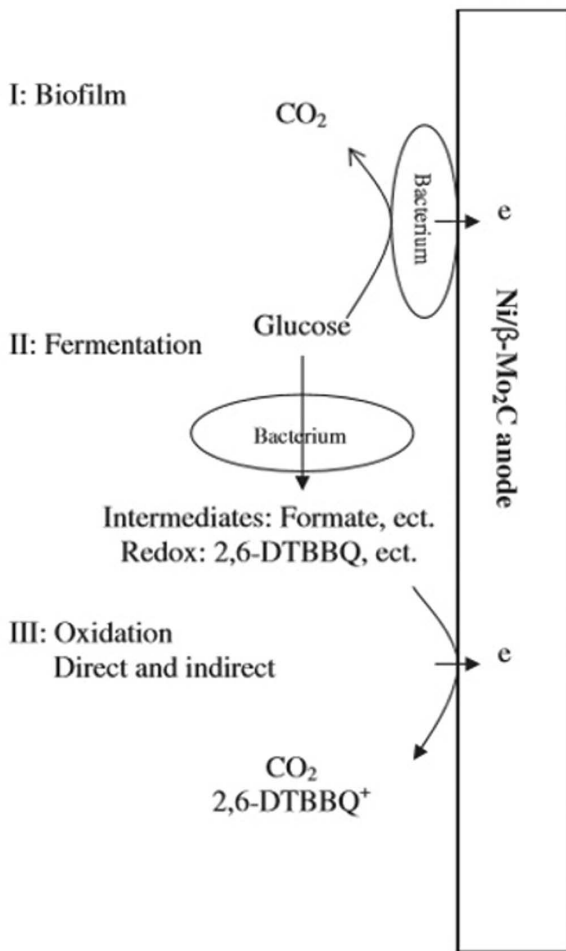d) the composites of conducting polymers with carbon.

Fig. 2: Schematic mechanism for electricity generation by K. pneumoniae on anode of MFC (after [100]).

the electrode, biocompatibility and the synergetic effect because of the interaction between graphene and tin(IV) oxide [108]. All listed above encouraged fast formation of a stable bacterial film.
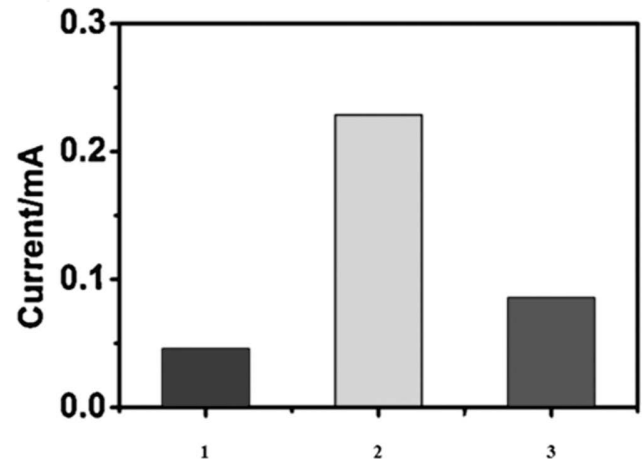

Fig. 3: Current obtained from bare carbon paper electrode with E. coli, CNT/Au/TiO$_2$ -1, nanocomposites modified carbon paper electrode with *E. coli* -2 and without *E. coli* -3 (after [107]).
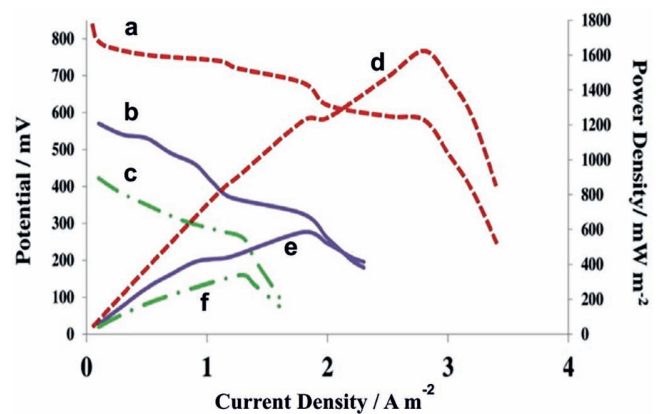

Fig. 4: Polarization curves for RGO-SnO$_2$/CC (a), RGO/CC (b) and bare CC (c); power density curves for RGO-SnO$_2$/CC (d), RGO/CC (e) and bare CC (f). Linear sweep voltammetry was applied for polarization tests at a scan rate of 0.1 mV·s^{-1} (after [108]).

As seen from the list, the composite should contain a material with intrinsic conductivity. As a rule, this function is carried out by carbon materials.

The anode material with a three-dimensional nanostructure is known to have been fabricated from the carbon nanotubes/Au/TiO$_2$ [107]. This composite anode demonstrated high conductivity, high porosity and specific surface area, which guaranteed easy absorption of *Escherichia coli*. Moreover, the modified anode had a more hydrophilic surface in contrast to the unmodified carbon paper (the edge angle of wetting is 90° versus 110°), which contributed to the effective adhesion of the bacterial film. Finally, the estimated power density of the testing MFC reached 2.4 mW·m^{-2}, which was three times higher than that of the MFC with the carbon paper anode. The nanocomposite anode performed higher catalytic activity in the reaction of glucose oxidation both in the presence as well as in the absence of bacteria than the carbon paper (Fig. 3) [107].

The composite anode material based on the reduced graphene oxide-SnO$_2$/carbon fibre where tin(IV) oxide had been obtained by a microwave synthesis significantly influenced the *Escherichia coli* bacterial film formation rate [108]. The power of the test MFC with the modified anode reached 1.624 W·m^{-2} (Fig. 4). This value was 4.8 times higher than that of the unmodified anode. The performance improvement of the MFC with the nanocomposite anode was explained based on the large surface area of

The composite anode made of SnO$_2$ nanotubes/glass carbon increased the maximum power density of an MFC up to 1.421 W·m^{-2} in the presence of *Escherichia coli* [103].

Another nanocomposite material of Fe$_3$O$_4$/carbon nanotubes obtained by means of precipitation of monodisperse Fe$_3$O$_4$ particles onto nanotubes with the solvothermal method may contain different mass percentages of Fe$_3$O$_4$ varying from 10 to 80 %. Finally, the composite anode fabricated from 30 % Fe$_3$O$_4$ nanotubes/carbon paper demonstrated the highest power density of an MFC in the presence of *Escherichia coli*. It demonstrated 0.830 W·m^{-2} [101], which was approximately 40 times higher than the power density of the anode made of unmodified carbon paper. The authors considered the high performance of the test MFC to be caused by the improved bacteria adhesion to the electrode surface as well as by the increase in electron transfer efficiency from the biolayer to the anode.

The composite anode material WO$_3$/C felt, where tungsten(VI) oxide was obtained by means of hydrothermal

synthesis, demonstrated high power density values for the test MFC with *Shewanella putrefaciens*. Moreover, the received data are very close to the anode material characteristics of the anode material of WO_3-Pt/C: 1.3 W·m^{-2} versus 1.5 W·m^{-2} [109]. The actual mechanism of the interaction between bacterial cells and the anode surface modified with tungsten(VI) oxide is not clear. Nevertheless, there are data confirming that WO_3 encourages regular fixation of the bacteria to the electrode surface owing to the large surface area. Besides, WO_3 is a more biocompatible material than the carbon material [110, 111]. Moreover, tungsten(VI) oxide interacts with the proteins produced by *Shewanella putrefaciens* or situated on the membrane surface of the bacterial cell. This contributes to the intensity of the electron transport from the biofilm to the MFC anode [103].

The MFC with the composite anode containing a conducting polymer also shows high electrical performance. The polyaniline-mWO$_3$/C felt-based anode tested with *E.coli* as a biocatalyst demonstrated power density of 0.98 W·m^{-2} [112].

A composite anode also fabricated on the basis of felt carbon was discussed in the paper [113]. Cerium(IV) oxide was used as the ceramic part of the composite. To obtain a homogeneous mixture, the oxide was mixed with carbon ultrasonically. Finally, the MFC with the composite electrode demonstrated higher power density performance of 2.94 W·m^{-2} in contrast to 1.70 W·m^{-2} for the unmodified carbon material (Fig. 5). The exogeneous populations of bacteria were used as a biocatalyst.
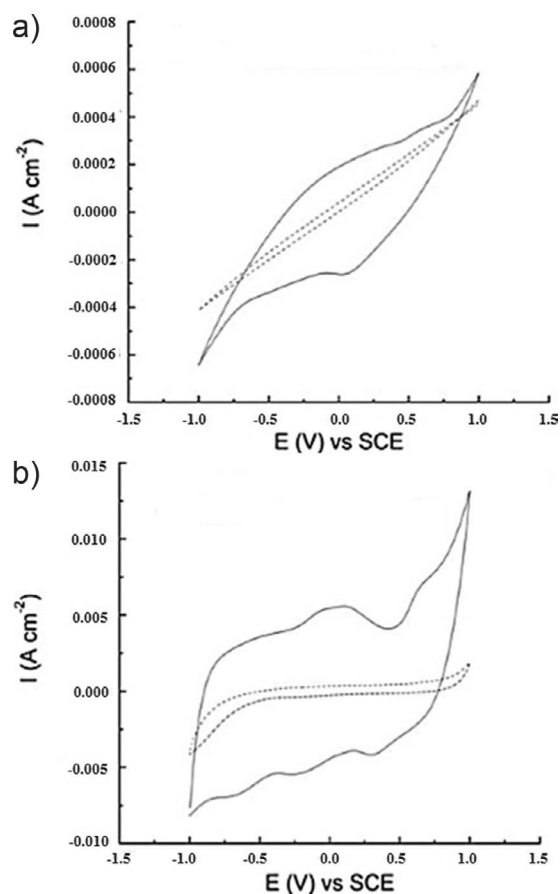

Fig. 5: Cyclic voltammograms for carbon felt (a) and nano-CeO$_2$ modified carbon felt (b) in PBS (phosphate buffer solution) and activated exoelectrogenes suspension lacking substrate (after [113]).

Thus, it is necessary that a ceramic powder should be a part of a composite in the anode of a MFC. This powder may not possess intrinsic electron conductivity, but is supposed to have high catalytic activity, biocompatibility and large surface area.

(3) The ceramic material deposited on the surface of a conducting support as a film

It should be noted that the ceramic material possessing intrinsic conductivity as well as ceramic-based composite material can be fabricated in the form of a bulk electrode or a film deposited onto a conductive support. That is why the classification of the ceramic materials discussed in subsections (1) and (2) of Section III is facultative.

The conventional conductive supports are listed in Table 2.

For instance, the anode material may consist of ruthenium(IV) oxide deposited electrochemically onto a carbon support [104]. The experimental MFC with *Shewanella decolorationis S12* reached the maximum power density of 0.308 W·m^{-2} while RuO_2-covered anode had the specific capacitance of 50 C·cm^{-2}. Meanwhile, the unmodified carbon support had the specific capacitance of about 0.1 C·cm^{-2}. Hence, the power density of the test MFC with the unmodified carbon anode is 16.7 times less than that of the modified one (Fig. 6). The authors of the paper consider the high performance of the testing MFC to be the consequence of the large surface area of the anode material as well as the capability of the ruthenium(IV) to be oxidized and reduced quickly, which contributes to the effective electron transfer from the biolayer to the anode and vice versa if necessary.

Table 2: Electrode materials for MFCs [114].

Anode material	Advantages	Disadvantages
Stainless steel	High conductivity, cheaper, easy accessibility	Low surface area, biocompatibility issues, corrosion
Graphite rod	High conductivity and chemical stability, cheaper, easy accessibility	Difficult to increase surface area
Graphite fibre brush	High specific area and easy construction	Clogging
Carbon cloth	Large relative porosity	Relatively expensive
Carbon paper	Easy wire connection	Fragile
Carbon felt	Large surface area	High resistance
RVC (reticulated vitreous carbon)	High electrical conductivity	Fragile, large resistance

Peng *et al.* [105] developed the anode coating on the basis of Fe_3O_4 (its intrinsic conductivity is up to $2 \cdot 10^2$ S/cm) and activated carbon. This mixture was applied to the stain-

less steel with the roll printing method. The MFC with the modified electrode AcFeM where Ac – activated carbon, M – steel mesh, in the presence of dissimilatory metal-reducing bacteria showed good specific capacitance, reaching the maximum of 574.6 C·m^{-2} in contrast to the MFC with the unmodified anode (AcM) (Fig. 7). The authors associate the MFC high capacitive performance with the facilitated electron transfer from the bacterial layer to the anode owing to the oxidation-reduction pair Fe_3O_4/Fe^{2+} working as an electron shuttle.
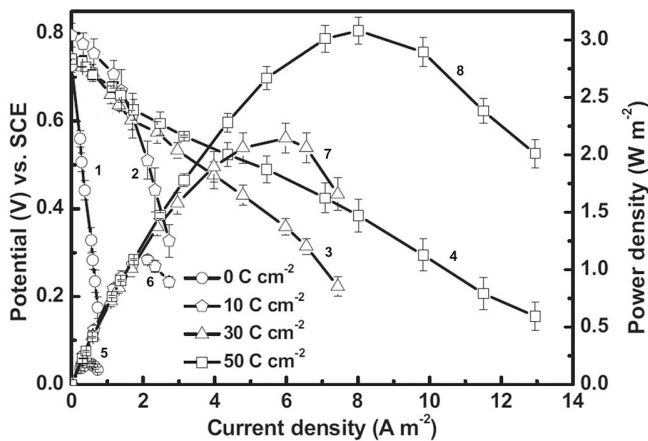

Fig. 6: Cell polarization (1, 2, 3, 4) and power density (5, 6, 7, 8) curves of four MFCs inoculated with *S. decolorationis* S12 varying in anodes modified with different RuO_2 surface concentration. The applied charge density for the formation of RuO_2 contained in four anodes was 0, 10, 30 and 50 C·cm^{-2}, respectively. The data point shown represents the average of triplicate measurements obtained from three independent experiments ± standard deviations (after [104]).
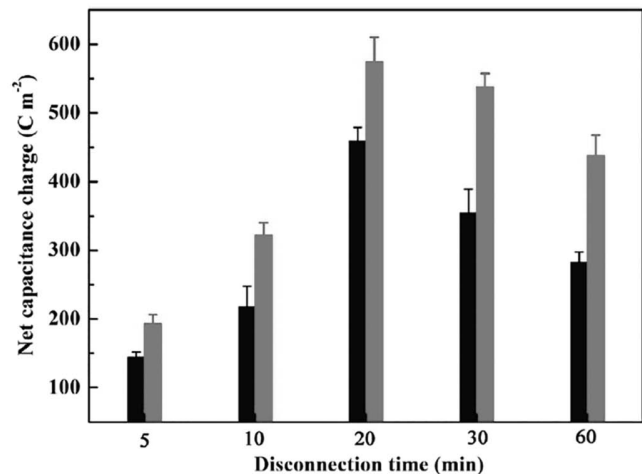

Fig. 7: The amount of net storage capacity (AcM – black, AcFeM – red) at each disruption time based on the charge-discharge experiment. Error bars ± SD were based on averages measured (after [105]).

