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Current state of research on microbial fuel cells: transfer mechanism, biofilm development, electrodes materials and architecture

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***Abstract*— The principle of operation of microbial fuel cells (MFC) is based on bio-electrochemical systems. In fact, they use bacteria to convert part of the energy available in a biodegradable substrate directly into electricity. Electricity is generated from redox reactions involved in the degradation of organic molecules by bacteria, resulting in the release of protons and electrons which can be transferred to electrodes. This technology offers various application prospects ranging from water treatment to electricity production or the design of biosensors.**

Recently, several studies have focused on the theme to lift the lock of the low power and density provided by the device.

The performance of an MFC in terms of power generation, output current and electrical efficiency depends on a complex set of parameters.

Thus, the identification of bacteria capable of producing electricity, the understanding of the mechanisms of electron transfer and adaptation of microbial communities, the impact of the nature of the electrodes and the configuration of the MFC on the generation of electricity are discussed.

In this study, we propose to make a synthesis of this work in order to highlight the technical challenges, the proposed solutions and the possible synergies for obtaining better energy conversion efficiency.

***Keywords*— fuel cell, microorganisms, biofilm, anode, cathode.**

I. INTRODUCTION

The increase in greenhouse gases from industrial production is a growing reality. According to the World Meteorological Organization, atmospheric concentrations of the three main greenhouse gases – carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) – broke new records in 2021[1]. These emissions, generated mainly by the combustion of fossil energy sources, lead to a disturbance of ecosystems, materialized by climate change. The increasingly reduced availability of these energy sources caused by their massive exploitation to satisfy the population explosion of recent decades, natural disasters with industrial damage, as well as the development of emerging countries leads to an increase in production costs and inequalities of access which require the search for alternative energy production technologies, based on the use of renewable fuels.

The 2022 Sustainable Development Goals Report indicates that the world continues to make progress towards sustainable energy targets but at a pace insufficient to achieve Goal 7 by 2030. Energy intensity improvements until 2030 should be 3.2% on average, while the average rate between 2010 and 2019 is estimated at 1.9% [2].

The development of renewable energies therefore seems essential in the medium term, given the considerable potential they offer and their intrinsic ecological qualities.

Microbial fuel cells, an energy source allowing both the removal of organic matter contained in wastewater and the generation of electricity, are a major component of the many technologies implemented in recent years in the field of renewable energies.

The global fuel cell market was valued at US$ 5.63 billion in 2021 and is expected to reach over US$ 42.3 billion by 2030 with a registered CAGR of 25.1% from 2021 to 2030 [3].

Fig. 1 Fuel cell market size, 2020 to 2030 USD billion [3].

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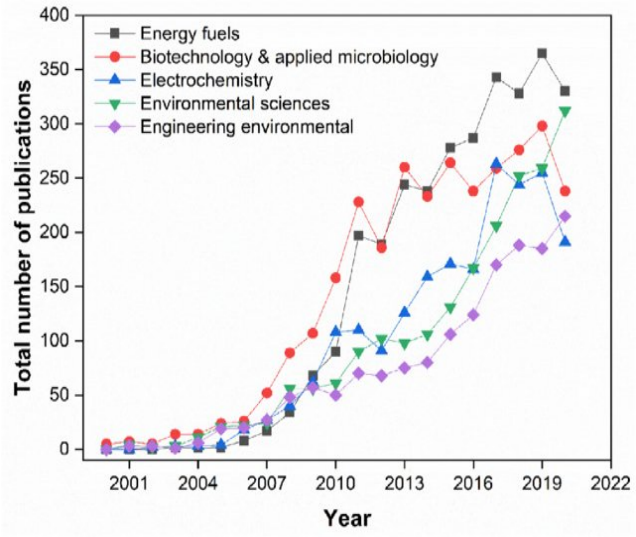

Fig. 2 Evolution of MFC subject categories [4].

Given the complexity of the system which involves microbiological, electrochemical and transfer phenomena within a reactor, it is important to analyze the performance of microbial fuel cells under various experimental conditions.

II. Principle of Operation of MFCs

The microbial fuel cell (MFC) is a device consisting of an anode and a cathode connected by a conductive wire. The anode is immersed in a substrate which is the source of organic matter. Bacteria naturally present in the substrate or inoculated into the anode compartment form a biofilm on the surface of the anode and oxidize the organic matter present in the substrate releasing electrons, protons and/or other cations.

The anodic oxidation reactions involved depend on the type of substrate used. In the case of acetate the reaction is such that [5]:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad (1)$$

Electrons are transferred from the biofilm to the anode by various mechanisms such as direct contact, nanowires or mediators [6]. Electrons migrate from the anode to the cathode through an external electrical circuit, while selected ions move through a separator membrane to complete the circuit.

