Chapter 5

The Role of Material Selection and Microfluidics for Optimized Energy Conversion in Microbial Fuel Cells

Giulia Massaglia and Marzia Quaglio

Additional information is available at the end of the chapter

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Abstract

This chapter book aims to present some key aspects, which play a crucial role to optimize the energy conversion process occurring in microbial fuel cells (MFCs): fluid dynamics and the materials selected as anodic electrodes. MFCs are (bio)-electrochemical devices that directly convert chemical energy into electrical energy, thanks to the metabolic activity of some bacteria. In the anodic compartment, these bacteria, named exoelectrogens, are able to oxidize the organic matter, directly releasing the electrons to the anode surface. The conversion process can be deeply influenced by how the electrolyte solution, containing the carbon-energy source, moves inside the device. For this reason, fluid dynamic modeling is an important tool to explain the correlation between the fluid flow and power output production, optimizing also the overall MFC performance. Moreover, the morphology of anode electrodes results to be essential to guarantee and enhance the bacteria proliferation on them, improving the energy conversion.

Keywords: microbial fuel cells, bioelectrochemical devices, exoelectrogenic bacteria, fluid dynamic, modeling

1. Introduction

Since in the next years, the high level of greenhouse gas emissions (GHG) must be reduced as confirmed by Kyoto protocol [1, 2], the development and investigation of renewable energy sources are of ever increasing importance, since they are expected to play a leading role to further improve the life quality all over the world [3].

As represented in **Figure 1**, the conventional energy sources, based on oil, coal and natural gas, are widely used comparing with the renewable energy ones that is only 10% of U.S energy

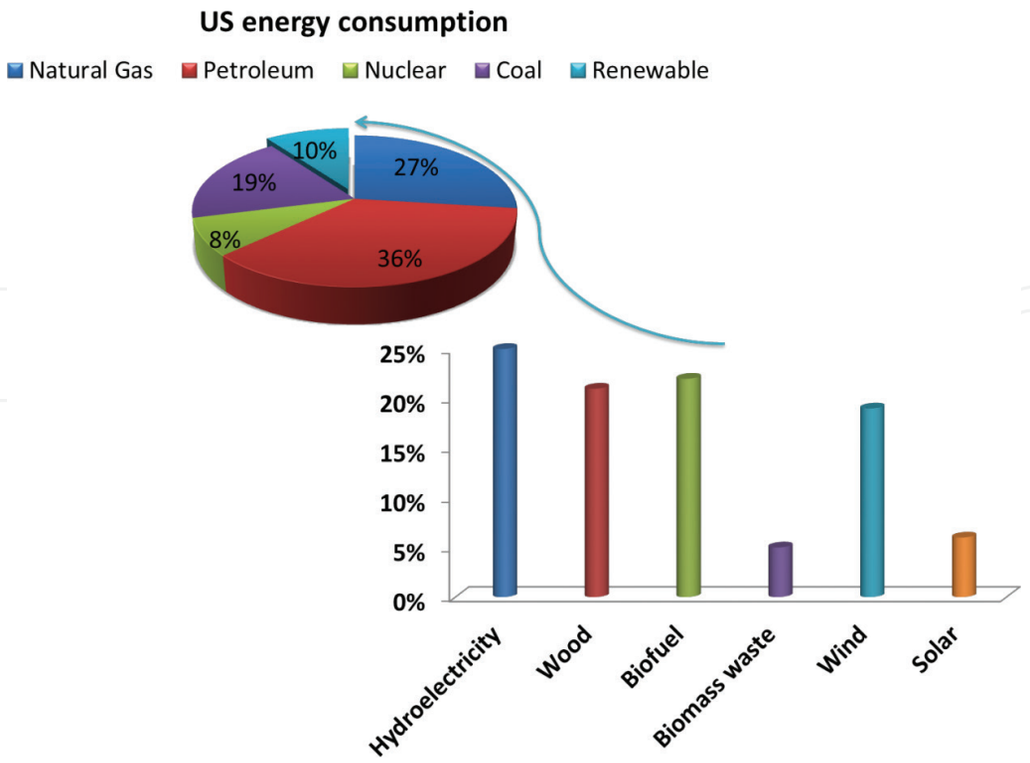

Figure 1. US energy consumption by energy sources in 2015.

consumption in 2015 [4]. The main targets of EU's Renewable Energy Directive are focused on two important aspects: (1) the renewable energy sources must represent the 20% of final/total energy consumption by 2020; (2) all EU countries must adopt national energy action plans, leading to carry out their renewable targets. Among all renewable energy sources, such as hydroelectricity, wood, geothermal, wind and solar, biofuel is produced/obtained/carried out/achieved through the biological processes, such as agriculture and anaerobic digestion, rather than a fuel obtained by geological processes, which are achieved in fossil fuels formation like coal and petroleum. Biofuels can be obtained directly from plants or derived indirectly by agricultural, commercial, domestic and/or industrial wastes. Furthermore, a biofuel cell is a device that realizes the conversion of chemical energy into electrical energy toward biochemical reactions. The electrons are produced by the oxidation reaction of a specific fuel. Among all different biofuel cells, microbial fuel cell (MFC) represents a promising technology as renewable energy sources.