In the research paper [115], a paste of manganese(IV) oxide and polypyrrole (a conducting polymer) composite obtained with a chemical method was applied to titanium wire covered with adsorbed felt carbon. Finally, the maximum power density of the MFC with the modified anode in the presence of sea bottom bacteria reached the value of 0.562 ± 5 W·m^{-2}, which was 2.2 times higher than the MFC power density with the unmodified anode. As seen from Fig. 8, the specific capacitance of the modified electrode is 3.1 times higher than that of the unmodified one.
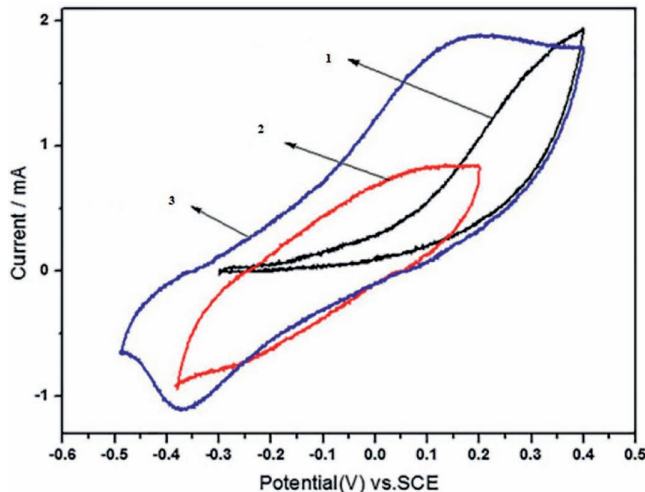

Fig. 8: Cyclic voltammetry plots of different electrodes: 1 – unmodified, 2 – polypyrrole, 3 – MnO_2/polypyrrole (after [115]).

A possible mechanism of electron transfer from the bacteria to the anode surface is suggested in Fig. 9. Manganese(IV) oxide is an electron carrier. The conducting polymer facilitates the electron transport owing to the oxidation-reduction activity. All this causes a high power density performance of the test MFC.
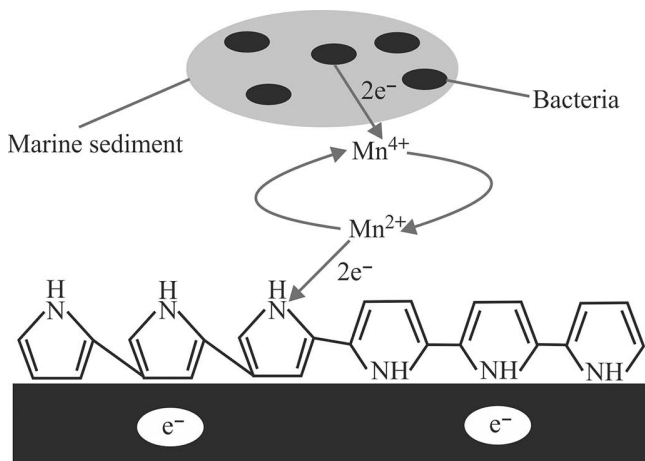

Fig. 9: Electron transfer mechanism of modified anode – polypyrrole/MnO_2 (after [115]).

Thus, ceramic anode materials significantly improve the electric performance of MFCs owing to their high catalytic activity, biological inertness, electrochemical stability and high energy capacitance.

IV. Ceramics as Cathode Functional Material

In terms of functioning, ceramics used for cathodes can be assigned two main purposes: supporting and catalytic functions.

(1) Ceramics as supporting material

The supporting function is based on the mechanical stability of calcined materials, biological compatibility with bacteria and high porosity. A number of publications is devoted to the use of natural ceramic materials such as terracotta, earthenware, Trojan clay, etc. in open-to-air cathodes [9–120]. Such cathodes play a double role, being simultaneously membranes in single-chamber MFCs. In this

section, the natural ceramic cathode materials operating primarily as supports are not discussed as they will be considered below in Section V devoted to membranes.

Nevertheless, it is worth mentioning that some ceramic powders like TiO_2 can be used instead of carbon as supports for cathode catalysts (Pt). The search for alternatives to carbon is necessitated by a number of its disadvantages [121, 122]. One of them is significant hydrophilicity, which results in deteriorated mass transport properties of a gas diffusion layer in open-to-air cathodes. This is of importance as the air contacting with the catalyst should remain humidified, otherwise ionic conductivity and catalytic activity will be worsened and MFC performance impaired.

Another drawback of carbon is a tendency to corrode, which leads to the worsening of the contact between the support and the catalyst particles. The particles consequently become more mobile and form larger aggregates or migrate out of the layer. In contrast to carbon, although TiO_2 possesses lower conductivity with a band gap of 3.2 eV for anatase and 3.0 eV for rutile, it shows more uniform dispersion of metal particles (Pt), improved corrosion resistance, higher catalytic stability and activity owing to its alloy formation with Pt [121, 123].

Venkatesan *et al.* (2016) [121] obtained TiO_2-supported metal nanocatalysts (Pt/TiO_2) with the liquid phase photo deposition method followed by calcination at 450 °C for 3 h. The cathode materials – Pt/TiO_2, Pt-Fe/TiO_2 and Pt/C – were tested in a single-chamber MFC to show the power densities of 110.5, 136.8 and 77 mW/m² respectively, thus, demonstrating a better performance of Pt-composites with titanium (IV) oxide support compared to that with carbon support. Besides, cyclic voltammetry experiments revealed a higher electrochemical stability of TiO_2 after 200 cycles than carbon.

The alternative materials including semi-conductive oxides (TiO_x, WO_x and SnO_2) or carbides [124] instead of carbon as support are in practice for polymer electrolyte membrane fuel cells (PEMFCs).

(2) Ceramics as catalytic material

Catalytic function is undoubtedly the major property of cathode materials as it determines the efficiency of molecular oxygen binding. Protons are transferred from the anode to the cathode through the membrane and electrons reach the cathode through the external circuit to reduce the molecular oxygen. Therefore, the need arises for a mediator hastening the reduction reaction. This role is played by catalysts owing to the presence of atoms/ions capable of changing their oxidation state and, hence, leading to intermediate bond formation.

Precious platinum has been considered the most effective catalyst so far. Thus, research has been directed towards finding new commercially available, effective catalytic materials capable of replacing the more expensive platinum. Numerous publications are devoted to the catalytic activity of thermally processed metal oxides and their composites along with metal compounds enriched with carbon and nitrogen, in oxygen reduction reactions (ORR) taking place at cathodes [125–183].

The spectrum of cathode catalytic materials is enormously wide. Hereafter, primarily heat-treated materials possessing crystalline structure and therefore qualifying as ceramics are highlighted.

(a) Metal oxides and composite materials based on them as catalysts

Manganese oxides are the most popular ORR catalysts among other oxide compounds owing to their low cost, abundance, non-toxicity, environmental safety and high catalytic activity [126]. The popularity is caused by the fact that manganese in oxides can adopt a variety of crystal structures and may exist in different valence states of 2+, 3+ and 4+. In the review [126], Stoerzinger, *et al.* (2015) considered the ORR kinetics for manganese(IV) oxide obtained by means of different techniques including hydrothermal methods and annealing steps. Crystal structures like perovskites and spinels were observed. It was presumed that the charge transfer process proceeded primarily via a four -electron route.

Li *et al.* (2010) [127] reported on a hydrothermally obtained (180 °C, 48 h) cryptomelane-type octahedral molecular sieve (OMS-2) structured from MnO_2 in a paper-like shape which was a better conductor than a bulk OMS-2 powder cathode because of its microporous network. Besides, catalytic performance of the composites Co-OMS-2, Cu-OMS-2 and Ce-OMS-2 was also determined and examined. The research revealed that among undoped and doped cathode catalysts, Co and Cu composites exhibited the best power generation with voltages of 217 mV and 214 mV respectively (in comparison with Pt catalyst producing 202 mV), although the maximum power densities attained by the materials were still below Pt catalyst performance.

In later research [128], Li *et al.* conducted 600-h continuous flow tests demonstrating that the fast reaction rate of OMS-2 cathodes enhanced power generation and chemical oxygen demand (COD) removal efficiency. Co-OMS-2 cathodes had the better performance than Cu-OMS-2 at high COD concentrations of 2000–4000 mg/L, with the power density of 897 mW/m² and COD removal efficiency of 46 %. Meanwhile, Cu-OMS-2 cathode was more suitable at low COD concentrations (1000 mg/L) exhibiting the highest power density of 201 mW/m².

Zhang *et al.* (2009) reported about three modifications of $MnO_2 – \alpha$, β and γ-structures [129]. β-structure was synthesized hydrothermally at 125 °C for 24 h followed by sintering at 300 °C for 5 h. The other α-and γ-structures were also obtained with the solution-based hydrothermal method, but without subsequent calcination. The results showed that α-MnO_2 tended to be of low crystallization extent and amorphous structure, and γ-MnO_2 was microspherical and tended to be agglomerated. Meanwhile, β-MnO_2 appeared in loose and claviform form, which contributed to it having the largest BET surface of the three samples. Hence, it was the β-MnO_2 that caused the highest MFC voltage, close to that for the MFC using Pt as catalyst (627 ± 18 mV). The maximum achieved output power was 3773 ± 347 mW/m³, and the maximum current density was 20 400 mA/m³ when a tube-type MFC con-

struction was used. The data on the high catalytic activity of β-MnO_2 in ORR are in accordance with Lu *et al.* (2011) [130].

Liu *et al.* (2010) [131] reported about nanostructured MnOx with the controllable size and morphology which could be readily obtained with the electrochemical deposition method. The MFC on the basis of such a cathode catalyst can generate electricity with the maximum power of 772.8 mW/m^3. Zhang P. *et al.* (2014) [132] obtained γ-MnO_2 carnation-like crystals with the potentiostatic method. The maximum power density (MPD) of the MFC equipped with the electrodeposited MnO_2/AC (activated carbon) air cathode reached 1554 $mW \cdot m^{-2}$.

Cheng *et al.* (2011) [133] described a rapid chemical synthesis of nanocrystalline spinel-like MnO_2 at room temperature, although its operation in MFCs was just proposed but not tested.

Liew *et al.* [134] (2015) and Y. Zhang *et al.* [135] (2011) studied hydrothermal synthesis of MnO_2 on carbon nanotubes (CNT) and functionalized nanotubes (f-CNT). According to Liew, the microbial fuel cell test showed that the composite MnO_2/f-CNT displayed higher power density (520 $mW \cdot m^{-2}$) compared to CNT (275 $mW \cdot m^{-2}$) and f-CNT (440 $mW \cdot m^{-2}$). According to Y. Zhang, the power density of 210 $mW \cdot m^{-2}$ produced by the MFC with *in situ* MnO_2/CNT cathode was 2.3 times that produced by the MFC using mechanically mixed MnO_2/CNTs (93 $mW \cdot m^{-2}$), and comparable to that of the MFC with a conventional Pt/C cathode (229 $mW \cdot m^{-2}$). One possible reason for the moderate performance is likely to be the amorphous structure.

Chen *et al.* (2012) [136] reported about the composite MnO_2/CNT on a steel mesh with the MPD of the corresponding MFC of 2676 $mW \cdot m^{-2}$ (normalized to the cathode surface area) or maximum power of 86 $W \cdot m^{-3}$ (normalized to the anode chamber volume). This advantage over the MFCs equipped with MnO_2/CNT observed above is likely to depend on the properties of PMPS (polymethylphenyl siloxane) used in a gas diffusion layer, and steel mesh. The need for the siloxane derivative was primarily caused by its water-repellent properties. And the steel mesh is a more conductive and adjustable support than the carbon cloth/paper applied in [134,135].

In research papers [137,138], the graphene and graphene oxide were also found to be effective substrates for manganese oxide. The MPD for a MFC operating with MnO_2/GNS (graphene nanosheets) achieved by Wen *et al.* (2012) was 2083 $mW \cdot m^{-2}$ compared to the one obtained by Gnana Kumar *et al.* (2014) for nanotubular α-MnO_2/graphene oxide, which was 3359 $mW \cdot m^{-2}$.

The intensive studies of catalytic materials based on MnO_2 have led to attempts of a more complex composite fabrication involving redox active organic conducting polymers. Yuan *et al.* (2015) [139] came up with the hydrothermal synthesis of multiwalled nanotubes MnO_2/polypyrrole/MnO_2. The corresponding MFC including this modified cathode catalyst exhibited an MPD of 721 ± 20 $mW \cdot m^{-2}$.

Cobalt oxides are the next frequently used cathode catalysts after manganese oxides [102, 140–147].

In the research papers [102, 140, 141], Gong *et al.* (2014), Ge *et al.* (2015) and Song *et al.* (2015) considered the use of cobalt oxide impregnated into a stainless steel mesh (SSM) [140], activated carbon (AC) [141] and nitrogen-doped carbon nanotubes (CNT) [102] respectively. In all cases the Co_3O_4 underwent high-temperature calcination (300–500 °C for 2–3 h). The first composite cathode SSM/Co_3O_4 was designated to operate in a dual-chamber MFC while the others equipped air single-chamber MFCs to produce the MPD of 1500 $mW \cdot m^{-2}$ [141] and 469 ± 17 $mW \cdot m^{-2}$ [102] correspondingly. The authors pointed out high or competitive catalytic performance of cobalt-oxide-based electrodes in ORR and emphasized their importance and economic efficiency in replacing platinum.

Ahmed *et al.* (2014) [142, 147] embedded CoO_x nanoparticles on carbon in order to enhance the catalytic activity of cobalt or iron phthalocyanine. The composite CoO_x-C was calcined at 400 °C for 1 h in ambient conditions for graphitic structural rearrangement of carbon and for the formation of cobalt oxide. The MPD of the MFC with cobalt phthalocyanine cathode catalyst doped with CoO_x nanoparticles was 50 % higher than without cobalt oxide and approximately equalled 780 $mW \cdot m^{-2}$ compared to 654 $mW \cdot m^{-2}$ for the cathode covered with iron phthalocyanine.

Iron oxides. Studies of ORR catalysts based on iron oxide are represented in the works [148, 149, 150]. The MPD performance of single-chambered MFCs is certainly higher for the high-temperature-treated iron oxides (1000 °C) [149, 150] than for the oxides just obtained based on decomposition of $Fe(CO)_5$ (165–175 °C) [148]. Moreover, Ma *et al.* (2015) [150] investigated silver composite on the basis of Fe_3O_4/GC (graphitic carbon) which increased the MPD from 1500 to 1700 $mW \cdot m^{-2}$.