At the cathode, oxygen is used as an oxidant in many cases, due to its availability and high reduction potential. Indeed, an ideal electron acceptor is necessary and must be durable, without interference or toxic effect on the microbial community or any other element of the system [7].

In the case of a proton exchange membrane, once the protons have diffused through the membrane, they can react with the oxygen present, leading to the generation of water according to the following reaction: [5]

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

The configuration of MFCs can vary widely to optimize power outputs. We thus distinguish various configurations such as MFC without membrane with single chamber, MFC with double chamber separated by a membrane, tubular or cylindrical MFC with a single compartment with membrane and MFC with single chamber with a configuration with several anodes [9].

The evolution of the proposed configurations is guided by the main constraints observed.

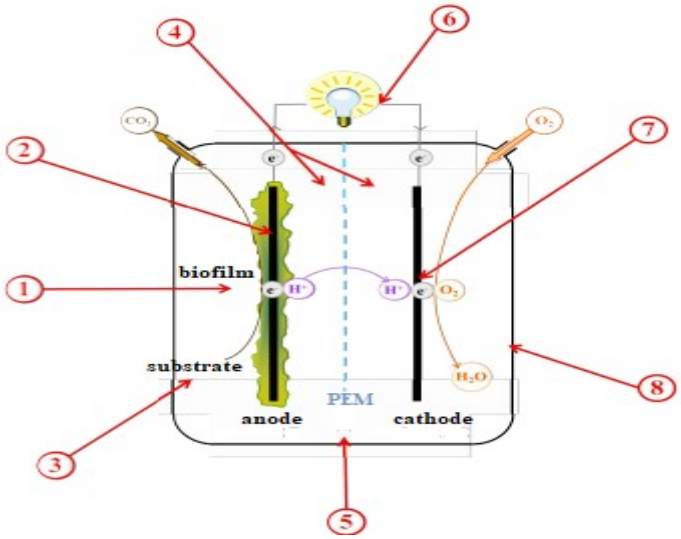

Fig. 3 The main components of an MFC: 1 biofilm, 2 anode, 3 substrate, 4 electrolytes, 5 anode/cathode separator, 6 external circuit, 7 cathode, 8 configuration [8].

III. Configuring MFCs

In the case of a single chamber configuration without membrane with an air cathode, the main constraint is related to the back diffusion of oxygen from the cathode to the anode which can be the source of contamination of the cathode by the development of a cathode biofilm. Indeed, the passage of oxygen to the anode is accompanied by a reduction in Coulomb efficiency due to the consumption of part of the oxygen by the development of the biofilm at the cathode to the detriment of oxidation from the substrate at the anode and therefore fouling of the cathode. [10].

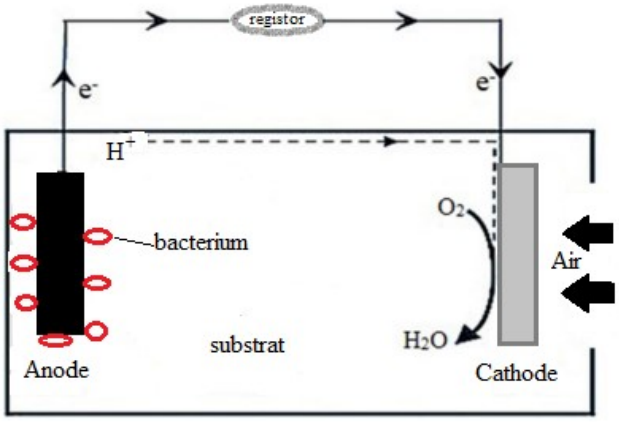

Fig. 4 Configuration of single-chamber MFC

In the presence of a membrane, the constraints are linked to the costs of the separator, particularly when it is a polymer electrolyte membrane (PEM) and to the limitations of the

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supply of oxygen to the cathode due to mass transfer problems leading to a slow oxygen reduction reaction (ORR). There is also an increase in the internal resistance due to the inter-electrode distance [10].

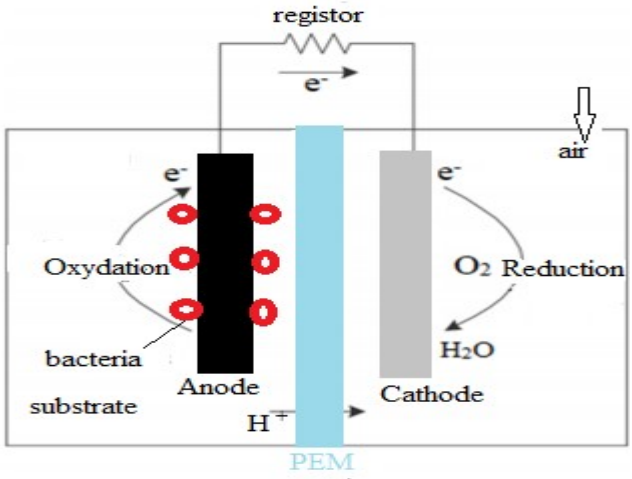

Fig. 5 Configuration of double-chamber MFC

Research has therefore focused on optimizing reduction at the cathode, optimizing mass transfer and fluid circulation, as well as developing lower cost membrane separators and electrodes.