In this chapter, MFC devices are proposed as bio-electrochemical devices that convert the chemical energy, embedded in organic compounds (fuel), into electrical energy by the action of exoelectrogenic microorganisms [5]. These electrochemical cells are based on a bio-anode, whose surfaces are colonized by microorganisms, which proliferate and drive/catalyse the oxidation reaction, occurring in the anodic compartment. In the past few decades, in order to validate the application of MFCs as energy production devices, different works in the literature focused their attention on different carbon energy sources as fuel [6–8]. Moreover, as highlighted by different works in the literature, both device architecture, which influence on the fluid dynamic distribution inside MFCs, and morphological properties of electrode materials play a crucial role to optimize/enhance overall performance/power output production. In this

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chapter, we also explained/described a growing interest in miniaturized these devices at the milliliter to microliter size [9–12]. In particular, the design of milliliter-size MFCs induced an optimization of carbon sources transport and the reduction of internal resistance of device, improving thus the power output production. The authors of several works in the literature demonstrate how the reduction/diminution of MFCs volume guarantees a small distance between electrodes, fast response time, a low Reynolds number and the possibility to investigate the electron transfer process due to the interaction between bacteria and anodic electrode.

2. MFCs technical aspects principle

The MFC is a bio-electrochemical device, where the microorganisms are used to convert chemical energy, trapped in an organic matter, into the electrical energy. The process is based on the concept that particular kind of microorganisms, named exoelectrogens, are able to oxidize the organic matter (also known as carbon energy sources) [13] and to directly transfer the produced electrons outside their cells exogenously [5]. Indeed, these microorganisms are capable to directly release the electrons to a chemical or materials that are not immediately the electron acceptor. Successively, the produced electrons flow from anodic electrode to terminal electron acceptor (TEA) through an external applied load. TEA acquires the electrons and becomes reduced in the cathode compartment (see **Figure 2**). Therefore, MFCs are characterized by three main compartments, as shown in **Figure 2**:

1. Anode chamber, where the organic matter oxidation reaction occurred, catalyzed by exoelectrogenic bacteria;
2. Cathode chamber, where the reduction reaction is carried out. The released electrons flow into cathode chamber through an external load applied, leading thus to reduce the terminal electron acceptor. Regarding the electrolyte in MFCs cathode compartment, many different chemical species accept the electron and then are reduced. One of them is the

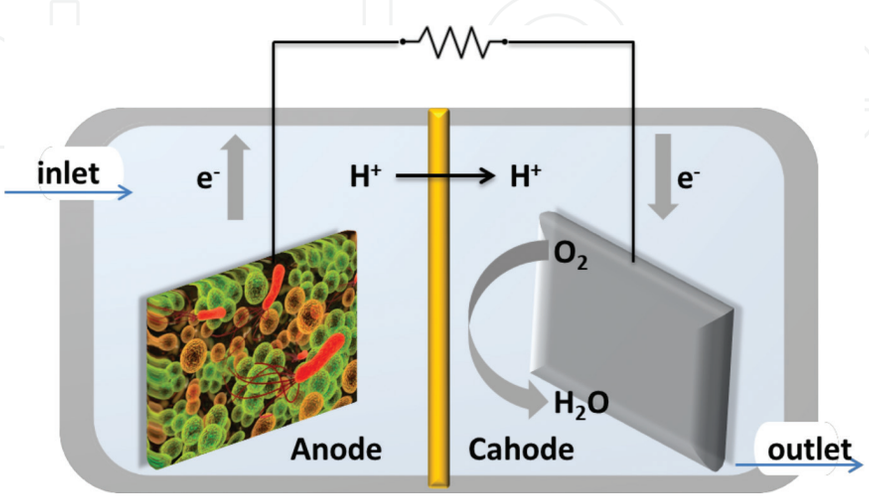

Figure 2. Scheme of working principle of microbial fuel cells (MFCs).

oxygen, dissolved into the electrolyte (normally electrolyte is based on water). The oxygen is reduced through a catalysed reaction of the electron with the protons, named oxygen reduction reaction (ORR). Many TEAs, such as oxygen, nitrate, sulphate and others, accept the electrons making some products that can diffuse outside the devices.

3. Proton exchange membrane (PEM), which is an anionic or cationic membrane that separates the anode and cathode chambers and ensure the protonic flow into the electrolyte.

3. Anode compartment

In the anode chamber bacteria grow on the electrode surface, generating a biofilm. According to IUPAC definition, the biofilm is an "Aggregate of microorganisms in which cells that are frequently embedded within a self-produced matrix of extracellular polymeric substance (EPS) adhere to each other and/or to a surface" [14]. The main difference between biofilm and planktonic microorganisms (bacteria that float in the liquid electrolyte) is represented by ability of bacteria to self-produce all the connections between among them and with anodic electrode surface. The adhesion of bacteria to the electrode surface is ensured by weak and reversible van der Waals forces. If the microorganisms are not immediately separated from the electrode surface, their anchorage became more effective and stronger by direct cell-adhesion by pili, and by a self-produced matrix of extracellular polymeric substances. The resulting biofilm in MFC's anode is formed by electrochemically active bacteria that oxidize the organic matter dissolved in the electrolyte, and acting as the carbon energy source in MFCs. In the last years, different works in the literature investigated the different electron transfer processes, carried out by bacteria in MFCs [15–20]. These processes can be divided into two mainly different ways:

1. electron shuttling via self-produced mediators [17, 18].
2. nanowires produced by some bacteria which are used as endogenous mediators [19, 20].