Nickel oxide. The heat-treated NiO (400 °C, 2 h) was examined in the composite with CNTs by Huang *et al.* (2015) [151] although the MPD was quite moderate (670 $mW \cdot m^{-2}$).

Copper oxides. Crystalline-structured copper oxides were successfully synthesized on activated carbon by means of electrochemical deposition without calcination [152, 153]. The corresponding MPD of single-chamber MFCs was about 1400–1500 $mW \cdot m^{-2}$, which can be considered quite remarkable and comparable with the MPD performance of many other calcined oxides.

Vanadium oxides are also prospective low-cost catalytic materials used for ORR in MFCs. Noori *et al.* (2016) [154] showed the advantage of the heat-treated (350 °C) flower-like V_2O_5 over α-MnO_2 nanotubes. which was revealed in a higher MPD, Coulombic efficiency and wastewater treatment efficiency. Ghoreishi *et al.* (2014) [155] compared performances of the MFCs with the composite material V_2O_5/PANI (polyaniline) (not calcined) and V_2O_5 (calcined), demonstrating the superiority of the composite.

Zirconium oxide is thoroughly examined in [156]. The achieved MPD was 600 $mW \cdot m^{-2}$.

Apart from transition metal oxides, the *non-transition metal oxides* also exhibit catalytic activity.

Lead oxide [157] and *tin oxide* [158] could also be employed as an alternative to platinum catalyst and co-catalyst respectively.

Hybrid metal oxides. Notably, the highest MPDs were demonstrated by combined dual inorganic oxides enhanced with AC. The urchin-like $NiCo_2O_4$/AC [143] exhibited 1730 mW·m^{-2} versus MnO_2/AC/CeO_2 with 2403 mW·m^{-2} [159]. The complex multi component perovskite- and spinel-like oxides are discussed in [145, 146].

(b) Metal oxide-based organic-inorganic composites as catalysts

The electroactive conducting organic polymers are frequently employed as components to metal oxides in organic-inorganic composites [139, 144, 155, 160]. To a large extent the demand for the former is caused by the combination of good conductivity with electrocapacitive behavior. The electrochemical activity of metal oxides is, however, limited by their semiconducting nature. Thus, the incorporation of metal oxides on a redox active polymer like polyaniline (PANI) or polypyrrole (PPy) can improve the catalytic performance of a ceramic material.

(c) Carbides, nitrides and borides as catalysts

Despite ubiquitous studies of ceramic oxides and their application as cathode catalytic materials in MFCs, nitrides, carbides and borides have not been researched sufficiently. Nevertheless, Wen *et al.* (2012) [161] reported about nitrogen-enriched core-shell structured Fe/Fe_3C-C nanorods derived from thermal decomposition of a nitrogen-containing polymer. Based on thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), the authors suggested that the heating was accompanied by simultaneous release of a large amount of carbon nitride gases (e.g. $C_2N_2^+$, $C_3N_2^+$, $C_3N_3^+$) which finally evolved into the core-shell composite N-Fe/Fe_3C@C. Multiple cyclic voltammetry experiments give the foundation to convince that the doped N and core-Fe_3C in the N-Fe/Fe_3C@C play a key role in improving the catalytic performance for ORR.

(d) Heat-treated M-N-C complexes as catalysts

Macrocyclic coordination compounds such as metal porphyrins and phthalocyanines are known to be effective catalysts of biological importance. Although their application in MFCs without preliminary processing is considered in a number of research articles [147, 162–164], a new approach based on pyrolysis of the compounds without substantial degrading has been gaining in popularity. Various research groups have reported that the heat treatment (up to 1000 °C) of transition metal macrocycles significantly improved their stability as electrocatalysts for oxygen reduction and in some instances, enhanced their overall catalytic activity [165] while maintaining the open framework structure with sufficient porosity and large surface area [166]. This class of materials is termed metal-nitrogen-carbon (M-N-C) catalysts or metal-organic-framework (MOF)-derived catalysts.

The most widely used precursors of these metal-organic framework catalysts are macrocyclic complexes of inexpensive transition metals (Fe, Co) with nitrogen-rich organic molecules like porphyrins [14, 167–170], phthalocyanines [14, 167–169, 171, 172], and naphthalocyanines [173], metal complexes of ethylenediamine (EDA) [174] and ethylenediaminetetraacetic acid [175] as well as metal-doped polymeric molecules evolved from imidazole [176], 2-methylimidazole [177], aniline [178, 179], pyrrole [180], melamine [181], aminoantipyrene [182], mebendazole [182], cyanamide [161], dicyandiamide [183], etc.

Fig. 10 depicts a possible route of the Co-MOF structure transformation upon thermal activation. X-ray photoelectron spectroscopy (XPS) data show that imidazolate groups are gradually converted to carbonaceous forms whereas a fraction of the nitrogen is retained as pyridinic or pyrrolic-like moieties with the former being the dominant component. The loss of hydrogen and some carbon and nitrogen as well as the segregation of the excess Co^{2+} ions and their conversion into Co^0 alter the structure of the framework with the formation of mesopores while maintaining a certain fraction of the micropores. Further increase of temperature to 900 °C graphitizes carbon, causing further loss of N for active sites and, therefore, reducing the activity of the catalyst [176]. Of the above-mentioned MOF-catalysts, the highest MPD of 2437 ± 55 mW·m^{-2} has been registered for a single-chamber MFC with the Fe-N-C cathode derived from the Fe-EDA derivative [174]. Such a high performance shows the advantage of the substances with the developed framework and, hence, multiple active sites for anchoring oxygen molecules.
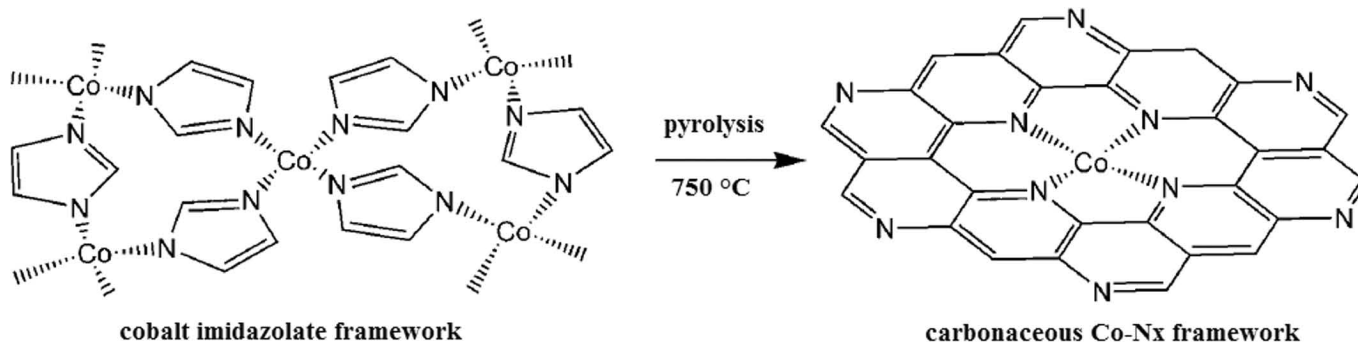

cobalt imidazolate framework → pyrolysis 750 °C → **carbonaceous Co-Nx framework**

Fig. 10: Proposed structural conversion from the MOF structure to the catalytic active site (after [176]).

(3) Biocathodes with ceramic materials (bacteria as catalysts)

Conventional MFCs consist of biological anodes and abiotic cathodes. In contrast to bioanodic MFCs (with bacteria being catalysts for hydrogen oxidation) that have been studied thoroughly [25, 26, 32, 38, 39], biocathodic MFCs (with bacteria being catalysts for oxygen reduction) have not gained the same popularity owing to the lower power generation [66] than those with chemically catalyzed cathodes [9, 116–121, 125–183]. Another drawback of biocathodes is that the MFC construction is more complicated, costly and infeasible on a large scale. Nevertheless, the interest in biocathode study and application is gradually increasing [184]. One possible explanation is that bacteria in biological cathodes accelerate cathodic electron transition, causing a decrease in internal resistance, which in turn contributes to power output performance [185].

Unfortunately, no data specifically related to the use of ceramic materials in biocathodes have been found. Though it is worth mentioning that some redox active bacteria placed in the cathodic compartment are able to interact with transition metal ions like Mn^{2+} and Fe^{2+}, facilitating oxygen reduction [65, 185, 186] in aerobic cathodes of MFCs. Rhoads *et al.* (2005) [186] reported on the use of *Lepthothrix discophora* SP-6 in oxidizing manganese ions Mn^{2+} into manganese dioxide MnO_2 in an aerated solution of Mn^{2+}. The microorganisms deposit MnO_2 on the cathode surface. Then the biomineralized manganese dioxide is subsequently reduced by two electrons from the anodic reaction. This results in the release of manganese ions. So the redox couple composed of manganese ions and manganese oxides can be considered a redox mediator in the cathodic reaction. In the study [185], Mao *et al.* (2010) investigated the performance of a biocathode microbial fuel cell based on the biocatalysis of ferro/manganese-oxidizing bacteria and revealed that it took 150 h to start up such a MFC reactor versus 60–100 h for an MFC with an abiotic cathode. So, further research is needed to minimize this period by optimizing the doses of iron and manganese compounds. Ferro/manganese-oxidizing microorganisms are omnipresent in natural waters, and using iron and manganese oxides as cathodic reactants in MFCs seems to be reasonable and profitable.

In summary, it should be emphasized that ceramic materials, particularly metal oxides, are prospective components of MFC cathodes capable of functioning both as supports and catalysts. Nevertheless, despite their high catalytic activity, they are lacking in conductivity and specific surface area, hence, limiting the number of active sites for binding oxygen. The resolution may lie in fabrication of composites combining redox activity of metal oxides with good conductivity and large surface area of carbon-based matrix (CNTs, f-CNTs, AC, graphene, GO, etc.) or conjugated polymers (polyaniline, polypyrrole, etc.). There is also another approach to enlarge the specific surface area while maintaining electrocapacitive efficiency. This involves pyrolytic-treated metal-organic macromolecules that owing to their developed framework structure can be effective substrates for oxygen binding.

V. Advantages of Porous Ceramics as Membrane Separators

The primary use of separators in electrochemical energy sources is to eliminate the interaction between the electrochemical processes occurring at the two electrodes, i.e. isolation of oxidation and reduction reactions in order to minimize losses in the voltage generated by the fuel cells.

Fuel cell separators are generally divided into two types: permeable and semipermeable separators. The permeable ones do not impede the bulk flow of fluid through the structure and, thus, do not provide for selection of ions or neutral molecules. In electrochemical processes, they are often called diaphragms. Through semipermeable separators selective transfer occurs depending on the molecular size or charge of the ions. In electrochemical processes, these are called "membranes".

An effective separator should possess a number of desirable properties such as chemical resistance, mechanical strength, as well as the absence of electronic conductivity, and good ionic conductivity. In addition to the general requirements for separators in a MFC, other factors have to be taken into account [2]:

a) Since the anode is anaerobic, it is necessary to prevent or minimize the transmission of oxygen into the anode chamber.

b) Further attention should be paid to the mechanism of ion transport in proton exchange membranes (PEM) under the presence of other cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) in the anolyte. Typically, a relatively low concentration of protons in solution and in the membrane and a higher affinity of negatively charged functional groups for most other kinds of cations leads to functional groups being occupied by other cations rather than protons. Consequently, the number of transferred protons becomes negligible compared to transport of other cation types. The proton transport number is 10^4 times lower than the sum of the transport numbers of other cation types.

c) Low proton transfer rate from the anode chamber into the cathode chamber (or the cathode) compared to the proton consumption rate at the cathode results in pH splitting, i.e. increase of the pH in the cathode chamber and decrease of the pH in the anode chamber. This reduces the stability of system and its bioelectrochemical performance.

d) A biofilm could potentially grow on the separator and cause gradual deterioration in the MFC performance.

e) The membranes should not, ideally, allow the transmission of non-ionic species to the cathode as the oxidation process would interfere with the cathodic oxygen reduction reaction. Crossover of organic matter leads to a loss of fuel and heterotrophic bacteria growth on the cathode, reducing the cathode potential. Frequently, in such circumstances the cathode has a negative potential (vs. Ag/AgCl), although it is expected to be a positive one [187] with the use of oxygen as an electron acceptor.

The most common MFC separators are proton exchange membranes (PEMs) (e.g. Nafion) [188–190]. Nevertheless, the problems associated with the use of PEM (e.g., insuf-

ficient proton conductivity, the presence of oxygen diffusion, biofouling, and high cost) impede the practical use of MFC technology [188–192]. Firstly, as noted above, diffusion capability of protons in the PEM degenerates highly as a result of joining of the PEM negatively charged functional groups with other prevailing anolyte cations. This induces a pH gradient between the anodic and cathodic chambers, which in turn reduces output power [13, 192]. Secondly, a relatively high oxygen permeability of PEM inhibits bacterial metabolism at the anode, resulting in the loss of electrons. Finally, the PEM can be impaired by contamination and chemical attacks [192–195].

Xu *et al.* [194] found that the PEM fouling layer increased the MFC internal resistance by 20 % and significantly reduced the output power (by 32.3 %). Nevertheless, the formation of a fouling layer on the PEM is inevitable during continuous operation [188, 193]. When the MFC works at actual sites, as a rule, physical or chemical decontamination is required. However, cleaning the membrane can cause its damage [194]. As occasionally contaminated PEMs have to be replaced with new ones, this increases the total cost of PEMs by 40 % of the total cost of the entire MFC (Nafion cost, the most common commercial PEM, costs about 1400 US $/m^2 [190]) [195]. Thus, there is an urgent need to explore more effective alternatives for PEM with a view to the successful commercialization of MFC technology.

Recently, diverse PEM materials have been evaluated, such as ion-exchange membranes (IEMs), salt bridges and porous materials depending on the output power density [187, 189, 191, 196–200]. Among these alternative separators, the polymeric porous separators (e.g. J-cloth, ultrafiltration membranes, microfiltration membranes, and forward osmosis membranes) usually demonstrate higher MFC efficiency compared with ion-exchange separators because of their excellent ability to transfer protons despite the high level of oxygen and fuel penetration [190]. Furthermore, polymeric porous membranes are considered more cost-effective [189, 190, 192]. However, these membranes originally designed for water treatment, inevitably deteriorate owing to biodegradation and fouling [196, 201]. Thus, periodic cleaning and replacement of membranes are required in long-term operation.

The application of porous ceramic materials characterized by high mechanical and chemical stability as the MFC membranes solves the above-mentioned problems [189]. Besides, interest in the development of ceramic membranes is growing because of the wide variety of types and methods of synthesis, which give a unique opportunity to use them.