A performance evaluation based on recent publications shows that substantial improvements result from the design, architecture and assembly of the cells.

To optimize the cost of MFC while preventing the formation of a biofilm at the cathode, Masoom Fatima and al. [11] developed a single-chamber MFC with an air cathode using oxygen and a conventional fiberglass separator. A peak anode current density of 0.59 Am^{-2} and a power density of 0.12 Wm^{-2} were achieved with a synthesized lignin-based electrospun carbon fiber bioanode supporting a Geobacter sulfurreducens biofilm for the oxidation of acetate and an air cathode, consisting of a mixture of macrocyclic catalysts pyrolyzed on carbon bound by polytetrafluoroethylene (PTFE).

To reduce the constraints related to mass transfers and to optimize the cost of electrodes Siti Kudnie Sahari and al. worked on a single-chamber MFC with a solid substrate (soil+poultry waste) and 51 cm^2 graphite activated carbon cloth electrodes. A power density of 904 mW/m^2 was obtained [12].

To improve the performance of single-chamber PCMs, they are usually used in series or multiple anode. Simona DiMicco and al. [13] showed that four reactors (28 mL x4) connected in parallel configuration give a volumetric power density of 1248.5 mW/m^3 (139.8 µW) at 0.291mA. Similarly, a reactor configuration with multiple tin-coated copper mesh (TCCM) anodes and a platinum-coated titanium mesh cathode produced a power density of 2965 mW/m^2. This high power density is more attributable to the high content of proteins, carbohydrates and lipids in the algal biomass used as substrate and the nature of the TCCM anode which enhanced bacterial attachment, increasing the collection capacity of electrons. [14].

An improvement in the performance of single-chamber PCMs was also noted by acting on the geometry of the reactor. Indeed, changing the configuration from cubic to cylindrical resulted in a substantial reduction in internal resistance from 127.21 Ω to 49.66 Ω on a carbon brush cylindrical PCM. This cylindrical cell inoculated with P. aeruginosa in gives a maximum power density of 3322 ± 38 mWm^{-2} with internal resistance of 34.0 ± 1.1 Ω [15].

TABLE I
Performance of SMFCs

Reference	**substrate**	**electrodes**	**Power density (mW/m^2)**
11	Acid Orange (AO5) with Geobacter sulfurreducens for acetate oxidation	bioanode of synthesized lignin-based electrospun carbon fiber. air-breathing cathode, consisting of a pyrolyzed macrocycle catalyst mixture on carbon bonded by polytetrafluoroethylene (PTFE)	0.12 Wm^{-2}
12	soil	graphite-activated carbon	904 mW/m^2
14	mixed-culture algae biomass	multi-anode reactor configuration which had tin-coated copper mesh (TCCM) anode and platinum-coated titanium mesh cathode	2965 mW/m^2
15	P. aeruginosa	cylindrical single-chamber and carbon brush anode	3322 ± 38 mW m^{-2}

The dual-chamber microbial fuel cell (DMFC) consists of two compartments, anodic and cathodic, respectively anaerobic and aerobic. The two chambers are separated either by a membrane.

Different types of membranes are used (cation exchangers, anion exchangers, bipolar membranes) taking into account their ability to conduct protons and prevent flux transfer [16].

Nafion 117, Flemion and Hyflon type membranes are the typical commercially available membranes used in MFC. Nafion membranes are the dominant material used in polymer electrolyte membrane (PEM) technologies due to their properties: high proton conductivity and high chemical stability in oxidation and reduction environments. However, they have limitations related to: reagent permeability, which results in reduced performance, dependence on water content

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to operate, preventing operation at higher temperatures or low humidity levels, and degradation chemical [17].

The use of non-fluorinated polymeric membrane materials such as sulfonated silicon dioxide (S-SiO2) in sulfonated polystyrene ethylene butylene polystyrene (SSEBS), sulfonated polyether ether ketone (SPEEK) and sulfonated polyether ether ketone membranes d Graphene Oxide (GO/SPEEK) has shown promising performance and proven to be an alternative material to Nafion 117. PEEK is a low cost polymer with good thermal stability and good mechanical properties [18]. There are many challenges in selecting an appropriate membrane for a large-scale MFC system for the technology to become technically and economically viable.