Direct electron transfer can be obtained by physical contact of redox active bacterial membrane organelle, such as cytochromes, with the anode electrode [21], as represented in **Figure 3a**. Otherwise, Gorbi et al. [19] investigated the conductive bacterial nanowires (or pili), produced

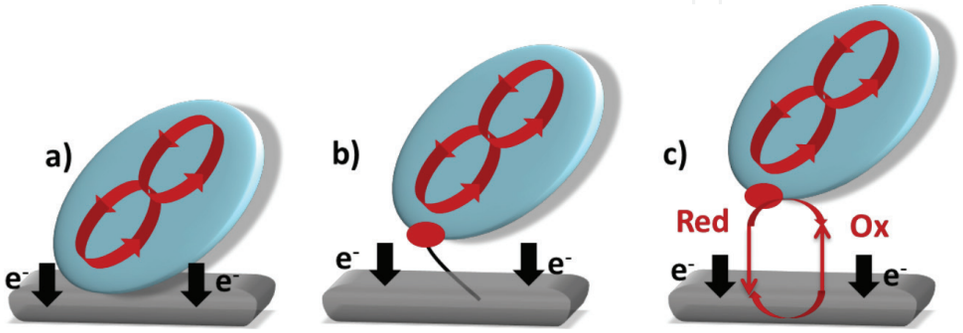

Figure 3. Scheme of the direct electron transfer pathway through (a) the membrane bound cytochromes, (b) nanowires self- produced by bacteria and (c) self-produced redox mediators.

by bacteria (Geobacter and Shewanella) as the pathway to direct transfer the electrons to anodic electrode, as shown in **Figure 3b**. Rabaey et al. [17, 18] defined the ability of certain bacteria to self-produce redox mediators, which then ensure the direct electron transfer to the anodic surface (see **Figure 3c**). He demonstrated that bacteria exist, which are able to generate exogenous redox mediators, which not have to be added to a culture. These self-produced mediators permit to shuttle the electrons to an electrode, inducing the power generation in a MFC.

4. Microbial fuel cells power output production

The theoretical concept, based on the power output production from MFCs, defined a direct correlation between power production and the measured voltage across the external applied load [22], as represented in Eq. (1):

$$P = I \cdot E_{MFC} \tag{1}$$

where I is the current produced from MFCs, E_{MFC} is voltage drop across the external applied resistor. One of the main parameters, that can affect produced current and consequently power production, is the surface area of anode electrode available for the microorganisms growth. For this reason, it is common to introduce the concept of power density, defined normalizing power production with anodic surface area (A_{anode}) [22]. Furthermore, since the measured current is defined as a function of the potential across the external resistance and it is needed to take into account the accessible surface area for bacteria proliferation, the power density output can be determined by Eq. (2):

$$P = \frac{{E_{MFC}}^2}{A_{anode} R_{external}} \tag{2}$$

As widely investigated by several works in the literature [22–24], the generated voltage by MFCs depends on both the microorganisms proliferation on anode electrode surface and anode and cathode voltages, as explained by Eq. (3):

$$E_{MFC} = E_{cathode} - E_{anode} \tag{3}$$

where $E_{cathode}$ and E_{anode} are respectively the cathode and anode voltages [22].

In particular, the anodic voltage is strictly correlated with the organic matter used as carbon energy source inside MFCs, the metabolic activity of the microorganisms and their adhesion on electrode surface, on which charge transfer depends. Different organic compounds are used as carbon energy sources inside MFCs [25, 26] to produce electricity. The most commonly used is sodium acetate, which can release a maximum of eight electrons when bacteria oxidized it [27, 28].

Chae et al. [28] investigated the single chamber microbial fuel cells (SCMFCs) performances with different substrates, such as acetate, butyrate, propionate and glucose. They demonstrated that the highest power output is associated with acetate feeding, followed by butyrate,

propionate and glucose. Despite of all kinds of organic matters, anodic open circuit voltage (a-OCV), defined as the highest potential reached by MFC when no external load is applied, is close to −0.3 V. At the cathode, the standard reduction potentials of all electrolytes, which must be reduced, influence the cathode voltage. Among all oxidants used in the cathode, such as metallic oxidants [29–35] (like U, Cd, Cr, Cu), the most commonly applied is oxygen, whose standard reduction potential is equal to 0.805 V. Nevertheless, direct oxygen reduction reaction (ORR) results to be thermodynamically disadvantageous due to its high reduction potential, low kinetics and high activation losses induced [22]. In order to evaluate the MFC voltage, it is mandatory to take into account the voltage losses caused by electrode overpotentials and ohmic losses, as represented by Eq. (4):

$$E_{MFC} = \sum V_{anode} + \left|\sum V_{cathode}\right| + IR_{\Omega} \tag{4}$$

where $\sum V_{anode}$ and $|\sum V_{cathode}|$ represent electrodes overpotentials and IR_{Ω} is the ohmic losses that are directly proportional to the generated current and internal resistance of MFCs. Theoretically, overpotentials consider all voltage drops required to favor, respectively, the electrons and protons transport inside the device. The electrode overpotentials are induced by three losses, as represented in **Figure 4** [5].