Practical suitability of such membranes in MFC has been confirmed in various experiments over the last decade. Park and Zeikus made the first attempt [82]. developing a porcelain septum separator for a single-chamber MFC using 100 % kaolin, which showed the potential of ceramics. Some years later an analogous system with a three-layer cathode composed of a cellulose acetate film, porcelain membrane and porous graphite plate was described [202]. This single-chamber MFC was linked with a solar cell to enhance power generation.

Ceramic membranes on the basis of clay minerals cause justified interest among researchers owing to their availability and low cost of raw materials. It has been found that ceramic material has certain conductivity and provides high rate of cation-exchange transfer [203, 204]. On this basis, it is expected that the clay membranes may play the role not only of physical separators, but also of proton exchange membranes. For efficient use of such ceramic membranes, the clay minerals they are made of should have a high cation exchange capacity. Besides cation exchange capacity, another essential characteristic of the membranes is their hydraulic resistance. This depends on the pore radius, which is typically small for clays. As shown in the paper [205], porosity of the MFC clay separators plays a vital role in the infiltration of fuel from the anode chamber into the cathode chamber.

Hereafter, the focus is on a number of works devoted to developing MFCs with these separators and the study of their properties over the past few years.

In 2010, the authors [187] used a commercially available 400-ml ceramic pot consisting of clay – 58 – 68 % kaolinite, 15 – 26 % illite and 5 – 9 % smectite to create an MFC. Installation demonstrated an output power of 16.8 W/m^3. Perhaps, this was the first study to show how low-cost common material could change the direction of MFC developments and accelerate their progress.

In subsequent research, the same group of researchers applied the clay pots to create a ceramic MFC that showed the production of energy comparable with a MFC based on IEM when rice mill wastewater was used as a fuel [206]. This work was promising, although potassium permanganate was used as the catholyte to increase the cathode potential. It is obvious that the system cannot really be considered environmentally friendly if at least one of its components (e.g. catholyte) is unstable.

In the studies discussed above, ceramic products available on the market were used, the design of which was not subjected to optimization. The researchers [207] used a different design and mode of operation, namely ceramic cylinders operating in a continuous stream. This design and operation mode confirmed the conclusions made with off-the-shelf pots that ceramics-based MFCs could be comparable with MFCs based on conventional ion exchange membranes. These communications show that the ceramics can be used as a structural material and as the passage for proton movement.

The most important factors determining the design and durability of MFC installations are thickness and porosity of the ceramics. Behera and Ghangrekar [208] studied the effect of different thickness of the ceramic membrane on the performance of the dual-chambered MFC, and found that the MFC with the membrane possessing the smallest thickness and, therefore, less internal resistance had the highest power output.

In 2012, the researchers stated that all the materials needed for the generation of electricity could be sourced locally in developing countries and supported it by making a single-chamber MFC from a terracotta pot (Fig. 11) [209]. This device showed the Coulombic efficiency of 21 ± 5 % with the power density of 33.13 mW/m ^{2}.
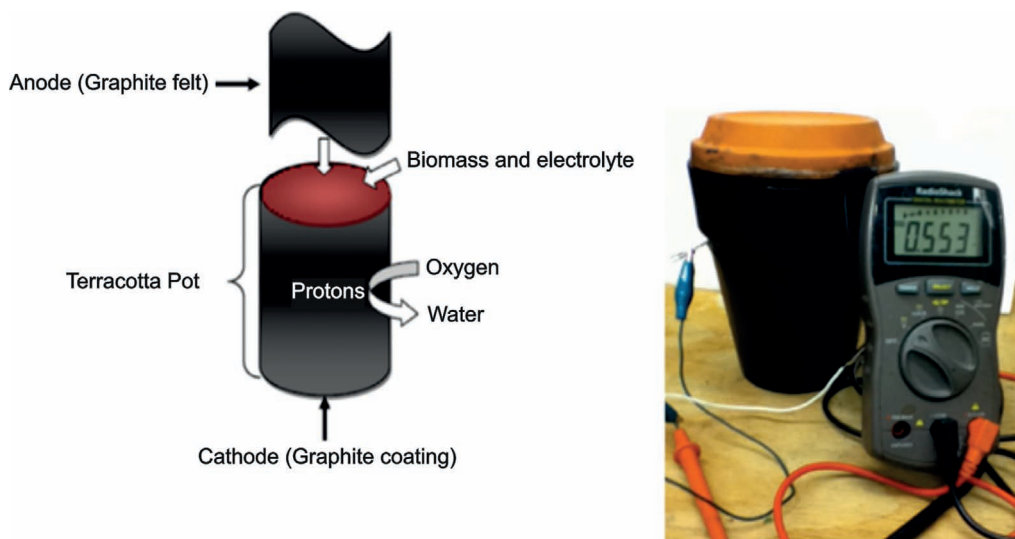
Fig. 11: Schematic diagram of the terracotta bio-battery and the bio-battery showing an open circuit voltage of 0.553 V after enrichment (after [209]).

Winfield *et al.* [200] reported that the ceramic MFC with an earthenware clay separator exhibited power density comparable to conventional PEM-based MFCs during long-term operation. In another study, Winfield *et al.* [119] also evaluated terracotta and earthenware for use as separators in an MFC and found them the least iron-rich and most porous materials compared to other ceramics. Besides, the more porous earthenware was a better material than terracotta.

The authors [120] used clay pots for MFCs and pointed out some of the problems of using ceramics including salt deposition on the cathode and electrolyte evaporation.

Anolyte loss caused by evaporation is an important problem associated with the use of ceramic materials as separators [119, 120, 209]. One way to avoid this is to use a gas diffusion hydrophobic layer, which at least restricts evaporative losses. Synthetic plastics can be used for sealing [209], but other methods including selective glazing may also be employed. The hydrophobic layers can be incorporated into the structure and introduced into the kiln-firing process by patterning the ceramics with a glazing agent.

Ghadge *et al.* [210] made a number of ceramic separators and investigated the effect of different soil properties like pH, conductivity, porosity and cation exchange capacity on the performance of a MFC. This study showed that the power generation of the MFC with a separator made of red soil was better than one made of black soil owing to the high cation exchange capacity, low pH, and higher electrical conductivity of red soil.

Components aiding performance can also be incorporated into the material prior to annealing. For example, in the paper [211], the ceramics were modified with the addition of cation exchangers such as montmorillonite and kaolinite before the kiln-firing stage. Montmorillonite showed the best characteristics in terms of power output and Coulombic efficiency. This was achieved owing to the presence of an ion exchanger, which improved cation transport ability and helped reduce crossover of the substrate and the diffusion of oxygen.

B. Midyurova *et al.* [118] reported on the development of ceramic membranes used as separators and templates for the next generation of electrodes. Two types of membranes were synthesized and used as templates for an air cathode in a single-chamber MFC. The first design of ceramic cathodes consisted of layers of Trojan clay, liquid Nafion® and steel mesh, whereas the second contained the ceramic Trojan clay membrane containing MnO_2 as a catalyst, carbon cloth and a layer of liquid Nafion®. The study confirmed the higher efficiency of the MFC with the composite ceramic separator/MnO_2-containing carrier compared with the ceramic membrane based on the clay without MnO_2.

Pasternak *et al.* [212] compared the performance and cost of four different ceramic materials in MFCs (i.e. mullite, earthenware, pyrophyllite, and alumina). Both short-term and long-term operation of pyrophyllite with wall thickness of 3 mm and porosity of 2 % provided the highest power density, 6.93 and 4.3 W/m^3 respectively.

To date, the cost of proton exchange membranes has become an obstacle to the progress of MFCs. Ceramics offer a cheap solution so that commercially available earthenware can be purchased for £ 4.14 per square metre, compared with £ 79.17 per square metre for conventional cation exchange membranes [212]. This significantly reduces the cost and some researchers believe that all the materials needed to produce one MFC unit can be purchased for less than £ 1 [187, 213].

Recent studies of commercial filtration membranes are also of interest owing to such properties as high mechanical strength, chemical stability and relatively low fouling propensities. E. Yang *et al.* [214] demonstrated the possibility of using the ceramic ultrafiltration membrane 15 KD (Sterlitech 15A) and the ceramic microfiltration membrane (Anodisc 13) as separators in MFCs. Despite higher rates of oxygen and fuel transfer through Anodisc 13 observed in the tests, the MFC having Anodisc 13 membrane generated more electricity compared to Nafion 117. Smaller Anodisc 13 membrane thickness and cylindrical pores of micron size resulted in a higher proton transfer rate and, therefore, less resistance. In this case, it should be noted that the cost of ceramic filtration membranes is generally ten times higher than that of polymeric filtration membranes [215]. However, the authors concluded that de-

spite their high initial introduction costs, commercial ceramic filtration membranes had great potential for use as separators for practical implementation of MFC technology. Notably, the long life of ceramic filtration membranes can reduce the total cost of a MFC by lengthening the replacement cycles for separators.

VI. Conclusions and Outlook

Microbiological fuel cells are the power sources of the future. These will be especially useful for operation in situations where the accessibility of installation is limited, for example, in remote areas, for wastewater treatment or in areas of emergency in the aftermath of disasters.

The most intense research in the field of bacteria selection and their adaptation to the MFC materials has been undertaken in the last few years. The bacteria species *Shewanella* and *Geobacter,* so-called metal-reducing bacteria capable of power generation, are mostly well studied. These bacteria are peculiar in that they are able to grow on behalf of intercellular oxidation of diverse organic substances combined with extracellular reduction of metal ions. Natural communities of sea microorganisms as well as fine species of bacteria are combined with ceramic materials of anodes and separating membranes. The key considerations with regard to using ceramics include the ability of these materials to work for a long time. Nevertheless, the delicate interaction of electroactive microorganisms with the electrode surface has not been sufficiently explored.

Ceramics can be successfully used for the fabrication of anode, cathode and membrane materials.

A ceramic anode in an MFC has a number of advantages in comparison with a typical carbon anode. These are the higher catalytic activity, electrochemical stability and redox activity. These properties contribute to the intensity of electron transport from a bacterial cell to the anode, thus increasing the efficiency of the MFC. Nevertheless, there are problems to be solved as the electron transfer from a bacterial cell to the anode surface should be intensified. It is necessary to study the mechanism of interaction between bacteria of different species and every particular ceramic material tested. Increasing electrical conductivity of the material as well as ensuring bacteria adhesion to the anode surface and biocompatibility are the current problems. Despite all listed benefits, composite materials (ceramics/carbon nanotubes/metal nanoparticles, ceramics/carbon materials, ceramics/conducting polymers) are the most preferential for anode fabrication for MFCs. By combining the advantages of their individual components, composite ceramic materials possess a synergetic effect that encourages electron transfer from a bacterium to the anode surface.

The ceramic materials are by all means promising in terms of their application in cathodes of MFCs owing to such properties as mechanical and morphological stability, biological compatibility with bacteria, redox activity, and electrochemical stability, low cost and environmental safety. These characteristics can play a crucial role in replacing platinum as the most widely used catalyst, and carbon as supporting matrix. However, there are still some disadvantages that need to be eliminated in further studies. These are the poor conductivity of ceramic materials and

low surface area. The poor conducting nature of ceramic material may be compensated, for instance, by making composites with substances possessing high conductivity such as metal nanoparticles and organic conducting polymers. Concerning the second drawback, one of the approaches to increase porosity of ceramics and, therefore, their surface area lies in an appropriate regime of thermal processing and the use of pore-forming agents.

To date, it has been found that ceramics are more stable than conventional membranes, for example Nafion®, but further work should be done towards reducing biofouling, clogging of pores and contamination – factors hindering MFC performance. The data available at the moment are promising and confirm the long-term viability of the ceramics. There are some problems to overcome, but it can be assumed that the ceramics will definitely be a more preferential material for the MFC membranes than the IEMs, encouraging the production of MFCs on an industrial scale.

In a relatively short period of time, the use of ceramics in MFCs has helped to reduce costs while improving performance, as supported by successful field tests. Nevertheless, questions still have to be answered based on a large number of studies.

References

[1] Rabaey, K., Verstraete, W.: Microbial fuel cells: Novel biotechnology for energy generation, *Trends Biotechnol.*, **23**, [6], 291 – 298, (2005),
doi: https://doi.org/10.1016/j.tibtech.2005.04.008.

[2] Scott, K., Yu, E.H. (Ed.): Microbial electrochemical and fuel cells. Fundamentals and applications, 1st edition. Woodhead Publishing, 2015.

[3] Ponomareva, A.A., Ivanova, A.G., Shilova, O.A., Kruchinina, I.Yu.: Current state and prospects of manufacturing and operation of methane-based fuel cells (review), *Glass Phys. Chem.*, **42**, [1], 1 – 19 (2016),
doi: https://doi.org/10.1134/S1087659616010120.

[4] Ishihara, T. (Ed): Perovskite oxide for solid oxide fuel cells. Chapter 2. Overview of intermediate-temperature solid oxide fuel cells, LLC, Springer Science Business Media, 17 – 43, 2009,
doi: https://doi.org/10.1007/978-0-387-77708-5.

[5] Guan, W.B., Zhai, H.J., Jin, L., Li, T.S., Wang, W.G.: Effect of contact between electrode and interconnect on performance of SOFC stacks, *Fuel Cells*, **11**, 445 – 450, (2011),
doi: https://doi.org/10.1002/fuce.201000176.

[6] Kalinina, M.V., Morozova, L.V., Egorova, T.L., Arsent'ev, M.Yu., Drozdova, I.A., Shilova, O.A.: Synthesis and physicochemical properties of a solid oxide nanocomposite based on a ZrO_2-Y_2O_3-Gd_2O_3-MgO system, *Glass Phys. Chem.*, **42**, [5], 505 – 511, (2016),
doi: https://doi.org/10.1134/S1087659616050060.

[7] Ramachandran, R., Chen, S-M., Kumar, G.P.G.: Enhancement of different fabricated electrode materials for microbial fuel cell applications: an overview, *Int. J. Electrochem. Sci.*, **10**, 7111 – 7137, (2015).

8   Yousefi, V., Mohebbi-Kalhori, D., Samimi, A.: Ceramic-based microbial fuel cells (MFCs): A review, *Int. J. Hydrogen Energ.*, **42**, [3], 1672–1690, (2017), doi: https://doi.org/10.1016/j.ijhydene.2016.06.054.

9   Winfield, J., Gajda, I., Greenman, J., Ieropoulos, I.: A review into the use of ceramics in microbial fuel cells, *Bioresource Technol.*, **215**, 296–303, (2016), doi: https://doi.org/10.1016/j.biortech.2016.03.135.

10   Logan, B.E. Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K.: Microbial fuel cells: methodology and technology, *Environ. Sci. Technol.*, **40**, 5181–5192, (2006).