A power density of 304.2 mW/m^2, was achieved with an ion-crosslinked nanocomposite membrane composed of cationic aniline-treated polysulfone (APSf) doped with anionic sulfonated multi-walled carbon nanotube (SMWCNT) to reduce oxygen crossing and improve chemical stabilities [19].

A disadvantage of the two-chamber configuration is that the cathode chamber must be fed regularly with fresh electrolytes or with a continuous air sparge, which is an energy-consuming process.

A quantitative comparison based on the configuration remains relatively difficult. Indeed, MFCs are complex systems governed by several interconnected factors. The performance observed may be due to the configuration, the electrode materials, the characteristics of the separator, the nature of the substrate or the properties of the microorganisms. The challenge is then to move towards experimental designs to separate and evaluate both the main effects and the possible interactions between the different control parameters. This approach will make it possible to model the system and thus be able to stabilize the parameters in the case of scaling up.

IV. ELECTRODES MATERIALS.

The scaling up of MFCs is significantly limited by a slow rate cathodic oxygen reduction (ORR) reaction and the development of a resilient anode microbial community. The choice of electrodes is therefore a determining factor in the study of the performance of MFCs because the bio-electrochemical reactions generally take place on the surface of the electrodes. Criteria such as chemical stability, conductivity, potential range, biocompatibility and cost should be considered [20]. Electrodes can be classified mainly into two groups, namely metal-based electrodes and carbon-based electrodes.

A. Anode

The anode chamber can be considered the heart of the MFC. Indeed, the design of the anode is essential to provide the bacteria with the environment and the surface necessary for their growth. The anode chamber is generally anaerobic to maximize microbial growth on the surface of the anode.

Various materials can be used as the anode to improve the performance of the MFC. The anode material must combine good conductivity and biocompatibility with bacteria. Metals such as copper, platinum and stainless steel are good conductors and therefore ideal for electrochemical activity but have poor compatibility for microbial activity. Some metals such as platinum and titanium have shown a strong ability to transport electrons over long distances but have limitations related to their high cost. Research then turns to alternative materials when scaling.

A comparison of the performance of an MFC with a metal-based anode (stainless steel brush SSB) and a carbon-based anode (carbon brushes CB) showed that the SSB anode generates a stable voltage of approximately 0 .4 V and a maximum power density of about 400 mW/m^2, while the CB anode system produces a voltage of about 0.5 V and a maximum power density of about 800 mW/m^2 [21].

To limit the resistance of the electrodes and improve the adhesion of the biofilm, the carbon-based electrodes are often modified by different techniques such as: acid treatment, electrochemical treatment, coating with a polymer, etc. The materials carbon materials used as anode include brush, felt, cloth, mesh, paper, rod, cross-linked glassy carbon, graphite.

Yasser A. Attia and al. [22] followed the variation of the performances of an MFC according to the nano material used. Graphene, carbon nanotubes and graphitic carbon nitride have been tested for their high electrical and thermal conductivity. The results showed that with electrodes coated with nanomaterial, the voltage generated by the MFC was stable with a maximum value of 1.367 V, i.e. a power density of 116 mW m-2. This same MFC with uncoated electrodes gives a variable voltage with a maximum power density of 23.6 mW m^{-2}.

In addition to finding conductive and biocompatible materials, it is important to consider the manufacturing cost for scaling up. Thus, natural waste enriched with organic matter can be a good alternative to commercial carbon-based materials.

Hung, Y.H. and al. demonstrated that coffee waste-derived activated carbon (CWAC) can serve as anode materials on a substrate enriched with Escherichia coli. By modifying the CWAC pore size, they achieved a power density of 3927 mW m^{-2}, higher than that of commercial activated carbon (975 mW m^{-2}). The improved power density of CWAC was attributed to its high conductivity and proper pore size distribution, which led to rapid electron transfer and bacterial adhesion. Additionally, the long-term performance of the MFC with the CWAC anode was investigated; it operated continuously for more than 100 h at a power density of 2000 mW m–2 without further nutrient replenishment [23].

Singh and al. [24] prepared an electrode by coating the surface of a stainless steel disc with spark plug soot. Physical, electrical and chemical characterization revealed that the electrode materials had good electrochemical and mechanical stability with hierarchically porous characteristics. Bias results revealed 0.68 ± 0.03 V as the highest circuit potential, 7135 ± 110 mA/m^2 as current density and 1650 ± 50 mW/m^2 power in a dual-chamber MFC. The preparation of carbon nanoparticle electrodes based on candle soot is recyclable, cost effective, scalable and reliable.

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The analysis of these different results shows that the challenge turns to the cost of anode fabrication for scaling up the MFC. Metal electrodes modified by binders or composite materials may be of interest. However, more research is needed on the types of materials with good conductivity. The use of carbonized waste also offers a promising prospect. The size and design of the electrode are very important aspects in the manufacture of anodes.