i. **Activation polarization losses** are due to the energy lost needed/necessary to start the oxidation or reduction reactions and to ensure electron transfer from the bacterial cells to the anode surface. The presence of catalyst at the cathode, the different bacteria in the anode compartment and the optimized electron transfer between bacteria and anode surface can minimize these losses. Furthermore, since the current density tends to be reduced when the anode surface increase, one of the strategies to overcome activation losses is related to use anode electrodes characterized by an high porosity and/or high roughness [36]. Another way can be represented by an improvement of interaction between bacteria and anodic electrodes, enhancing thus the electron transfer outside the microbe cells to anode surface. As shown in **Figure 4**, it is possible to appreciate that the activation losses result to be more evident at low current values.

ii. **Ohmic losses** are strictly correlated with internal resistance (R_{Ω}) of MFCs. Ohmic losses are due to all parameters that can increase the internal device resistance. The internal resistance is defined as the resistance to the electrons flow in electrodes and connections, and the resistance to ionic transport in the electrolyte and through PEM, if is present. They can be defined by Ohm's Law, as explained in Eq. (5):

$$\eta_{\Omega} = IR_{\Omega} \tag{5}$$

The distance between anode and cathode electrodes, the biofilm formation on anode surface, the fluid dynamic distribution of electrolyte inside the device and consequently the designed architecture of MFCs can influence the ohmic losses. In order to improve overall device performance, ohmic losses must be overcome. In particular, increasing of electrical conductivity of anode materials, minimizing the distance between anode and cathode leading to favor electrons flow and optimizing the contact between electrodes and electron collectors can

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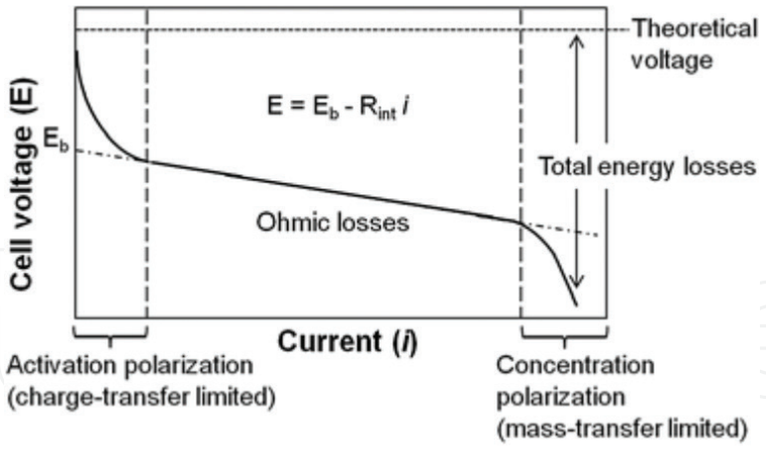

Figure 4. The polarization curve for typical MFCs. Reprinted with the permission from (chemical society reviews, 2012, 41, 7228–7246) copyright (2012) Royal Society of Chemistry.

avoid ohmic losses, as much as possible. Xie et al. [37] demonstrated how three-dimensional structure of anode electrode increases the surface area to volume ratio, improving thus the interaction between microorganisms and electrodes and consequently ensuring a higher electron transport. Another important parameter is the distance between anode and cathode electrodes, lower is this distance, lower is the internal resistance since the electron and protonic pathway is reduced. Liu et al. [38] compared the power outputs obtained by MFCs when two different spacing, equal to 4 cm ad 2 cm, between two electrodes are used, highlighting that power density, when the distance is of 2 cm, is double than the one reached when distance is 4 cm. Different works in the literature also underlined how the proton exchange membrane (PEM) increases the internal resistance of MFCs [39]. Indeed, the removal of PEM not only simplifies the design of device, but it can also reduce ohmic losses and consequently increases the power output production.

iii. Mass transports losses carry out when the amount of reactants to the electrodes or products from electrodes is insufficient, leading thus to minimize the reaction rate. These losses, moreover, can be modified the metabolic activities of microorganisms. These losses not only limit the power generation of MFCs, but they increase the pH, hindering/minimizing the proton diffusion and consequently reducing significantly the current density production. Mass transport losses achieved at high current densities.

Moreover, among all voltage losses, it is needed to consider the bacterial metabolism, which induces a voltage drop due to the energy suitable for bacteria sustainability.