11   Logan, B.E., Regan, J.M.: Electricity-producing bacterial communities in microbial fuel cells, *Trends Microbiol.*, **14**, 512–518, (2006).

12   Bond, D.R., Lovley, D.R.: Electricity production by *Geobacter sulfurreducens* attached to electrodes, *Appl. Environ. Microbiol.*, **69**, 1548–1555, (2003).

13   Rozendal, R.A., Hamelers, H.V., Buisman, C.J.: Effects of membrane cation transport on pH and microbial fuel cell performance, *Environ. Sci. Technol.*, **40**, 5206–5211, (2006).

14   Zhao, F., Harnisch, F., Schröder, U., Scholz, F., Bogdanoff, P., Herrmann, I.: Challenges and constraints of using oxygen cathodes in microbial fuel cells, *Environ. Sci. Technol.*, **40**, 5193–5199, (2006).

15   Rahimnejad, M., Bakeri, G., Ghasemi, M., Zirepour, A.: A review on the role of proton exchange membrane on the performance of microbial fuel cell, *Polym. Adv. Technol.*, **25**, 1426–1432, (2014).

16   Kim, J.R., Cheng, S., Oh, S.E., Logan, B.E.: Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells, *Environ. Sci. Technol.*, **41**, 1004–1009, (2007).

17   Rozendal, R.A., Hamelers, H.V., Molenkamp, R.J., Buisman, C.J.: Performance of single chamber biocatalyzed electrolysis with different types of ion exchange membranes, *Water Res.*, **41**, 1984–1994, (2007).

18   Rozendal, R.A., Sleutels, T.H., Hamelers, H.V., Buisman, C.J.: Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater, *Water Sci. Technol.*, **57**, 1757–1762, (2008).

19   Arends, J.B.A., Verstraete, W.: 100 years of microbial electricity production: three concepts for the future, *Microbial. Biotechnol.*, **5**, 333–346, (2012).

20   Potter, M.C.: Electrical effects accompanying the decomposition of organic compounds, *P. R. Soc.*, **84**, 260–276, (1911).

21   Cohen, B.: The bacterial culture as an electrical half-cell, *J. Bacteriol.*, **21**, 18–19, (1931).

22   Davis, J.B., Yarbrough, H.F.: Preliminary experiments on a microbial fuel cell, *Science*, **137**, 615–616, (1962).

23   Lewis, K.: Biochemical fuel cells, *Bacteriol. Rev.*, **30**, 101–113, (1966).

24   Yahiro, A.T., Lee, S.M., Kimble, D.O.: Bioelectrochemistry. I. enzyme utilizing bio-fuel cell studies, *Biochim. Biophys. Acta*, **88**, 375–383, (1964).

25   Schröder, U.: Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency, *Phys. Chem. Chem. Phys.*, **9**, 2619–2629, (2007).

26   Philips, J., Verbeeck, K., Rabaey, K., Arends, J.B.A.: Electron transfer mechanisms in biofilms. In: Microbial electrochemical and fuel cells. Elsevier. Woodhead Publishing, Boston, Cambridge, UK, 2016.

27   Caccavo, J.F., Lonergan, D.J., Lovley, D.R., Davis, M., Stolz, J.F., Mcinerney, M.J.: *Geobacter sulfurreducens* sp. nov., a hydrogen- and acetate-oxidizing dissimilatory metal-reducing microorganism, *Appl. Environ. Microbiol.*, **60**, 3752–3759, (1994).

28   Kim, B.H., Ikeda, T., Park, H.S., Hyun, M.S., Kano, K., Takagi, K., Tatsumi, H.: Electrochemical activity of an Fe(III)-reducing bacterium, *Shewanella putrefaciens* IR-1, in the presence of alternative electron acceptors, *Biotechnol. Tech.*, **13**, 475–478, (1999).

29   Kim, B.H., Kim, H.J., Hyun, M.S, Park, D.H.: Direct electrode reaction of Fe(III)-reducing bacterium, *Shewanella putrefaciens, J. Microbiol. Biotechnol.*, **9**, 127–131, (1999).

30   Kim, B.H., Park, D.H., Shin, P.K., Chang, I.S., Kim, H.J.: Mediator-less biofuel cell. U.S. Patent Application **5**, 976, 719, (1999).

31   Holmes, D.E., Bond, D.R., O'Neil, R.A., Reimers, C.E., Tender, L.R., Lovley, D.R.: Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments, *Microb. Ecol.*, **48**, 178–190, (2004).

32   Logan, B.E.: Exoelectrogenic bacteria that power microbial fuel cells, *Nat. Rev. Microbiol.*, **7**, 375–381, (2009).

33   Galushko, A.S., Schink, B.: Oxidation of acetate through reactions of the citric acid cycle by *Geobacter sulfurreducens* in pure culture and in syntrophic coculture, *Arch. Microbiol.*, **174**, 314–321, (2000).

34   Thauer, R.K.: Citric-acid cycle, 50 years on. modifications and an alternative pathway in anaerobic bacteria, *Eur. J. Biochem.*, **176**, 497–508, (1988).

35   Kracke, F., Vassilev, I., Krömer, J.O.: Microbial electron transport and energy conservation – the foundation for optimizing bioelectrochemical systems, *Front. Microbiol.*, **6**, 575, (2015).

36   Scott, J.H., Nealson, K.H.: A biochemical study of the intermediary carbon metabolism of *Shewanella putrefaciens, J. Bacteriol.*, **176**, 3408–3411, (1994).

37   Matsuda, S., Liu, H., Kouzuma, A., Watanabe, K., Hashimoto, K., Nakanishi, S.: Electrochemical gating of tricarboxylic acid cycle in electricity-producing bacterial cells of *Shewanella. PLoS ONE*, **8**, e72901, 10.1371/journal.pone.0072901, (2013).

38   Grobbler, C., Virdis, B., Nouwens, A., Harnisch, F., Rabaey, K., Bond, P.L.: Use of SWATH mass spectrometry for quantitative proteomic investigation of *Shewanella oneidensis* MR-1 biofilms grown on graphite cloth electrodes, *Syst. Appl. Microbiol.*, **38**, 135–139, (2015).

39   Kouzuma, A., Kasai, T., Hirose, A., Watanabe, K.: Catabolic and regulatory systems in *Shewanella oneidensis* MR-1 involved in electricity generation in microbial fuel cells, *Front. Microbiol.*, **16**, 609, (2015).

40   Shi, L., Squier, T.C., Zachara, J.M., Fredrickson, J.K.: Respiration of metal (hydr)oxides by *Shewanella* and *Geobacter*: a key role for multihaem c-type cytochromes, *Mol. Microbiol.*, **65**, 12–20, (2007).

41   Coursolle, D., Baron, D.B., Bond, D.R., Gralnick, J.A.: The Mtr respiratory pathway is essential for reducing flavins and electrodes in *Shewanella oneidensis, J. Bacteriol.*, **192**, 467–474, (2010).

42   Gorby, Y.A., Yanina, S., McLean, J.S., Rosso, K.M., Moyles, D., Dohnalkova, A., Beveridge, T.J., Chang, I.S., Kim, B.H., Kim, K.S., Culley, D.E., Reed, S.B., Romine, M.F., Saffarini, D.A., Hill, E.A., Shi, L., Elias, D.A., Kennedy, D.W., Pinchuk, G., Watanabe, K., Ishii, S., Logan, B., Nealson, K.H., Fredrickson, J.K.: Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms, *Proc. Natl. Acad. Sci. USA*, **103**, 11358–11363, (2006).

43   Reguera, G., McCarthy, K.D., Mehta, T., Nicoll, J.S., Tuominen, M.T., Lovley, D.R.: Extracellular electron transfer via microbial nanowires, *Nature*, **435**, 109–1101, (2005).

44   Reguera, G., Nevin, K.P., Nicoll, J.S., Covalla, S.F., Woodard, T.L., Lovley, D.R.: Biofilm and nanowire production leads to increased current in *Geobacter sulfurreducens* fuel cells, *Appl. Environ. Microbiol.*, **72**, 7345–7348, (2006).

45 Shi, L.A., Richardson, D.J., Wang, Z.M., Kerisit, S.N., Rosso, K.M., Zachara, J.M., Fredrickson, J.K.: The roles of outer membrane cytochromes of *Shewanella* and *Geobacter* in extracellular electron transfer, *Environ. Microbiol. Rep.*, **1**, 220–227, (2009).

46 Leang, C., Qian, X.L., Mester, T., Lovley, D.R.: Alignment of the c-type cytochrome OmcS along pili of *Geobacter sulfurreducens*, *Appl. Environ. Microbiol.*, **76**, 4080–4084, (2010).

47 McLean, J.S., Wanger, G., Gorby, Y.A., Wainstein, M., McQuaid, J., Ishii, S.I., Bretschger, O., Beyenal, H., Nealson, K.H.: Quantification of electron transfer rates to a solid phase electron acceptor through the stages of biofilm formation from single cells to multicellular communities, *Environ. Sci. Technol.*, **44**, 2721–2727, (2010).

48 Nielsen, L.P., Risgaard-Petersen, N., Fossing, H., Christensen, P.B., Sayama, M.: Electric currents couple spatially separated biogeochemical processes in marine sediment, *Nature*, **463**, 1071–1074, (2010).

49 Luo, S., Guo, W., Nealson, K.H., Feng, X., He, Z.: ^{13}C pathway analysis for the role of formate in electricity generation by *Shewanella oneidensis* MR-1 using lactate in microbial fuel cells, *Sci. Rep.*, **12**, 20941, (2016).

50 Malvankar, N.S., Yalcin, S.E., Tuominen, M.T., Lovley, D.R.: Visualization of charge propagation along individual pili proteins using ambient electrostatic force microscopy, *Nat. Nanotechnol.*, **9**, 1012–1017, (2014).

51 Pirbadian, S., Barchinger, S.E., Leung, K.M., Byun, H.S., Jangir, Y., Bouhenni, R.A., Reed, S.B., Romine, M.F., Saffarini, D.A., Shi, L., Gorby, Y.A., Golbeck, J.H., El-Naggar, M.Y.: *Shewanella oneidensis* MR-1 nanowires are outer membrane and periplasmic extensions of the extracellular electron transport components, *Proc. Nat. Acad. Sci. USA*, **111**, 12883–12888, (2014).

52 Xiao, K., Malvankar, N.S., Shu, C., Martz, E., Lovley, D.R, Sun, X.: Low energy atomic models suggesting a pilus structure that could account for electrical conductivity of *Geobacter sulfurreducens* pili, *Sci. Rep.*, **6**, 23385, (2016).

53 Sure, S.K., Ackland, L.M., Torriero, A.A., Adholeya, A., Kochar, M.: Microbial nanowires: an electrifying tale, *Microbiol.*, **162**, 2017–2028, (2016).

54 Lovley, D.R., Malvankar, N.S.: Seeing is believing: novel imaging techniques help clarify microbial nanowire structure and function, *Environ. Microbiol.*, **17**, 2209–2215, (2015), doi: https://doi.org/10.1111/1462-2920.12708.

55 Tan, Y., Adhikari, R.Y., Malvankar, N.S., Ward, J.E., Nevin, K.P., Woodard, T.L., Smith, J.A., Snoeyenbos-West, O.L., Franks, A.E., Tuominen, M.T., Lovley, D.R.: The low conductivity of *Geobacter uraniireducens* pili suggests a diversity of extracellular electron transfer mechanisms in the genus *Geobacter*, *Front. Microbiol.*, **7**, 980, (2016), doi: https://doi.org/10.3389/fmicb.2016.00980.

56 Chung, Y., Hyun, K.H., Kwon, Y.: Fabrication of a biofuel cell improved by the π-conjugated electron pathway effect induced from a new enzyme catalyst employing terephthalaldehyde, *Nanoscale*, **8**, 1161–1168, (2016), doi: https://doi.org/10.1039/c5nr06703k.

57 von Canstein, H., Ogawa, J., Shimizu, S., Lloyd, J.R.: Secretion of flavins by *Shewanella* species and their role in extracellular electron transfer, *Appl. Environ. Microbiol.*, **74**, 615–623, (2008).

58 Reimers, C.E., Tender, L.M., Fertig, S., Wang, W.: Harvesting energy from the marine sediment-water interface, *Environ. Sci. Technol.*, **35**, 192–195, (2001).

59 Koch, C., Harnisch, F.: Is there a specific ecological niche for electroactive microorganisms?, *ChemElectroChem.*, **3**, 1282–1295, (2016).

60 Fedorovich, V., Knighton, M.C., Pagaling, E., Ward, F.B., Free, A., Goryanin, I.: Novel electrochemically active bacterium

61 Rotaru, A.E., Woodard, T.L., Nevin, K.P., Lovley D.R.: Link between capacity for current production and syntrophic growth in *Geobacter* species, *Front. Microbiol.*, **21**, 744, doi: https://doi.org/10.3389/fmicb.2015.00744 (2015).

62 Wrighton, K.C., Thrash, J.C., Melnyk, R.A., Bigi, J.P., Byrne-Bailey, K.G., Remis, J.P., Schichnes, D., Auer, M., Chang, C.J., Coates, J.D.: Evidence for direct electron transfer by a gram-positive bacterium isolated from a microbial fuel cell, *Appl. Environ. Microbiol.*, **77**, 7633–7639, (2011), doi: https://doi.org/10.1128/AEM.05365-112011.

63 Koch, C., Harnisch, F.: What is the essence of microbial electroactivity?, *Front. Microbiol.*, **7**, 1890, (2016).

64 Gregory, K.B., Bond, D.R., Lovley, D.R.: Graphite electrodes as electron donors for anaerobic respiration, *Environ. Microbiol.*, **6**, 596–604, (2004).

65 He, Z., Angenent, L.: Application of bacterial biocathodes in microbial fuel cells, *Electroanalysis*, **18**, 2009–2015 (2006), doi: https://doi.org/10.1002/elan.200603628.

66 Huang, L., Regan, J.M., Quan, X.: Electron transfer mechanisms, new applications, and performance of biocathode microbial fuel cells, *Bioresour. Technol.*, **102**, 316–323, (2011), doi: https://doi.org/10.1016/j.biortech.2010.06.096.

67 Rahimnejad, M., Adhami, A., Darvari, S., Zirepour, A., Oh, S.E.: Microbial fuel cell as new technology for bioelectricity generation: a review, *Alexandria Engineering* J., **54**, 745–756, (2015).

68 Miyahara, M., Kouzuma, A., Watanabe, K.: Effects of NaCl concentration on anode microbes in microbial fuel cells, *AMB Express*, **5**, 34, (2015), doi: https://doi.org/10.1186/s13568-015-0123-6.

