



Bioelectrochemical systems: Sustainable bio-energy powerhouses

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ABSTRACT

Bioelectrochemical systems comprise of several types of cells, from basic microbial fuel cells (MFC) to photo-synthetic MFCs and from plant MFCs to biophotovoltaics. All these cells employ bio entities at anode to produce bioenergy by catalysing organic substrates while some systems convert solar irradiation to energy. The current review epitomizes the above-mentioned fuel cell systems and elucidates their electrical performances. Microbial fuel cells have advantages over conventional fuel cells in terms of being sustainable whilst producing impressive power efficiencies without any net carbon emissions. They can be utilized for several environmentally friendly applications including wastewater treatment and bio-hydrogen generation, apart from producing clean and green electricity. Multifarious heterotrophic and autotrophic microbes and plants have been studied for their potential as imperative components of fuel cell technology. MFCs also display some interesting applications, such as integration of plant MFCs into architecture to produce “green” cities. Biophotovoltaic technology is the current hot cake in this field, which aspires to achieve significant electrical efficiencies by light-induced water splitting mechanisms. Furthermore, the utilization of BPVs in space renders it a technology for the future. Compared with other fuel cell systems, this technology is still in its inception and requires further efforts to endeavour its use on commercial or industrial level.

1. Introduction

The aggravating global energy challenge is imposing a limitation on the use of fossil fuels while endorsing the renewable energy resources with infinitesimal repercussion on the environment. The depleting non-renewable energy reserves such as coal and increasing environmental pollution is causing a gradual transformation towards sustainable energy resources, encompassing thermal, hydro and solar (Pospischil et al., 2014; Haldane and Toman, 2015; L. Lu et al., 2015; Rehman et al., 2015; Furlan and Mortarino, 2017). Fossil fuel consumption has a negative impact on the environment culminating in the production of carbon dioxide. The consequence of using non-renewable resources through generations has jeopardized not only human health but also the ecosystem (Machol and Rizk, 2013). Furthermore, climate change and global warming are among the adverse aftermaths of continuous fossil fuel utilization.

A contemplated alternative energy generation method is the fuel cell technology (FC). A fuel cell transforms chemical energy from a fuel into electrical energy (O'hayre et al., 2016). The hydrogen combustion reaction is split into two half electrochemical reactions. Electrons are thus emanated from the fuel because of the spatial separation in these reactions (Spiegel, 2007). These electrons stream into an external

circuit causing the generation of electricity (Dicks and Rand, 2018). An FC contains two electrodes in an electrolyte where the two half electrochemical reactions occur. William Grove first invented the fuel cell in 1839 (Appleby, 1990). FCs can be considered as the manufacturing plants that generate electricity until provided with some fuel. They commingle the benefits of batteries and engines. They provide higher energy potential and are rapidly rechargeable than batteries and unlike engines they are highly reliable with minimum toxic emissions (Hoogers, 2002).

One such neoteric energy generating system is the biological entities based electrochemical cells that convert energy either from a substrate or from sunlight into chemical and electrical energy. Biological fuel cell technology emerged as a confluence of microbiology, chemistry and physics (or more specifically the electrochemistry) (Rabaey and Verstraete, 2005; Logan and Elimelech, 2012; Mohan et al., 2014; Dicks and Rand, 2018). Fig. 1 displays a timeline depicting important events that lead to the current emerging technology of next generation green energy production.