5. Anodic materials and their influence on power output production

Among all parameters that influence the overall device performance, the materials used at the anode, the electrochemical active biofilm at the electrode, and the device configuration play an important active role to establish the MFCs power output production. In particular, anodic electrodes must satisfy several properties [22] in order to enhance bacteria proliferation on them

and consequently to improve the overall device performance: (1) biocompatibility for microorganisms proliferation; (2) high electrical conductivity and high chemical resistance; (3) high specific area to volume ratio, with pores size of order of some micrometers to enhance bacteria proliferation on electrode surface and to facilitate the diffusion of carbon energy source inside the electrode; (4) cheap production cost. Among all these properties, the electrical conductivity, the morphology and the porosity of anodic material can mainly influence the device performance, especially in terms of the power output production. In recent years, some works in the literatures investigate some metals and their alloys as anodic materials, thanks to their high electrical conductivity, combined with good mechanical properties [40, 41]. One of the main limit of metals and their alloys, designed as anodes in MFCs, is related to their chemical resistance. Since these materials do not satisfy the no corrosive requirements, different surface treatment are provided to overcome the corrosive limit and at the same time to induce a certain roughness on the surface, ensuring thus the bacteria adhesion on it. As proposed in the literature, only stainless steel and titanium are suitable to be applied as anodes in MFCs. Dumas et al. [42] tested stainless steel plates as both anodic and cathode electrodes inside device, demonstrating that the power density (close to 23 mW/m^2) result to be limited by anode. As reported in other work of literature, Dumas et al. [43] confirm worst performance of MFCs, when a stainless steel plate is used as anode, than the one reached when graphite anode. Titanium wires are commonly used as current collector in MFCs. Heijne et al. demonstrate the lowest performance reached when untreated titanium is employed as anodes in the cells [44]. Few works in the literature [6, 45] focused their attention on gold anodes, which enhance the growth of Geobacter on its surface, generating a current density close to the one obtained by MFCs with graphite anodes. Since carbon-based materials show a high biocompatibility for bacterial proliferation, good chemical resistance, good electrical conductivity and low cost production, they result to be the most promising anodes in MFCs [46]. Generally, carbon-based materials conjugate the best chemical surface and morphological properties, able to enhance the biofilm formation [47]. It is possible to divide these kinds of materials in three different groups, according to their structure [46]: (1) plane organization, (2) packed organization and (3) brush organization.

5.1. Planar structure of anode electrodes

Among all carbon materials with a planar structure, carbon paper, carbon cloth, graphite plates or sheets are widely applied as anodes in MFCs [48, 49]. Both carbon paper and carbon cloth are cheaper than graphite based electrodes. Nevertheless, these samples are characterized by a low thickness and an enough dense structure, able to reduce the porosity of electrodes, minimizing the surface area and the bacteria growth [46]. Graphite sheets show a higher mechanical resistance than the one offered by carbon cloth or carbon paper. In particular, Heijne et al. [44] highlighted that the anodes, based on graphite sheets with a certain roughness degree, show a higher power output than smooth graphite sheets. In order to overcome the high production cost of all these carbon materials, Wang et al. [50] investigated a carbon mesh electrodes, treated with ammonia gas and compared to a carbon cloth, on which the same treatment was employed. They demonstrated that treated carbon mesh reached a power output greater than the one obtained by carbon cloth. In particular, many works in the literature demonstrated how the ammonia gas treatment enhances the positive charge of carbon surfaces, maximizing the bacterial proliferation and increasing the

overall device performance [51]. Furthermore, surface treatments of carbon-based materials, especially nitrogen-based functionalization, demonstrated to significantly improve microbial proliferation on anode and thus the overall device performances [50, 51].

Since high porosity is an important property that anode electrode must satisfy, two classes of materials can be considered: graphite or carbon felt and graphite foam. Generally, the structure of felt samples are made of fibres, with a total thickness greater than the one of previously described carbon materials [30]. These materials showed pores size distribution of some micrometers, able to increase the bacterial growth, which, however, is restricted by diffusion of carbon energy sources inside the electrodes [30]. Another porous carbon material that is not commonly used as anodes in MFCs is graphite foam [52]. Chaudhuri et al. [52] confirmed that the current density obtained with graphite foam results to be 2.4 times higher than the one reached with graphite rod.

5.2. Packed structure of anode electrodes

Different arrangement of above described carbon-based materials has been investigated in order to obtain the packed structure of anode electrodes, able to increase the surface area of electrodes, available for microorganisms proliferation [53–56]. One of these kinds of structures is granular graphite. Rabey et al. designed granular graphite as anode in MFCs. Li et al. [55] reported a power density of 557 mW/m^2 achieved with granular activated carbon anode, which is double than the one reached with carbon cloth. This good result confirmed how the enhanced surface area of anode guarantees a better bacterial proliferation and then an improved electron transfer from bacteria to anode surface. Aelterman et al. [53] analyzed overall device performance when different anodes, as carbon felt, graphite felt and granular graphite, are applied. They defined a large/great power density, close to 386 W/m^3, carried out by graphite felt as anode electrode.