69 Lefebvre, O., Tan, Z., Kharkwal, S., Ng, H.Y.: Effect of increasing anodic NaCl concentration on microbial fuel cell performance, *Bioresour. Technol.*, **112**, 336–340, (2012) doi: https://doi.org/10.1016/j.biortech.2012.02.048.

70 Miyahara, M., Kouzuma, A., Watanabe, K.: Sodium chloride concentration determines exoelectrogens in anode biofilms occurring from mangrove-grown brackish sediment, *Bioresour. Technol.*, **218**, 674–679, (2016), doi: https://doi.org/10.1016/j.biortech.2016.07.015.

71 Pfennig, N., Biebl, H.: *Desulfuromonas acetoxidans* gen. nov. and sp. nov., a new anaerobic, sulfur-reducing, acetate-oxidizing bacterium, *Arch. Microbiol.*, **110**, 3–12, (1976)

72 Gebhardt, N.A., Thauer, R.K., Linder, D., Kauflers, P.M., Pfennig, N.: Mechanism of acetate oxidation to CO_2 with elemental sulfur in *Desulfuromonas acetoxidans*, *Arch. Microbiol.*, **141**, 392–398, (1985).

73 Paulsen, J., Kröger, A., Thauer, R.K.: ATP-driven succinate oxidation in the catabolism of *Desulfuromonas acetoxidans*, *Arch. Microbiol.*, **144**, 78–83, (1986).

74 Badalamenti, J.P., Summers, Z.M., Chan, C.H., Gralnick, J.A., Bond, D.R.: Isolation and genomic characterization of 'Desulfuromonas soudanensis WTL', a metal- and electrode-respiring bacterium from anoxic deep subsurface brine, *Front. Microbiol.*, **7**, 913, (2016), doi: https://doi.org/10.3389/fmicb.2016.00913.

75 Sun, D., Call, D., Wang, A., Cheng, S., Logan, B.E.: *Geobacter* sp. SD-1 with enhanced electrochemical activity in high-salt concentration solutions, *Environ. Microbiol. Rep.*, **6**, 723–729, (2014).

76 Fan, Y., Hu, H., Liu, H.: Sustainable power generation in microbial fuel cells using bicarbonate buffer and proton transfer mechanisms, *Environ. Sci. Technol.*, **41**, 8154–8158, (2007), doi: https://doi.org/10.1021/es071739c.

phylogenetically related to *Arcobacter butzleri*, isolated from a microbial fuel cell, *Appl. Environ. Microbiol.*, **75**, 7326–7334, (2009).

77 Shleev, S., Bergel, A., Gorton, L.: Biological fuel cells: divergence of opinion, *Bioelectrochemistry*, **106**, 1–2, (2015).

78 Galushko, A.S., Kiesele-Lang, U., Kappler, A.: Degradation of 2-methylnaphthalene by a sulfate-reducing enrichment culture of mesophilic freshwater bacteria, *Polyc. Arom. Comp.*, **23**, 207–218, (2003).

79 Bertin, L., Lampis, S., Todaro, D., Scoma, A., Vallini, G., Marchetti, L., Majone, M., Fava, F.: Anaerobic acidogenic digestion of olive mill wastewaters in biofilm reactors packed with ceramic filters or granular activated carbon, *Water Res.*, **44**, 4537–4549, (2010).

80 Pendergast, M.T.M., Hoek, E.M.V.: A review of water treatment membrane nanotechnologies, *Energ. Environ. Sci.*, **4**, 1946–1971, (2011).

81 Lowy, D.A., Tender, L.M., Zeikus, J.G., Park, D.H., Lovley, D.R.: Harvesting energy from the marine sediment-water interface II. kinetic activity of anode materials, *Biosens. Bioelectron.*, **21**, 2058–2063, (2006), doi: https://doi.org/10.1016/j.bios.2006.01.033.

82 Park, D.H., Zeikus, J.G.: Improved fuel cell and electrode designs for producing electricity from microbial degradation, *Biotechnol Bioeng.*, **81**, [3], 348–55, (2003), doi: https://doi.org/10.1002/bit.10501.

83 Schroeder, U., Harnisch, F., Angenent, L.T.: Microbial electrochemistry and technology: terminology and classification, *Energ. Environ. Sci.*, **8**, 513–519, (2015), doi: https://doi.org/10.1039/C4EE03359K.

84 Zhou, M., Chi, M., Luo, J., He, H., Jin, T.: An overview of electrode materials in microbial fuel cells, *J. Power Sources*, **196**, 4427–4435, (2011) doi: https://doi.org/10.1016/j.jpowsour.2011.01.012.

85 Chen, S., He, G., Carmona-Martinez, A.A., Agarwal, S., Greiner, A., Hou, H., Schröder, U.: Electrospun carbon fiber mat with layered architecture for anode in microbial fuel cells, *Electrochem. commun.*, **13**, 1026–1029, (2011), doi: org/10.1016/j.elecom.2011.06.009.

86 Chen, S., He, G., Liu, Q., Harnisch, F., Zhou, Y., Chen, Y., Hanif, M., Wang, S., Peng, X., Hou, H., Schröder, U.: Layered corrugated electrode macrostructures boost microbial bioelectrocatalysis, *Energ. Environ. Sci.*, **5**, 9769–9772, (2012), doi: https://doi.org/10.1039/C2EE23344D.

87 Guo, K., Prévoteau, A., Patil, S.A., Rabaey, K.: Engineering electrodes for microbial electrocatalysis, *Curr. Opin. Biotechnol.*, **33**, 149–156, (2015), doi: https://doi.org/10.1016/j.copbio.2015.02.014.

88 Richter, H., Nevin, K.P., Jia, H., Lowy, D.A., Lovley, D.R., Tender, L.M.: Cyclic voltammetry of biofilms of wild type and mutant Geobacter sulfurreducens on fuel cell anodes indicates possible roles of OmcB, OmcZ, type IV pili, and protons in extracellular electron transfer, *Energ. Environ. Sci.*, **2**, 506–516, (2009), doi: https://doi.org/10.1039/B816647A.

89 Kuzmicheva, E.V., Reshetov, V.A., Kazarinov, I.A., Ignatov, O.V.: Discharge performance of the microbial fuel cell based on the bacterial species EscherichiaColi, in Russian, Elektrochimicheskaya energetika (Electrochemical energetics), 7, [1], 33–37, (2007).

90 Kusacheva, S.A., Chernyaev, S.I., Saschenko, I.I., Grishakova, V.V., Zhukova, Yu.M., Morozenko, D.N.: Justfication of the choice of designs and materials of bio-power generation system, in russian, *Sovremennye naukoemkie tekhnologii, (Modern high technologies)*, **6**, [1], 51–54, (2016).

91 Thorne, R., Hu, H., Schneider, K., Bombelli, P., Fisher, A., Peter, L.M., Dentc, A., Cameron, P.J.: Porous ceramic anode materials for photo-microbial fuel cells, *J. Mater. Chem.*, **21**, 18055–18060, (2011), doi: https://doi.org/10.1039/c1jm13058 g.

92 Bowen, C.R., Thomas, T.: Macro-porous Ti_2AlC MAX-phase ceramics by the foam replication method, *Ceram. Int.*, **41**, (9), 12178–12185, (2015), doi: https://doi.org/10.1016/j.ceramint.2015.06.038.

93 The online chemical encyclopedia http://www.xumuk.ru/encyklopedia

94 Zhong, Y., Xia, X., Shi, F., Zhan, J., Tu, J., Fan, H.J.: Transition metal carbides and nitrides in energy storage and conversion, *Adv. Sci.* **3**, 1500286, 1 of 28, (2016), doi: https://doi.org/10.1002/advs.201500286.

95 Benda, K.V., Binder, H., Köhling, A., Sandstede, G.: Electrochemical behaviour of tungsten carbide electrodes. In: G. Sandstede (Ed.), From Electrocatalysis to Fuel Cells. The University of Washington Press, Seattle, 1972.

96 Palanker, V.S., Gajyev, R.A., Sokolsky, D.V.: On adsorption and electro-oxidation of some compounds on tungsten carbide; their effect on hydrogen electro-oxidation, *Electrochim. Acta*, **22**, 133–136, (1977), doi: https://doi.org/10.1016/0013-4686(77)85025-1.

97 Zeng, L., Zhang, L., Li, W., Zhao, S., Lei, J., Zhou, Z.: Molybdenum carbide as anodic catalyst for microbial fuel cell based on *Klebsiella pneumoniae*, *Biosens. Bioelectron.*, **25**, 2696–2700, (2010), doi: https://doi.org/10.1016/j.bios.2010.05.002.

98 Zhang, L.X., Zhou, S.G., Zhuang, L., Li, W.S., Zhang, J.T., Lu, N., Deng, L.F.: Microbial fuel cell based on *Klebsiella pneumoniae* biofilm, *Electrochem. Commun.*, **10**, 1641–1643, (2008), doi: https://doi.org/10.1016/j.elecom.2008.08.030.

99 Zeng, L.Z., Zhao, S.F., Li, W.S.: Ni_3Mo_3C as anode catalyst for high-performance microbial fuel cells, *Appl. Biochem. Biotechnol.*, 2637–2646, (2015), doi: https://doi.org/10.1007/s12010-014-1458-1.

100 Zeng, L.Z., Zhao, S.F., Wang, Y.Q., Li, H., Li, W.S.: Ni/ß-Mo_2C as noble-metal-free anodic electrocatalyst of microbial fuel cell based on klebsiella pneumonia, *Int. J. Hydrogen Energ.*, **37**, 4590–4596, (2012), doi: https://doi.org/10.1016/j.ijhydene.2011.05.174.

101 Park, I.H., Christy, M., Kim, P., Nahm, K.S.: Enhanced electrical contact of microbes using Fe_3O_4/CNT nanocomposite anode in mediator-less microbial fuel cell, *Biosens. Bioelectron.*, **58**, 75–80, (2014), doi: org/10.1016/j.bios.2014.02.044.

102 Song, T.S., Wang, D.B., Li X., Liang, Y., Xie, J.: Cobalt oxide/ nanocarbon hybrid materials as alternative cathode catalyst for oxygen reduction in microbial fuel cell, *Int. J. Hydrogen Energ.*, **40**, 3868–3874, (2015), doi: https://doi.org/10.1016/j.ijhydene.2015.01.119.

103 Mehdinia, A., Ziaei, E., Jabbari, A.: Multi-walled carbon nanotube/SnO_2 nanocomposite: A novel anode material for microbial fuel cells, *Electrochim. Acta*, **130**, 512–518, (2014), doi: https://doi.org/10.1016/j.electacta.2014.03.011.

104 Lv, Z., Xie, D., Yue, X., Feng, C., Wei, C.: Ruthenium oxide-coated carbon felt electrode: A highly active anode for microbial fuel cell applications, *J. Power Sources*, **210**, 26–31, (2012), doi: https://doi.org/10.1016/j.jpowsour.2012.02.109.

105 Peng, X., Yu, H., Ai, L., Li, N., Wang, X.: Time behavior and capacitance analysis of nano-Fe_3O_4 added microbial fuel cells. *Bioresour. Technol.*, **144**, 689–692, (2013), doi: https://doi.org/10.1016/j.electacta.2013.07.166.

106 Qiao, Y., Bao, S.J., Li, C.M., Cui, Q.Q., Lu, Z.S., Quo, J.: Nanostructured Polyaniline/Titanium fuel cells, *ACS Nano*, **2**, 113–119, (2008), doi: https://doi.org/10.1021/nn700102s.

107 Wu, Y., Zhang, X., Li, S., Lv, X., Cheng, Y., Wang, X.: Microbial biofuel cell operating effectively through carbon nanotube blended with gold-titania nanocomposites modified electrode, *Electrochim. Acta*, **109**, 328–332, (2013), doi: https://doi.org/10.1016/j.electacta.2013.07.166.

108 Mehdinia, A., Ziaei, E., Jabbari, A.: Facile microwave-assisted synthesized reduced graphene oxide/tin oxide nanocomposite and using as anode material of microbial fuel cell to improve power generation, *Int. J. Hydrogen Energ.*, 39, 10724–10730, (2014), doi: https://doi.org/10.1016/j.ijhydene.2014.05.008.

109 Varanasi, J.L., Nayak, A.K., Sohn, Y., Pradhan, D., Das, D.: Improvement of power generation of microbial fuel cell by integrating tungsten oxide electrocatalyst with pure or mixed culture biocatalysts, *Electrochim. Acta*, 199, 154–163, (2016), doi: https://doi.org/10.1016/j.electacta.2016.03.152.

110 Read, S.T., Dutta, P., Bond, P.L., Keller, J., Rabaey, K.: Initial development and structure of biofilms on microbial fuel cell anodes, *BMC Microbiol*, 10, 98, 1 of 10, (2010), doi: https://doi.org/10.1186/1471-2180-10-98.

111 Pham, T.H., Aelterman, P., Verstraete, W.: Bioanode performance in bioelectrochemical systems: recent improvements and prospects, *Trends Biotechnol.*, 27, 168–178, (2009), doi: https://doi.org/10.1016/j.tibtech.2008.11.005.

112 Wang, Y., Li, B., Zeng, L., Cui, D., Xiang, X., Li, W.: Polyaniline/mesoporous tungsten trioxide composite as anode electrocatalyst for high-performance microbial fuel cells, *Biosens. Bioelectron.*, 41, 582–588, (2013), doi: https://doi.org/10.1016/j.bios.2012.09.054.

113 Yin, Y., Huang, G., Zhou, N., Liu, Y., Zhang, L.: Increasing power generation of microbial fuel cells with a nano-CeO_2 modified anode, *Energ. Source. Part A*, 38, 1212–1218, (2016), doi: https://doi.org/10.1080/15567036.2014.898112.

114 Mustakeem, M.: Electrode materials for microbial fuel cells: nanomaterial approach, *Mater. Renew. Sustain. Energy*, 4, 1–11, (2015), doi: https://doi.org/10.1007/s40243-015-0063-8.

115 Chen, W., Liu, Z., Su1, G., Fu1, Y., Zai, X., Zhou, C., Wang, J.: Composite-modified anode by MnO_2/polypyrrole in marine benthic microbial fuel cells and its electrochemical performance, *Int. J. Energy Res.*, 41, 845–853, (2016), doi: https://doi.org/10.1002/er.3674.

116 Santoro, C., Artyushkova, K., Gajda, I., Babanova, S., Serov, A., Atanassov, P., Greenman, J., Colombo, A., Trasatti, S., Ieropoulos, I.: Cathode materials for ceramic based microbial fuel cells (MFCs), *Int. J. Hydrogen Energ.*, 40, [42], 14706–14715, (2015a).

117 Midyurova, B., Nenov, V., Ates, M., Uludag, N.: Improvements of MFC's proton exchange membranes and cathodes, *J. Mater. Environ. Sci.*, 7, [1], 85–95, (2016).