B. Cathode

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The cathode of an MFC is composed of an electrode support, a catalyst and an air diffusion layer. Cathode performance is rated based on high electrical conductivity, high mechanical strength, and catalytic efficiency. The main constraint identified in the functioning of the cathode is related to slow oxygen reduction (ORR). Indeed, the cathodic compartments are often filled with water and therefore a neutral pH and at mild temperatures. Under these conditions, the rate of oxygen reduction is very low, which leads to increased surges and thus limits the performance of an MFC. The same electrode materials used for the anode can be used for the cathode but must be modified with catalysts. Platinum is the most commonly used cathode catalyst due to its high efficiency in oxygen reduction. The use of expensive metal catalysts as cathode materials in MFCs limits the practical applications of MFC technology. Besides their high cost, platinum catalysts are more susceptible to fouling when used with poor quality water. Many research efforts have been made to reduce the cost of cathode catalysts by finding cheaper alternatives to platinum without sacrificing performance [26].

Thus, mixed transition metal oxides of nickel and copper (Ni and Cu), supported on a graphene (G) electro catalyst (NiO–CuO/G), were synthesized and tested as a cost-effective cathode for the ORR in MFCs. Electrochemical measurements of the electrocatalyst were carried out and compared to a reference Pt/C catalyst. The NiO-CuO/G electro catalyst showed high selectivity towards ORR with a power density of 21.25 mW m $^{-2}$ in an air cathode MFC. This value is lower than that of the Pt/C-based MFC which is 50.4 mW m $^{-2}$. [27]

Chang and al. proposed a low cost air cathode. This was obtained from Balsa wood chips by pyrolysis at 800 ˚C. A maximum power density of 200 mW/m^2 has been achieved in an SMFC. The cathode thus developed could be used directly without the need to apply expensive catalysts, binders and gas diffusion layers. [28]

The analysis of research results on cathode materials shows that bio cathodes can be a good alternative to the use of expensive materials. In effect; when working with a membraneless SMFC, the likely development of a biofilm at the cathode can be leveraged in the form of a biocatalyst to accept electrons from the cathode substrate. The challenge will then be to optimize the start of the cathode.

Besides the impact of the electrode materials on the energy performance, the impact of the configuration parameters such as the inter-electrode space or the electro-active surface must be analyzed. Indeed, these two parameters can have an influence on the formation of the biofilm and the transfer of electrons.

Fig.6 Mostly used anode electrodes (A) carbon paper, (B) carbon cloth, (C) carbon fibre, (D) reticulated vitrified carbon, (E) carbon mesh, (F) graphitic granular, (G) carbon brushes, (H) graphite rod, (I) polycrystalline graphite, (J) carbon felt, (K) platinum mesh, (L) different metal electrode strips, (M) conductive polymer-based strips..[25]

V. SUBSTRATE CARACTERIA

Biodegradable substrates can be of different types ranging from pure constituents such as acetate, glucose, cysteine, ethanol and bovine serum albumin, to complex mixtures of organic substances such as wastewater, garden or agricultural waste.

With glucose as fuel, the efficiency of a single chamber MFC with an air cathode has been successfully demonstrated to degrade penicillin combinations or penicillin on pharmaceutical effluents. Indeed, the glucose-penicillin combination is involved in the production of energy. When used individually in an SMFC, 1 g L^{-1} glucose (14.7 W m^{-3}) and 50 mg L^{-1} penicillin (2.1 W m^{-3}) had a power density six times lower than the combination of 1 g L^{-1} glucose + 50 mg L^{-1} penicillin (101.2 W m^{-3}). When 50 mg of penicillin L^{-1} was used, the peak current density was 3.5 times higher (10.73 A m^{-2}) than when no penicillin was used (3.03 A m^{-2}).

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Penicillin improves the permeability of bacterial cell membranes, facilitating the transport of electrons from the microbe to the anode via the cell membranes while lowering the internal resistance of the MFC and increasing the power density. These results clarified that some hazardous and bio-refractory organic compounds, such as antibiotic effluents, could constitute a valuable resource for energy production from MFCs [29].

Papaya waste was used as a substrate to assess sucrose productivity. The maximum observed power density was 583.09 mW/cm^2. The presence of sucrose also had an impact on the internal resistance. Indeed, the cell without sucrose was 0.1952 ± 0.00214 KΩ and with 20% it was 0.044306 ± 0.0014 KΩ [30].

These different results show that the use of mixed effluents offers new perspectives. Indeed, the use of MFCs often aims at a double objective which is the treatment of effluents and the production of electricity. The challenge could be to optimize the performance of MFCs in the case of industrial effluents, which are difficult to biodegrade, especially with the presence of heavy metals.