5.3. Brushed structure of anode electrodes

The graphite brush materials are classified as an ideal electrode, able to conjugate high surface area, high porosity and great electrical conductivity. Logan et al. [22] designed brushes anodes made of carbon fibres that covered two titanium wires. In particular, they developed two brush anodes characterized by different dimensions: the smaller one (2.5 cm in diameter and 2.5 in long) and a greater one (5 cm in diameter and 7 cm in long). The MFCs with the smaller anodes achieve a power density of 2.4 W/m^2, higher than the one reached with greater brush anode (1.43 W/m^2). Both achieved power densities result to be higher than the one obtained with plain carbon paper, used as anode. The worst performance of large brush anodes can be explained by the fact that an excessive amount of fibres can hinder bacterial proliferation and consequently the diffusion of organic matter inside the anode.

5.4. Composite carbon-based anodes

The anodic surface plays a crucial role to influence the microorganisms adhesion on it, the electrical connections, self-produced by bacteria, with the electrode and consequently the overall MFCs performance [40, 57, 58]. One of the several strategies, which can be carried

out to properly modify the electrode surfaces, is based on the coating materials deposition on the electrode. This coating layer must be able to improve the biofilm formation, while the electrical conductive backbone part ensures the charge transfer [40, 57]. Many works in the literature developed composite anodes, made of metals as backbone electrode part and carbon-based materials as interface layer between all electrode and bacteria. These anodic configurations improve not only the bacterial growth on the electrode surface but simultaneously the power output production [50, 59, 60].

6. Device configurations

Two main configurations of MFCs are widely used in the literature [22]: (1) dual chamber microbial fuel cells (DC-MFCs), characterized by two different chambers, respectively anode and cathode, normally divided by proton exchange membrane (PEM) and (2) single chamber microbial fuel cells (SC-MFCs), where anode and cathode compartments constitute only one chamber. Typically, SCMFCs are membrane-less device and the electrolyte result to be in common between anode and cathode. **Figure 5a** shows DC-MFCs, where the electrolyte inside the cathode is based on chemical solutions, like hexacyanoferrate of potassium. This architecture requires the presence of a cationic membrane, which allows the protons transfer between the anode and cathode and create two different and separate compartments: the anode and the cathode chamber. In this way, the produced electrons, which flow into the cathode, can be recombined with protons. **Figure 5b** represents SC-MFCs configuration, characterized by only one chamber. The electrolyte is unique and common with anode and cathode. Different works in the literature developed this configuration in order to use oxygen, dissolved into the electrolyte, as the final electron acceptor.

As confirmed by some works in the literature [14], the main advantage of DC-MFCs is strictly due to the presence of water-soluble electrolyte as a terminal electron acceptor. Indeed, if the electrolyte contains potassium hexacyanoferrate, its standard reduction potential is very low, close to 0.361 V, leading thus to favor the reduction reaction. On the contrary, the presence of a chemical compound as TEA in the cathode chamber minimizes/limits the application of these devices in the environment. In order to overcome this limitation, SC-MFCs are designed.

In the latter configuration, oxygen is usually used as unique terminal electron acceptor, without the presence of other chemical compounds, ensuring then the environmental-friendly application of MFCs. Nevertheless, the direct oxygen reduction reaction (ORR) shows low kinetics and requires a high reduction potential (close to 0.805 V) to carry out, causing several overpotentials in the devices. Indeed, the development of catalyst layer, to accelerate and favor direct ORR, is required [61]. Logan et al. [61] designed/investigated/proposed the development of a catalyst layer (CL) and a diffusion layer (DL) in order to overcome/avoid all disadvantage of SC-MFCs. The diffusion layer is made of several polytetrafluorethylene (PTFE) layers, able to enhance the diffusion of oxygen from outside to inside the devices, while the catalyst layer is typically based on platinum, which is considered the ideal catalyst for ORR.

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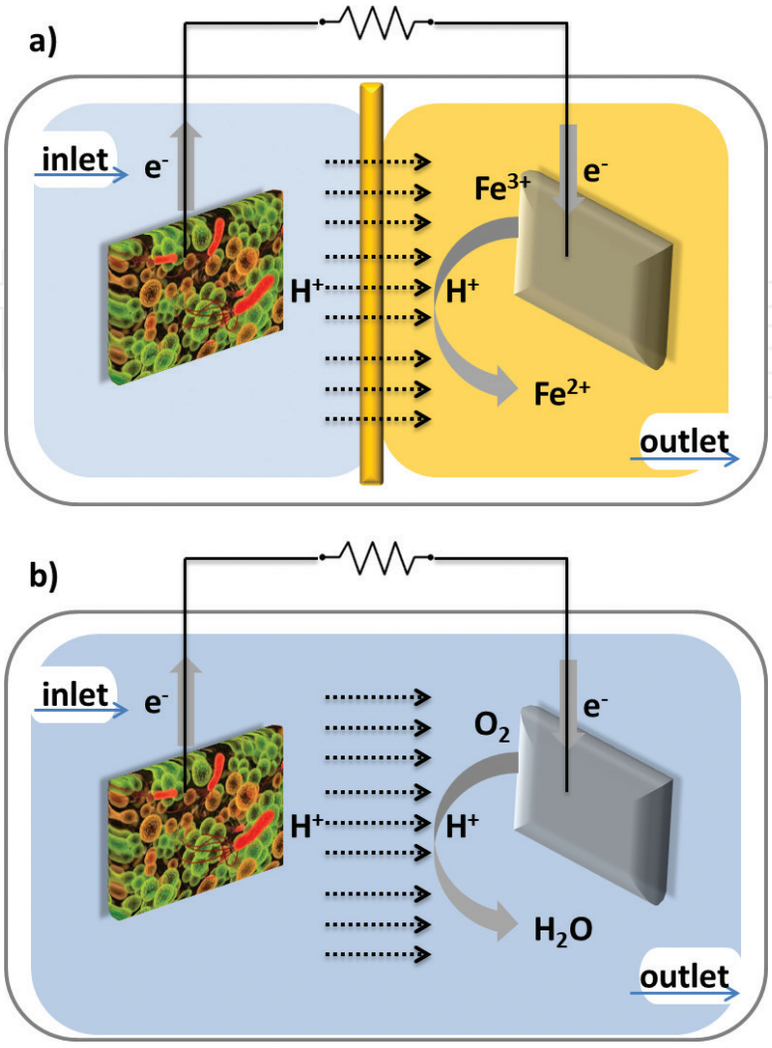