118 Midyurova, B., Yemendzhiev, H., Tanev, P., Nenov, V.: Application of different ceramic materials to the microbial fuel cell design, *J. Chem. Technol. Metallurg.*, 50, [4], 543–550, (2015).

119 Winfield, J., Greenman, J., Huson, D., Ieropoulos, I.: Comparing terracotta and earthenware for multiple functionalities in microbial fuel cells, *Bioprocess Biosyst. Eng.*, 36, [12], 1913–1921, (2013a), doi: https://doi.org/10.1007/s00449-013-0967-6.

120 Chatterjee, P., Ghangrekar, M.M.: Design of clayware separator-electrode assembly for treatment of wastewater in microbial fuel cells, *Appl. Biochem. Biotechnol.*, 173, 378–390, (2014a), doi: https://doi.org/10.1007/s12010-014-0846-x.

121 Venkatesan, P.N., Dharmalingam, S.: Synthesis and characterization of pt, Pt-Fe/TiO_2 cathode catalysts and its evaluation in microbial fuel cell, *Mater Renew Sustain Energy*, 5:11, (2016).

122 Maass, S., Finsterwalder, F., Frank, G., Hartmann, R., Merten, C.: Carbon support oxidation in PEM fuel cell cathodes, *J. Power Sources*, 176, [2], 444–451, (2008).

123 Jinfeng, Z., Peng, Z., Jianjun, L., Jiaguo, Y.: New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO_2, *Phys. Chem. Chem. Phys.*, 16, 20382–20386, (2014).

124 Wang, Y.J., Wilkinson, D.P., Zhang, J.: Noncarbon support materials for polymer electrolyte membrane fuel cell electrocatalysts, *Chem. Rev.*, 111, [12], 7625–7651, (2011).

125 Yuan, H., Hou, Y., Abu-Reesh, I.M., Chen, J., He, Z.: Oxygen reduction reaction catalysts used in microbial fuel cells for energy-efficient wastewater treatment: a review, *Mater. Horiz.*, 3, 382–401, (2016).

126 Stoerzinger, K.A., Risch, M., Han, B., Shao-Horn, Y.: Recent insights into manganese oxides in catalyzing oxygen reduction kinetics, *ACS Catal.*, 5, 6021–6031, (2015).

127 Li, X., Hu, B., Suib, S., Lei, Y., Li, B.: Manganese dioxide as a new cathode catalyst in microbial fuel cells, *J. Power Sources*, 195, 2586–2591, (2010).

128 Li, X., Hu, B., Suib, S., Lei, Y., Li., B.: Electricity generation in continuous flow microbial fuel cells (MFCs) with manganese dioxide (MnO_2) cathodes, *Biochem. Eng. J.*, 54, 10–15, (2011).

129 Zhang, L., Liu, C., Zhuang, L., Li, W., Zhou, S., Zhang, J.: Manganese dioxide as an alternative cathodic catalyst to platinum in microbial fuel cells, *Biosens. Bioelectron.*, 24, 2825–2829, (2009).

130 Lu, M., Kharkwal, S., Ng, H.Y., Li, S.F.Y.: Carbon nanotube supported MnO_2 catalysts for oxygen reduction reaction and their applications in microbial fuel cells, *Biosens. Bioelectron.*, 26, 4728–4732, (2011).

131 Liu, X.-W., Sun, X.-F., Huang, Y.-X., Sheng, G.-P., Zhou, K., Zeng, R.J., Dong, F., Wang, S.-G., Xu, A.-W., Tong, Z.-H., Yu, H.-Q.: Nano-structured manganese oxide as a cathodic catalyst for enhanced oxygen reduction in a microbial fuel cell fed with a synthetic wastewater, *Water Res.*, 44, 5298–5305, (2010).

132 Zhang, P., Li, K., Liu, X.: Carnation-like MnO_2 modified activated carbon air cathode improve power generation in microbial fuel cells, *J. Power Sources*, 264, 248–253, (2014).

133 Cheng, F., Shen, J., Peng, B., Pan, Y., Tao, Z., Chen, J.: Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts, *Nat. Chem.*, 3, 79–84, (2011).

134 Liew, K.B., Daud, R.W., Chasemi, M., Loh, K.S., Ismail, M., Lim, S.S., Leong, J.X.: Manganese oxide/functionalised carbon nanotubes nanocomposite as catalyst for oxygen reduction reaction in microbial fuel cell, *Int. J. Hydrogen Energ.*, 40, [35], 11625–11632, (2015).

135 Zhang, Y., Hu, Y., Li, S., Sun, J., Hou, B.: Manganese dioxide-coated carbon nanotubes as an improved cathodic catalyst for oxygen reduction in a microbial fuel cell, *J. Power Sources*, 196, 9284–9289, (2011).

136 Chen, Y., Lv, Z., Xu, J., Peng, D., Liu, Y., Chen, J., Sun, X., Feng, C., Wei, C.: Stainless steel mesh coated with MnO_2/carbon nanotube and polymethylphenyl siloxane as low-cost and high-performance microbial fuel cell cathode materials, *J. Power Sources*, 201, 136–141, (2012), doi: https://doi.org/10.1016/j.jpowsour.2011.10.134.

137 Wen, Q., Wang, S., Yan, J., Cong, L., Pan, Z., Ren, Y., Fan, Z.: MnO_2-graphene hybrid as an alternative cathodic catalyst to platinum in microbial fuel cells, *J. Power Sources*, 216, 187–191, (2012), doi: https://doi.org/10.1016/j.jpowsour.2012.05.023.

138 Kumar, G.G., Awan, Z., Nahm, K.S., Xavier, J.S.: Nanotubular MnO_2/graphene oxide composites for the application of open air-breathing cathode microbial fuel cells, *Biosens. Bioelectron.*, 53, 528–534, (2014), doi: https://doi.org/10.1016/j.bios.2013.10.012.

139 Yuan, H., Deng, L., Tang, J., Zhou, S., Chen, Y., Yuan, Y.: Facile synthesis of MnO_2/polypyrrole/MnO_2 multiwalled nanotubes as advanced electrocatalysts for the oxygen reduction reaction, *ChemElectroChem*, 2, 1152–1158, (2015).

140 Gong, X.-B., You, S.-J., Wang, X.-H., Zhang, J.-N., Gan, Y., Ren, N.-Q.: A novel stainless steel mesh/cobalt oxide hybrid

electrode for efficient catalysis of oxygen reduction in a microbial fuel cell, *Biosens. Bioelectron.*, **55**, 237–241, (2014).

141 Ge, B., Li, K., Fu, Z., Pu, L., Zhang, X.: The addition of ortho-hexagon nano spinel Co_3O_4 to improve the performance of activated carbon air cathode microbial fuel cell, *Bioresour. Technol.*, **195**, 180–187, (2015).

142 Ahmed, J., Kim, H.J., Kim, S.: Embedded cobalt oxide nano particles on carbon could potentially improve oxygen reduction activity of cobalt phthalocyanine and its application in microbial fuel cells, *RSC Adv.*, **4**, 44065–44072, (2014).

143 Ge, B., Li, K., Fu, Z., Pu, L., Zhang, X., Liu, Z., Huang, K.: The performance of nano urchin-like $NiCo_2O_4$ modified activated carbon as air cathode for microbial fuel cell, *J. Power Sources*, **303**, 325–332, (2016).

144 Khilari, S., Pandit, S., Das, D., Pradhan, D.: Manganese cobaltite/polypyrrole nanocomposite-based air-cathode sustainable power generation in the single-chambered microbial fuel cells, *Biosens. Bioelectron.*, **54**, 534–540, (2014).

145 Hu, D., Wang, H., Wang, J., Zhong, Q.: Carbon-supported Cu-doped Mn-Co spinel-type oxides used as cathodic catalysts for the oxygen reduction reaction in dual-chambered microbial fuel cells, *Energy Technol.*, **3**, 48–54, (2015), doi: https://doi.org/10.1002/ente.201402110.

146 Dong, H., Yu, H., Wang, X., Zhou, Q., Sun, J.: Carbon-supported perovskite oxides as oxygen reduction reaction catalyst in single chambered microbial fuel cells, *Chem. Technol. Biotechnol.*, **88**, 774–778, (2013), doi: https://doi.org/10.1002/jctb.3893.

147 Ahmed, J., Yuan, Y., Zhou, L., Kim, S.: Carbon supported cobalt oxide nanoparticles-iron phthalocyanine as alternative cathode catalyst for oxygen reduction in microbial fuel cells, *J. Power Sources*, **208**, 170–175, (2012).

148 Wang, P., Lai, B., Li, H., Du, Z.: Deposition of fe on graphite felt by thermal decomposition of $Fe(CO)_5$ for effective cathodic preparation of microbial fuel cells, *Bioresour. Technol.*, **134**, 30–35, (2013).

149 Ma, M., Dai, Y., Zou, J.-L., Wang, L., Pan, K., Fu, H.-G.: Synthesis of iron oxide/partly graphitized carbon composites as a high-efficiency and low-cost cathode catalyst for microbial fuel cells, *ACS Appl. Mater. Interfaces*, **6**, 13438–13447, (2014).

150 Ma, M., You, S., Gong, X., Dai, Y., Zou, J., Fu, H.: Silver/iron oxide/graphitic carbon composites as bacteriostatic catalysts for enhancing oxygen reduction in microbial fuel cells, *J. Power Sources*, **283**, 74–83, (2015).

151 Huang, J., Zhu, N., Yang, T., Zhang, T., Wu, P., Dang, Z.: Nickel oxide and carbon nanotube composite (NiO/CNT) as a novel cathode non-precious metal catalyst in microbial fuel cells, *Biosens. Bioelectron.*, **72**, 332–339, (2015), https://doi.org/10.1016/j.bios.2015.05.035.

152 Liu, Z., Li, K., Zhang, X., Ge, B., Pu, L.: Influence of different morphology of three-dimensional Cu_xO with mixed facets modified air-cathodes on microbial fuel cell, *Bioresour. Technol.*, **195**, 154–161, (2015).

153 Zhang, X., Li, K., Yan, P., Liu, Z., Pu, L.: N-type Cu_2O doped activated carbon as catalyst for improving power generation of air cathode microbial fuel cells, *Bioresour. Technol.*, **187**, 299–304, (2015).

154 Noori, M.T., Ghangrekar, M.M., Mukherjee, C.K.: V_2O_5 microflower decorated cathode for enhancing power generation in air-cathode microbial fuel cell treating fish market wastewater, *Int. J. Hydrogen Energ.*, **41**, 3638–3645, (2016).

155 Ghoreishi, K.B., Ghasemi, M., Rahimnejad, M., Yarmo, M.A., Daud, W.R.W., Asim, N., Ismail, M.: Development and application of vanadium oxide/polyaniline composite as a novel cathode catalyst in microbial fuel cell, *Int. J. Energ. Res.*, **38**, 70–77, (2014), doi: https://doi.org/10.1002/er.3082.

156 Mecheri, B., Iannaci, A., D'Epifanio, A., Mauri, A., Licoccia, S.: Carbon-supported zirconium oxide as a cathode for microbial fuel cell applications, *ChemPlusChem*, **81**, 80–85, (2016).

157 Morris, J.M., Jin, S., Wang, J., Zhu, C., Urynowicz, M.A.: Lead dioxide as an alternative catalyst to platinum in microbial fuel cells, *Electrochem. Commun.*, **9**, 1730–1734, (2007).

158 Garino, N, Sacco, A., Castellino, M., Munõz-Tabares, J.A., Chiodoni, A., Agostino, V., Margaria, V., Gerosa, M., Massaglia, G., Quaglio, M.: Microwave-assisted synthesis of reduced graphene oxide/SnO_2 nanocomposite for oxygen reduction reaction in microbial fuel cells, *ACS Appl. Mater. Interfaces*, **8**, 4633–4643, (2016), doi: https://doi.org/10.1021/acsami.5b11198.

159 Singh, I., Chandra, A.: Use of the oxygen storage material CeO_2 as co-catalyst to improve the performance of microbial fuel cells, *Int. J. Hydrogen Energ.*, **41**, 1913–1920, (2016).

160 Khilari, S., Pandit, S., Varanasi, J.L., Das, D., Pradhan, D.: Bifunctional manganese ferrite/polyaniline hybrid as electrode material for enhanced energy recovery in microbial fuel cell, *ACS Appl. Mater. Interfaces*, **7**, 20657–20666, (2015).

161 Wen, Z., Zhang, S.Ci.F., Feng, X., Cui, S., Mao, S., Luo, S., He, Z., Chen, J.: Nitrogen-enriched core-shell structured Fe/Fe_3C-C nanorods as advanced electrocatalysts for oxygen reduction reaction, *Adv. Mater.*, **24**, 1399–1404, (2012), doi: https://doi.org/10.1002/adma.201104392.

162 Chen, R., Li, H., Chu, D., Wang, G.: Unraveling oxygen reduction reaction mechanisms on carbon-supported Fe-phthalocyanine and Co-phthalocyanine catalysts in alkaline solutions, *J. Phys. Chem.*, **113**, 20689–20697, (2009).

163 Burkitt, R., Whiffen, T.R., Yu, E.H.: Iron phthalocyanine and MnOx composite catalysts for microbial fuel cell applications, *Appl. Catal.*, *B*, **181**, 279–288, (2016).

164 Zhang, Y., Mo, G., Li, X., Ye, J.: Iron tetrasulfophthalocyanine functionalized graphene as a platinum-free cathodic catalyst for efficient oxygen reduction in microbial fuel cells, *J. Power Sources*, **197**, 93–96, (2012), doi: https://doi.org/10.1016/j.jpowsour.2011.06.105.

165 Gupta, S., Tryk, D., Bae, I., Aldred, W., Yeager, E.: Heat-treated polyacrylonitrile-based catalysts for oxygen electroreduction, *J. Appl. Electrochem.*, **19**, 19–27, (1989).

166 You, S., Gong, X., Wang, W., Qi, D., Wang, X., Chenand, X., Ren, N.: Enhanced cathodic oxygen reduction and power production of microbial fuel cell based on noble-metal-free electrocatalyst derived from metal-organic frameworks, *Adv. Energy Mater.*, **6**, (2016), doi: https://doi.org/10.1002/aenm.201501497.

167 Zhao, F., Harnisch, F., Schröder, U., Scholz, F., Bogdanoff, P., Herrmann, I.: Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells, *Electrochem. Commun.*, **7**, 1405–1410, (2005), doi: https://doi.org/10.1016/j.elecom.2005.09.032.

168 Birry, L., Mehta, P., Jaouen, F., Dodelet, J.P., Guiot, S.R., Tartakovsky, B.: Application of iron-based cathode catalysts in a microbial fuel cell, *Electrochim. Acta*, **56**, 1505–1511, (2011).