VI. BIOFILM DEVELOPMENT

The development of an efficient anodic biofilm has a significant impact on the energy performance of MFCs. It depends on the nature of the microorganisms, the nature of the substrate and the affinity with the electrodes.

Biofilm development is controlled by a density-dependent communication mechanism known as quorum sensing [31]. QS is a method of bacterial communication in which cells release, sense, and respond to tiny, diffusible signal molecules that regulate physiological processes in microbial populations [32].

Polymeric extracellular substances (EPS), one of the major components of a biofilm, determine the composition and density of the bacterial biofilm. The EPS consists of extracellular proteins (70%), lipids (20%), nucleic acids (5%) and other substances [33].

MFCs use two types of microorganisms: reducing ones that effect the reduction of the electrodes and the movement of electrons to the anode, and oxidizing ones involved in the oxidation of organic components and their subsequent transfer. These can be inoculated into the anode compartment (pure strain) or naturally present in the medium (mixed cultures). It is therefore essential to understand the effects of the nature of the inoculum on bacterial anodic diversity and to establish its relationship with the energy performance of the system.

Among pure strains, Archaebacteria have the potential to serve as electrogens in MFCs under particular conditions. Two species of halophilic archaea, Haloferax volcanii and Natrialba magadii, were tested as electricogens in the anode of an MFC. Without any exogenous mediator, a power density of 11.87 and 4.57 µW/cm^2 was for H. volcanii and N. magadii, respectively. With the addition of a mediator (neutral red), an increase in power density is noted for both species with better performance than that of Escherichia coli under the same conditions [34].

So-called photosynthetic MFCs (PMFCs) have been developed using a pure strain of cyanobacteria. These species are environmentally friendly and photosynthetic microorganisms. PMFCs work with light as an energy source and generate electricity through the oxidation of water by light.

A newly isolated cyanobacterium, Nostoc sp. ATCC 27893, was also applied in the anode of a PMFC, which generated current and power densities of 250 mA/m^2 and 35 mW/m^2. When 1,4-benzoquinone was added as an electron mediator, a significant improvement in power generation capacity was observed (maximum current density of 2300 mA/m^2 and maximum power density of 100 mW/m^2) [34].

In the case of mixed cultures of microorganisms various sources are used such as soil or marine sediments, the natural microbial community and brewery wastewater [35], domestic water, activated sludge, metal reduction, municipal wastewater.

The optimization of the system consists in favoring the presence of electroactive bacteria over methanogenic bacteria. Methanogens can decrease coulombic efficiency. Pre-treatment of the inoculum reduces methanogens and therefore increases energy production.

Raychaudhuri, A and al. (2019) compared the influence of three inoculum treatment methods, namely heat treatment (MFC1), ultrasound (MFC2) and air exposure (MFC3), on the suppression of methanogenesis using wastewater from the rice mill. MFC2 and MFC3 exhibited a peak volumetric power density of 525.62 mW/m^3 and 656.10 mW/m^3, respectively, which were 1.7 and 2.1 times higher than that of MFC1.[36]

The electroactive organisms present in the anode chamber often consist of Geobacter, Rhodobacter and Turicibacter [37] which are powerful electrogens. Other species were detected depending on the characteristics of the substrate.

Chao Li and al. developed a spatial electroactive biofilm on the carbon skeleton derived from the phenolic foam, which greatly enhanced the biocapacity and Geobacter abundance of the bioanode. Compared with the carbon cloth anode (CC), the optimal spatial electroactive biofilm (3DP_900) enriched the abundance of Geobacter up to 56.8% from 17.2%, and obtained a biomass load extraordinary electroactive of about 339 ± 63 µg cm^{-2} and a remarkable biocapacity of about 3.4 F. The space biofilm also strongly reduced barriers to electron transfer (Rct) and mass transfer (Rd) in the oxidation reaction of the anodic substrate. They thus obtained the lowest Rct of 2.0 ± 0.2 Ω with an Rd of 35 ± 3.3 Ω in 3DP_900, which also supports the highest power density at 0.347 ± 0.027 W m^{-2} and the highest coulombic CR recovery at 69.2%. A numerical analysis showed that due to the mature preparation technology, carbonized phenolic foam (2 cm thick pieces) reduces the investment cost of electrode preparation by three orders of magnitude, from 1157, 3 USD m^{-2} from CC to 5.2 USD [38].

It emerges from this analysis that the use of pure strains, although offering better performance in terms of power density, may have limits in the case of scaling up. The challenge is therefore to optimize the formation of the biofilm from the bacteria naturally present in the effluents or waste.