Figure 5. Two different electrochemical schemes describing two different architectures of MFCs: (a) shows the dual chamber MFCs where the reduced species in the cathode is hexacyanoferrate of potassium; (b) represents the single chamber MFCs where on the contrary, the oxygen in the cathode is reduced into the water.

7. Role of fluid dynamics inside the device

The necessity to improve the power output produced by MFCs demanded different strategies, focused on scaling-up MFCs [62], using different kinds of microbial communities and exploring several substrates (i.e., derived from wastes) [25]. However, during the last decades, different works in the literature considered these devices in terms of small dimensions and optimized fluid dynamic distribution, in order to minimize the internal ohmic resistance, leading thus to improve the overall MFCs performance [63]. Fluid dynamic modeling can be implemented to define the correlation between the fluid distribution inside the device and its overall performance [64, 65]. Furthermore, this kind of simulation can have a predictive role of fundamental importance in driving the design of the reactors toward the optimal MFC configuration.

Massaglia et al. [65] analyzed two different architectures of open air cathode MFCs, (drop-MFCs and square-MFCs), with an inner volume of few milliliters. They demonstrated a direct correlation between the fluid distribution inside MFCs and the power output production. In this work, Drop-MFCs, indeed, represented the best architecture design, maximizing the fluid dynamic distribution and consequently the power density output. **Figure 6** shows the fluid dynamic distribution inside both drop-MFCs and square-MFCs, obtained implementing two different flow rate values. The presented results confirm the better fluid distribution inside drop-MFCs for both flow rates.

Qian et al. reported the advantages of design MFCs with smaller volumes of the order of milliliter. They demonstrated how this configuration results to be effective for reducing internal electrical resistance device and enhancing mass transport. Ringeisen et al. [66] achieved great power densities of 500 W/m^3 with a MFCs with an internal volume of 1.2 mL.

Fan et al. [67] investigated the power density production, close to 1 W/m^3, obtained with an open air cathode configuration MFCs, characterized by a volume of 2.5 mL. Both the interaction between biofilm and anode electrode and consequently the metabolic activity of microorganisms that drive the oxidation reaction in anodic chamber show a pivotal role to define the power output production. Nevertheless macro-size MFCs and milliliter-size MFCs show higher output performance, the miniaturization of MFCs to microliter-size (μL-MFCs)