169 Deng, L., Zhou, M., Liu, C., Liu, L., Liu, C., Dong, S.: Development of high performance of Co/Fe/N/CNT nanocatalyst for oxygen reduction in microbial fuel cells, *Talanta*, **81**, 444–448, (2010), doi: https://doi.org/10.1016/j.talanta.2009.12.022.

170 Schulenburg, H., Stankov, S., Schünemann, V., Radnik, J., Dorbandt, I., Fiechter, S., Bogdanoff, P., Tributsch, H.: Catalysts for the oxygen reduction from heat-treated iron(III) tetramethoxyphenylporphyrin chloride: structure and stability of active sites, *J. Phys. Chem. B*, **107**, 9034–9041, (2003).

171 Yu, E.H., Cheng, S., Logan, B.E., Scott, K.: Electrochemical reduction of oxygen with iron phthalocyanine in neutral media, *J. Appl. Electrochem.*, **39**, 705–711, (2008), doi: https://doi.org/10.1007/s10800-008-9712-2.

172 Nguyen, M.-T., Mecheri, B., Iannaci, A., D'Epifanio, A., Licoccia, S.: Iron/polyindole-based electrocatalysts to enhance oxygen reduction in microbial fuel cells, *Electrochim. Acta*, **190**, 388–395, (2006).

173 Kim, J.R., Kim, J.-Y., Han, S.-B., Park, K.-W., Saratale, G.D., Oh, S.-E.: Application of Co-naphthalocyanine (CoNPc) as alternative cathode catalyst and support structure for microbial fuel cells, *Bioresour. Technol.*, **102**, 342–347, (2011), doi: https://doi.org/10.1016/j.biortech.2010.07.005.

174 Pan, Y., Mo, X., Li, K., Pu, L., Liu, D., Yang, T.: Iron-nitrogen-activated carbon as cathode catalyst to improve the power generation of single-chamber air-cathode microbial fuel cells, *Bioresour. Technol.*, **206**, 285–289, (2016), https://doi.org/10.1016/j.biortech.2016.01.112.

175 Xia, X., Zhang, F., Zhang, X., Liang, P., Huang, X., Logan, B.E.: Use of pyrolyzed iron ethylenediaminetetraacetic acid modified activated carbon as air-cathode catalyst in microbial fuel cells, *ACS Appl. Mater. Interfaces*, **5**, 7862–7866, (2013), https://doi.org/10.1021/am4018225.

176 Ma, S., Goenaga, G.A., Call, A.V., Liu, D.-J.: Cobalt imidazolate framework as precursor for oxygen reduction electrocatalysts, *Chem. – Eur. J.*, **17**, 2063–2067, (2011), doi: https://doi.org/10.1002/chem.201003080.

177 Tang, H., Cai, S., Xie, S., Wang, Z., Tong, Y., Pan, M., Lu, X.: Metal-organic-framework-derived dual metal- and nitrogen-doped carbon as efficient and robust oxygen reduction reaction catalysts for microbial fuel cells, *Adv. Sci.*, **3**, 1500265, (2016), doi: https://doi.org/10.1002/advs.201500265.

178 Tang, X., Li, H., Wang, W., Du, Z., Ng, H.Y.: A high-performance electrocatalytic air cathode derived from aniline and iron for use in microbial fuel cells, *RSC Adv.*, **4**, 12789–12794, (2014), doi: https://doi.org/10.1039/c3ra47931e.

179 Tang, X., Li, H., Du, Z., Ng, H.Y.: Polyaniline and iron based catalysts as air cathodes for enhanced oxygen reduction in microbial fuel cells, *RSC Adv.*, **5**, 79348–79354, (2015), doi: https://doi.org/10.1039/C5RA16148G.

180 Su, Y., Jiang, H., Zhu, Y., Zou, W., Yang, X., Chen, J., Li, C.: Hierarchical porous iron and nitrogen co-doped carbons as efficient oxygen reduction electrocatalysts in neutral media, *J. Power Sources*, **265**, 246–253, (2014), https://doi.org/10.1016/j.jpowsour.2014.04.140.

181 Chan, Y.-Z., Dai, Y., Li, R., Zou, J.-L., Tian, G-H., Fu, H.-G.: Low-temperature synthesized nitrogen-doped iron/iron carbide/partly-graphitized carbon as stable cathode catalysts for enhancing bioelectricity generation, *Carbon*, **289**, 8–19, (2015), doi: https://doi.org/10.1016/j.carbon.2015.03.026.

182 Santoro, C., Serov, A., Narvaez Villarrubia, C.W., Stariha, S., Babanova, S., Schuler, A.J., Artyushkova, K., Atanassov, P.: Double-chamber microbial fuel cell with a non-platinum-group metal Fe-N-C cathode catalyst, *ChemSusChem*, **8**, 828–834, (2015), doi: https://doi.org/10.1002/cssc.201402570.

183 Li, S., Hu, Y., Xu, Q., Sun, J., Hou, B., Zhang, Y.: Iron- and nitrogen-functionalized graphene as a non-precious metal catalyst for enhanced oxygen reduction in an air-cathode microbial fuel cell, *J. Power Sources*, **213**, 265–269, (2012), doi: https://doi.org/10.1016/j.jpowsour.2012.04.002.

184 Milner, E.M.: Development of an aerobic biocathode for microbial fuel cells, PhD thesis, Chemical Engineering and Advanced Materials, Newcastle University, pp. 251, (2015).

185 Mao, Y., Zhang, L., Li, D., Shi, H., Liu, Y., Cai, L.: Power generation from a biocathode microbial fuel cell biocatalyzed by ferro/manganese-oxidizing bacteria, *Electrochim. Acta*, **55**, 7804–7808, (2010), doi: https://doi.org/10.1016/j.electacta.2010.03.004.

186 Rhoads, A., Beyenal, H., Lewandowski, Z.: Microbial fuel cell using anaerobic respiration as an anodic reaction and biomineralized manganese as a cathodic reactant, *Environ. Sci. Technol.*, **39**, 4666–4671, (2005).

187 Behera, M., Jana, P.S., Ghangrekar, M.M.: Performance evaluation of low cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode, *Bioresour. Technol.*, **101**, 1183–1189, (2010), doi: https://doi.org/10.1016/j.biortech.2009.07.089.

188 Chae, K.J., Choi, M., Ajayi, F.F., Park, W., Chang, I.S., Kim, I.S.: Mass transport through a proton exchange membrane (Nafion) in microbial fuel cells, *Energy Fuels*, **22**, 169–176, (2008), doi: https://doi.org/10.1021/ef700308u.

189 Daud, S.M., Kim, B.H., Ghasemi M., Daud, W.R.W.: Separators used in microbial electrochemical technologies: current status and future prospects, *Bioresour. Technol.*, **195**, 170–179, (2015), doi: https://doi.org/10.1016/j.biortech.2015.06.105.

190 Dhar, B.R., Lee, H.-S.: Membranes for bioelectrochemical systems: challenges and research advances, *Environ. Technol.*, **34**, 1751–1764, (2013), doi: http://dx.doi.org/10.1080/09593330.2013.822007.

191 Kim, K.-Y., Chae, K.-J., Choi, M.-J., Yang, E.-T., Hwang, M.H., Kim, I.S.: High-quality effluent and electricity production from non-CEM based flow-through type microbial fuel cell, *Chem. Eng. J.*, **218**, 19–23, (2013), doi: https://doi.org/10.1016/j.cej.2012.12.018.

192 Li, W.W., Sheng, G.P., Liu, X.W., Yu, H.Q.: Recent advances in the separators for microbial fuel cells, *Bioresour. Technol.*, **102**, 244–252, (2011), doi: https://doi.org/10.1016/j.biortech.2010.03.090.

193 Choi, M.-J., Chae, K.-J., Ajayi, F.F., Kim, K.-Y., Yu, H.-W., Kim, C.-W., Kim, I.S.: Effects of biofouling on ion transport through cation exchange membranes and microbial fuel cell performance, *Bioresour. Technol.*, **102**, 298–303, (2011), doi: https://doi.org/10.1016/j.biortech.2010.06.129.

194 Xu, J., Sheng, G.-P., Luo, H.W., Li, W.W., Wang, L.F., Yu, H.Q.: Fouling of proton exchange membrane (PEM) deteriorates the performance of microbial fuel cell, *Water Res.*, **46**, 1817–1824, (2012), doi: https://doi.org/10.1016/j.watres.2011.12.060.

195 Ter Heijne, A., Hamelers, H.V.M., De Wilde, V., Rozendal, R.A., Buisman, C.J.N.: A bipolar membrane combined with ferric iron reduction as an efficient cathode system in microbial fuel cells, *Environ. Sci. Technol.*, **40**, 5200–5205, (2006), doi: https://doi.org/10.1021/es0608545.

196 Kim, K.-Y., Yang, E., Lee, M.-Y., Chae, K.-J., Kim, C.-M., Kim, I.S.: Polydopamine coating effects on ultrafiltration membrane to enhance power density and mitigate biofouling of ultrafiltration microbial fuel cells (UF-MFCs), *Water Res.*, **54**, 62–68, (2014), doi: https://doi.org/10.1016/j.watres.2014.01.045.

197 Ge, Z., Ping, Q., Xiao, L., He, Z.: Reducing effluent discharge and recovering bioenergy in an osmotic microbial fuel cell treating domestic wastewater, *Desalination*, **312**, 52–59, (2013), doi: https://doi.org/10.1016/j.desal.2012.08.036.

198 Werner, C.M., Logan, B.E., Saikaly, P.E., Amy, G.L.: Wastewater treatment, energy recovery and desalination using a forward osmosis membrane in an aircathode microbial osmotic fuel cell, *J. Membrane Sci.*, **428**, 116–122, (2013), doi: https://doi.org/10.1016/j.memsci.2012.10.031.

199 Zhang, F., Brastad, K.S., He, Z.: Integrating forward osmosis into microbial fuel cells for wastewater treatment, water extraction and bioelectricity generation, *Environ. Sci. Technol.*, **45**, 6690–6696, (2011), doi: https://doi.org/10.1021/es201505t.

200 Winfield, J., Chambers, L.D., Rossite, J., Ieropoulos, I.: Comparing the short and long term stability of biodegradable, ceramic and cation exchange membranes in microbial fuel cells, *Bioresour. Technol.*, **148**, 480–486, (2013), doi: https://doi.org/10.1016/j.biortech.2013.08.163.

201 Ge, Z., He, Z.: Effects of draw solutions and membrane conditions on electricity generation and water flux in osmotic microbial fuel cells, *Bioresour. Technol.*, **109**, 70–76, (2012), doi: https://doi.org/10.1016/j.biortech.2012.01.044.

202 Seo, H.N., Lee, W.J., Hwang, T.S., Park, D.H.: Electricity generation coupled with wastewater treatment using a microbial fuel cell composed of a modified cathode with a ceramic membrane and cellulose acetate film, *J. Microbiol. Biotechnol.*, **19**, [9], 1019–1027, (2009), doi: https://doi.org/10.4014/jmb.0812.663.

203 Jackson, M.L.: Significance of kaolinite intercalation in clay mineral analysis, *Clay. Clay Miner.*, **9**, 424–430, (1960).

204 Tertre, E., Hubert, F., Bruzac, S., Pacreau, M., Ferrage, E., Pret, D.: Ion-exchange reactions on clay minerals coupled with advection/dispersion processes. application to Na^+/Ca^{2+} exchange on vermiculite: Reactive-transport modeling, batch and stirred flow-through reactor experiments, *Geochim. Cosmochim. Acta*, **112**, 1–19, (2013), doi: https://doi.org/10.1016/j.gca.2013.02.028.

205 Matthews, G.P., Laudone, G.M., Gregory, A.S., Bird, N.R.A., Matthews, A.D. G., Whalley, W.R.: Measurement and simulation of the effect of compaction on the pore structure and saturated hydraulic conductivity of grassland and arable soil, *Water Resour. Res.*, **46**, W05501, (2010), doi: https://doi.org/10.1029/2009WR007720.

206 Behera, M., Jana, P.S., More, T.T., Ghangrekar, M.M.: Rice mill wastewater treatment in microbial fuel cells fabricated using proton exchange membrane and earthen pot at different pH, *Bioelectrochemistry*, **79**, 228–233, (2010), doi: https://doi.org/10.1016/j.bioelechem.2010.06.002.

207 Jana, P.S., Behera, M., Ghangrekar, M.M.: Performance comparison of up-flow microbial fuel cells fabricated using proton exchange membrane and earthen cylinder, *Int. J. Hydrogen Energ.*, **35**, 5681–5686, (2010), doi: https://doi.org/10.1016/j.ijhydene.2010.03.048.

208 Behera, M., Ghangrekar, M.M.: Electricity generation in low cost microbial fuel cell made up of earthenware of different thickness, *Water Sci. Technol.*, **64**, 2468–2473, (2011), doi: https://doi.org/10.2166/wst.2011.822.

209 Ajayi, F.F., Weigele, P.R.: A terracotta bio-battery, *Bioresour. Technol.*, **116**, 86–91, (2012), doi: https://doi.org/10.1016/j.biortech.2012.04.019, Epub 2012 Apr 17.

210 Ghadge, A.N., Sreemannarayana, M., Duteanu, N., Ghangrekar, M.M.: Influence of ceramic separator's characteristics on microbial fuel cell performance, *J. Electrochem. Sci. Eng.*, **4**, [4], 315–326, (2014), doi: http://dx.doi.org/10.5599/81.

211 Ghadge, A.N., Ghangrekar, M.M.: Development of low cost ceramic separator using mineral cation exchanger to enhance performance of microbial fuel cells, *Electrochim. Acta.*, **166**, 320–328, (2015), doi: https://doi.org/10.1016/j.electacta.2015.03.105.

212 Pasternak, G., Greenman, J., Ieropoulos, I.: Comprehensive study on ceramic membranes for low-cost microbial fuel cells, *Chemsuschem*, **9**, 88–96, (2016), doi: https://doi.org/10.1002/cssc.201501320.

213 Ieropoulos, I.A., Ledezma, P., Stinchcombe, A., Papaharalabos, G., Melhuish, C., Greenman, J.: Waste to real energy: the first MFC powered mobile phone, *Phys. Chem. Chem. Phys.*, **15**, [37], 15312–15316, (2013), doi: https://doi.org/10.1039/c3cp52889h.

214 Yang, E., Chae, K., Kim, I.S.: Assessment of different ceramic filtration membranes as a separator in microbial fuel cells, *Desalination and Water Treatment.*, **57**, [58], 1–9, (2016), doi: https://doi.org/10.1080/19443994.2016.1183523.

215 Ciora, R., Liu, P.K.: Ceramic membranes for environmental related applications, *Fluid/Particle Sep. J.*, **15**, 51–60, (2003).