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To do this, further studies on the characterization of biofilms are needed in order to better understand the electron transfer mechanisms of the different bacteria identified. Existing techniques for probing the electrochemical activity of bacteria involve culturing large batches of cells and measuring protein activity, a painstaking and time-consuming process.

VII. TRANSFER MECHANISMS

Following the formation of the biofilm on the surface of the anode, a determining aspect in the performance of MFCs is the mechanism of adhesion of microorganisms to the surface of the electrode and the transfer of electrons. This is because electrons must be transferred from the living microbial cell membrane to the inside of the outer membrane. This extracellular electron transfer must result in a redox active species that can electronically link the bacterial cell to the electrode. This species can be a soluble redox shuttle, a reduced primary metabolite, or an outer membrane redox protein. The transfer of extracellular electrons (EET) between the microorganisms and the electrodes can therefore be direct (DET) or indirect or mediated (MET).

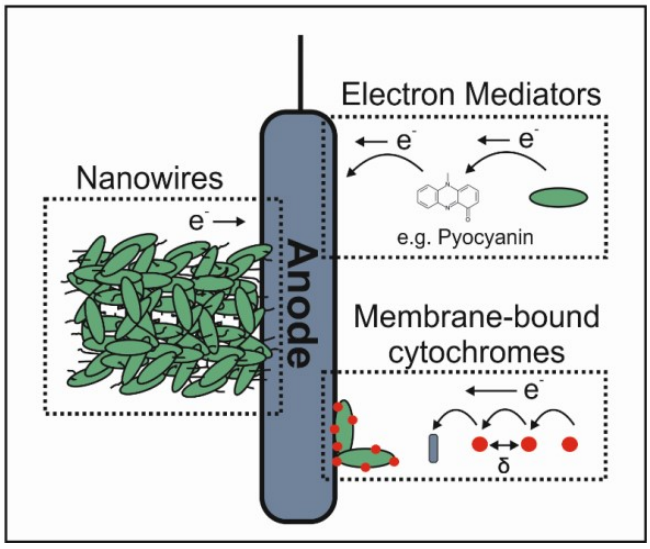

Fig. 7 : The three known methods of electron transfer demonstrated by exoelectrogenic bacteria, including; direct electron transfer – conductive pili, denoted within the literature as nanowires; redox-active proteins; and indirect electron transfer by electron shuttles.[39]

The most obvious case of transfer is that of direct electron transfer. This type of transfer is possible because these bacteria all have an electron transfer pathway different from that described for the respiratory chain allowing the transport of electrons from the internal membrane (where the respiratory chain is located in Gram -) towards the outer membrane, the latter exhibiting on its surface cytochromes which can be reduced (therefore capture the electrons resulting from the oxidation of cellular respiration) and which can oxidize on contact with a surface in order to transmit these electrons to it. Among the bacterial species known for their anodic exo-electrogenic metabolism, the best known and studied are Geobacter sulfurreducens and Shewanella oneidensis [6].

The conductive pili or bacterial “nano-threads” have been identified in the species Geobacter sulfurreducens, via conductive atomic force microscopy (C-AFM) making it possible to visualize the passage of electric current in these structures [6].

The last solution that electro-active organisms have at their disposal to increase the range of their electron transfer to a solid is the synthesis and use of intermediate electronic shuttles between the cell and the solid.

The electronic shuttle is initially reduced by the bacterium which will give it the electrons resulting from its catabolism (and therefore from the oxidation of a substrate). The electronic shuttle will then be dropped into the medium until it reaches the level of the terminal acceptor, namely the solid where it will oxidize in order to transmit its electrons to it.

There may also be cases where several intermediate oxidation-reduction reactions take place, with the transmission of electrons from one chemical compound to another until the terminal acceptor. It can be noted that these electronic shuttles can be divided into two categories, those synthesized directly by organisms (such as flavins and phenazines) but also compounds naturally present in the environment (such as metal ions, for example) [6].

Non-electroactive microorganisms require redox mediators to transfer their electrons to electrode surfaces. Several synthetic electron mediators have been commonly used to transfer electrons by replacing oxygen to accept electrons during the microbial respiration chain between the microbe and the electrode, called mediated electron transfer. There are two types of widely used artificial mediators, i.e. hydrophilic mediators (such as potassium ferricyanide) and lipophilic mediators such as benzoquinone, menadione, dichloroindophenol,2,3,5,6 tetramethylphenylenediamine [40].

Shirkosh M and al. evaluated the performance of an MFC using Escherichia coli and Shewanella oneidensis MR-1 as biocatalysts. They compared the different electron transfer mechanisms and evaluated the interactions between the anode and the microorganisms. Thus, using aluminum, zinc, copper, nickel and tin anodes, they noted that the bacterial colony in the case of Shewanella oneidensis MR-1 as biocatalyst was more abundant with aluminum. If the density of the biofilm is favorable to the production of electricity in the case of Shewanella oneidensis MR-1, this is not the case for Escherichia coli.