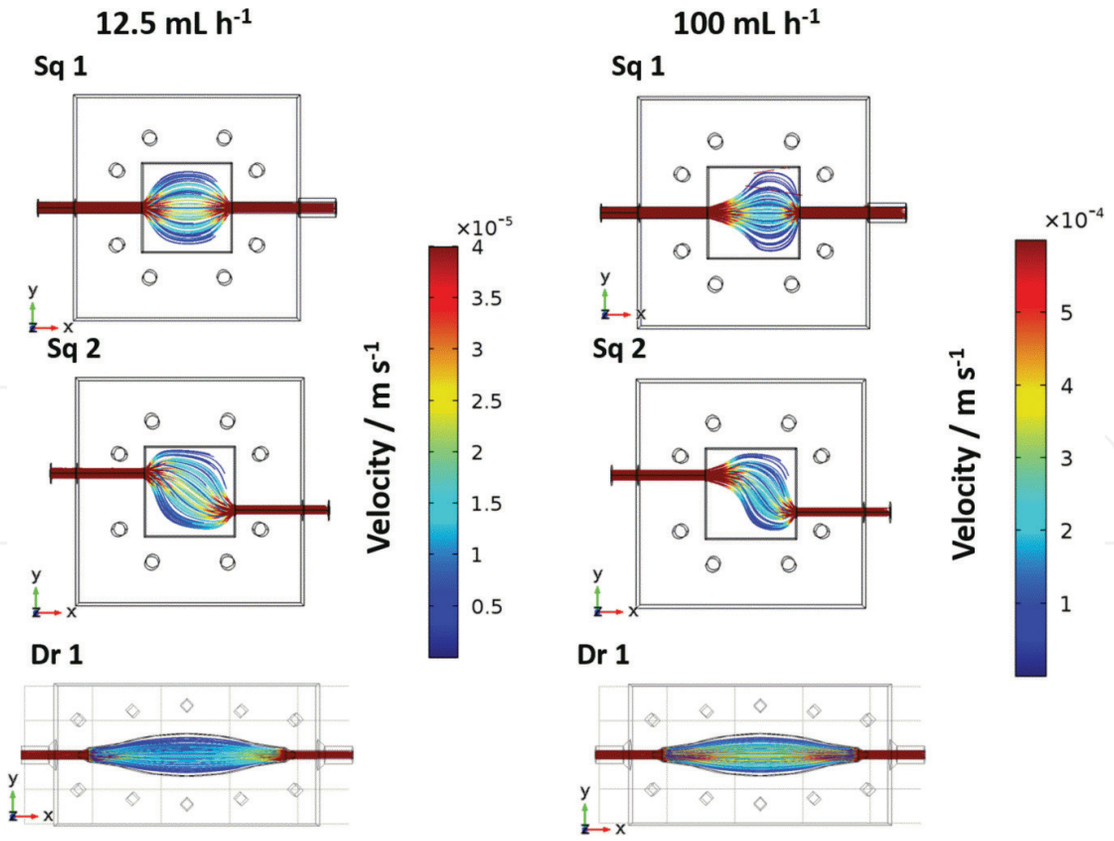

Figure 6. Results of simulations of fluid distribution inside drop-MFCs and square-MFCs, implemented two different values of flow rate, 25 mL h^{-1} and 100 mL h^{-1}. Reprinted with the permission from (Fuel Cell, 2017, 17, 627–634) Copyright (2017) Wiley online library.

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resulted to be needed to deeply understand/investigate the relationship and the interconnection between all the biological, chemical and electrical parameters. Since some parameters, such as mass transport, reaction kinetics and ohmic resistance deeply influence overall MFC performance, the design of microliter-size MFCs (μL-MFCs) is required to better investigate electrochemically active bacteria and electrode performance. μL-MFCs, in particular, employ important and pivotal features:

1. Lower electrode distance for reducing the ohmic internal resistance and optimizing the mass transport;
2. Laminar fluid dynamic inside the device for ensuring a better distribution of organic matter to be oxidized;
3. Device fast response time.

Several works underline/confirm advantageous characteristics of these devices, as high surface area to volume ratio, lower electrode distance and fast response time [11]. The designed micro-channels ensures a laminar flow of electrolyte, containing the organic matter to be oxidized, minimizing the mixing with the oxidant species and consequently avoiding the use of PEM, decreasing then the ohmic resistance [39]. Some works in the literature focused their attention on the critical role of the relationship between the size and electrode distance, demonstrating that μL-MFCs equipped with small electrodes could maximize the performances and minimize the amount of residual fuel [9, 68]. Furthermore, the selection of the most promising anode materials, together with the reduction of device impedance, plays a crucial role to improve the performance of these microscale devices. Qian and Morse [68] studied a carbon cloth anode applied in μL-MFCs with a volume of 4 μL, achieving a power density of 62.5 W/m^3. Lee et al. [9] demonstrates from a fluid dynamic point of view that nano-sized anodes electrodes ensure the best performance of microfluidic devices.

8. Conclusion

The proper selection of anode electrodes and deep study of fluidic distribution inside MFCs play a pivotal role to define the overall devices performance. In particular, several works in the literature demonstrated how the morphology of anode electrodes must be optimized in order to improve the bacteria proliferation on their surface, maximizing then the energy conversion. For this reason, all anode electrodes must satisfy key properties: (1) biocompatibility for microorganisms proliferation; (2) high electrical conductivity and high chemical resistance; (3) high specific area to volume ratio, with pores size of order of some micrometers to enhance bacteria proliferation on electrode surface and to facilitate the diffusion of carbon energy source inside the electrode and (4) cheap production cost. Among all possible materials, carbon-based results to be the most promising ones to be applied as anode in this bioelectrochemical devices. It has also been evidenced that fluid management inside the reactor is of critical importance, since an optimal chemical energy to electrical energy conversion is possible only if proper interactions of fluids (i.e. the electrolyte) and the bioanode are possible.

In this perspective, fluid dynamic modeling is a key tool to design systems with optimized electrolyte/bioanode interfaces. During the last few years, different strategies were implemented to enhance the power output production. Among all them, the optimization of fluid distribution and the reduction of MFC dimensions were employed. Nevertheless, macro-sized MFCs and milliliter-size MFCs show higher output performance, the miniaturization of MFCs to microliter-size (μL-MFCs) resulted to be needed to deeply understand/investigate the relationship and the interconnection among all the biological, chemical and electrical parameters.

Author details

Giulia Massaglia[1,2]* and Marzia Quaglio[1]

*Address all correspondence to: giulia.massaglia@polito.it

1 Center For Sustainable Future Technologies@Polito, Istituto Italiano Di Tecnologia, Torino, Italy

2 Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino, Italy

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