It is clear that the nanowire-based direct electron transfer mechanism enables the transport of electrons through a complex network of interconnected nanowires. This may explain why a denser and thicker S. oneidensis MR-1 biofilm can produce a higher power density [41].

In order to improve the electron transfer rate, many attempts have been made to overcome kinetic and thermodynamic obstacles.

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Das, S and al. evaluated the impact of quorum detectors. Indeed, quorum sensing molecules (QSM) extracted from anaerobic sludge can help to improve the overall productivity of the algal culture, thereby decreasing the unit production cost of algal biofuel. Biomass extracted from quorum-sensing-induced algal lipids (LEB-QSA) was applied in the anode chamber of the MFC to function as a substrate and mediator, which improved the coulombic efficiency of this MFC by 74% per compared to the control MFC running without LEB-QSA. Thus, this exploration demonstrated successful improvement of macromolecular properties of algal culture dosed with QSMs and improved performance of MFCs with application of LEB-QSA as mediator and substrate [42].

The role of extracellular polysaccharides (EPS) in electron transfer was studied with Geobacter sulfurreducens. Rollefson and al. showed a role for EPS as binding sites for peripheral redox proteins that allow multicellular communities to transfer electrons to distant acceptors, where the mutant lacking the gene coding for exopolysaccharide matrix production failed to develop electrogenic biofilms on the electrodes. It has thus been observed that G.sulfurreducens possesses genes which encode extracellular anchoring polysaccharides which contain binding sites for type c cytochromes, essential for the transfer of electrons to the electrode [43].

We note through the analysis of these different studies that the electron transfer mechanism depends on the nature of the microorganisms and the affinities with the anode materials. The challenges then turn to the exploitation of self-producing microorganism mediators to make MFCs work as an alternative to artificial mediators. This requires the isolation and analysis of a large number of microbes capable of producing endogenous mediators.

There is also a need for further research on the modelling of transfer mechanisms. Belleville and al. developed a model to describe the growth of the biofilm and the local segregation of the biomass in the electro-active biofilm which made it possible to see the positive impact of EPS [44].

VIII. CONCLUSION AND PERSPECTIVES

MFCs are an innovative and sustainable technology for energy production. Remember that the objective of this review is to take stock of research on MFCs for energy production to see the limits, the solutions proposed, the possible synergies and the challenges for scaling up. We have seen that for most researchers, the objective was to combine the production of energy with the elimination of a pollutant. The results are therefore more focused on the effectiveness of the MFC according to different parameters. Parameters such as configuration, electrode materials, substrate, microorganisms, biofilm and transfer mechanisms have been investigated. It is then necessary to push more research towards the optimization of these parameters. Effective operation of the MFC system depends on a stable internal and external environment. Scaling of MFC systems should be supported by proper control of operating conditions. Operating parameters such as temperature, pH, cell biomass concentration, substrate concentration and electron mediator concentration can be optimized through experimental design and modelling. Temperature remains the primary external factor affecting the performance of MFC systems.

Regarding the configuration, various advantages and disadvantages are associated with each model. Scaling up a standardized, compact, high-performance design is a challenge. Power generation is improved by stacking MFCs in vertical, horizontal, cylindrical, and flat configurations in parallel and series connections.

In the choice of electrodes, beyond biocompatibility and conductivity, it will be necessary to take into account possible modifications induced by the thermodynamic and kinetic properties of biological and electrochemical processes. The modification of electrodes by the addition of metal oxides, carbon-based materials and their composites has significantly improved the performance of microbial fuel cells. However, the use of certain materials, such as graphene and graphene oxide, is not a sustainable alternative due to their price. This same observation holds true for platinum-like catalysts, used to reduce cathode activation over potential and improve MFC power output. The challenge would be to move towards new cost-effective and affordable cathode catalysts.

At the cathode, growth inhibition and periodic removal of non-electroactive biofilms are conducive to maintaining oxygen reduction efficiency during long-term operation of the MFC. It is therefore necessary to see the feasibility of this approach in the large-scale application of MFCs.

At the anode level the challenge is in maintaining microbial activity in the long term.

The characteristics of biofilms (composition, morphology, physical properties and thickness) have a remarkable impact on the production of electricity. Understanding of EET mechanisms is limited to bacteria such as Geobacter spp. and Shewanella spp. Research should be directed towards other exogenous generators for a better understanding of the properties of biofilm and the genetic modification of organisms.

The power densities obtained so far remain relatively low and limit the application of MFCs to low power equipment. The challenges identified for scaling up, while numerous, are attainable.

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