2. Microbial fuel cells

The idea of microbial fuel cells dates back to 1911 in the study

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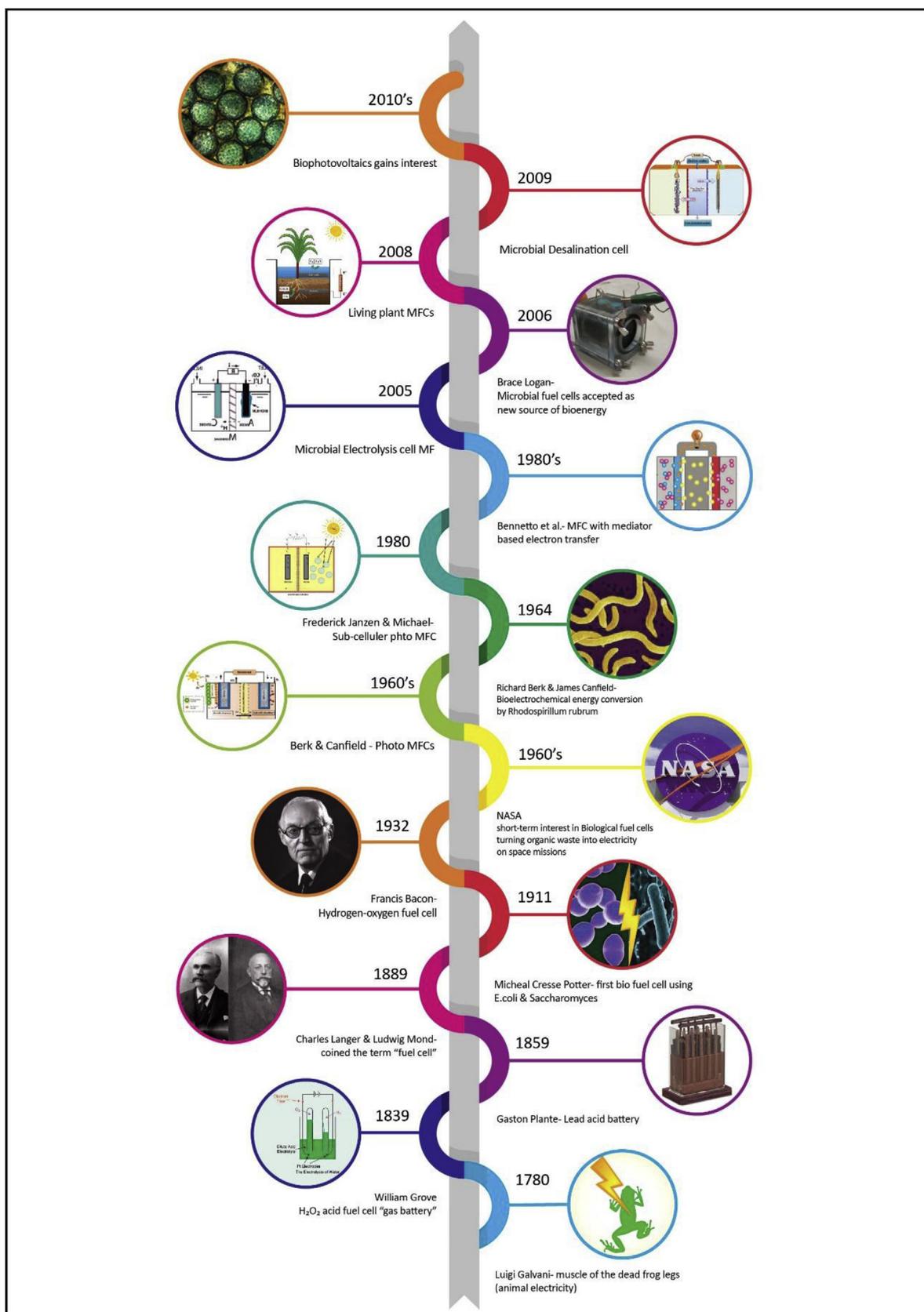


Fig. 1. Timeline displaying some important events during the innovation of fuel cell technology leading to biophotovoltaics.

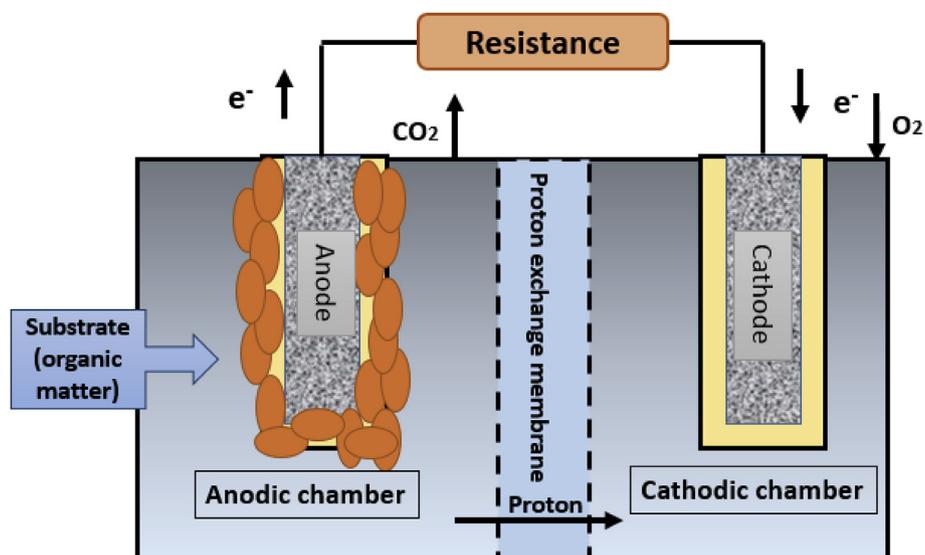


Fig. 2. A basic dual chambered microbial fuel cell.

conducted by Potter (1911). He scrutinized the generation of electricity by insertion of platinum electrode in the *E. coli* suspension. However, the technology became dormant in the following decades and gained prominent spotlight in the late 1990s. The microbial fuel cells (MFCs) convert the chemical energy of a substrate (sometimes wastewater) into electricity by a cascade of catalytic redox reactions of microbes (Fig. 2). The substrate (organic matter) is oxidized at the anode, electrons are generated by the microorganisms that are passed through the cathode to the external circuit resulting in an electrical current (Rabaey and Verstraete, 2005; Ou et al., 2017). MFCs are different from conventional electrochemical cells in the sense that they utilize electrogenic microbes such as bacteria (*Clostridium cellulolyticum* and *G. sulfurreducens*, *Enterobacter cloacae*, *Clostridium butyricum*) and fungi (*Aspergillus awamori* and *Phanerochaete chrysosporium*) (Ren et al., 2008; Rezaei et al., 2009; Kalathil et al., 2011; Ray and Ghangrekar, 2015). These exoelectrogenic bio-agents increase the complexity of the traditional electrochemical cells. The biochemical pathways of the microbial cells convert the chemical energy of fuels to electrical energy (Meunier et al., 2011). However, the low cost-effectiveness of these cells due to high material costs and mediocre power generation impedes the feasibility of this technology at a larger scale (Zhou et al., 2013).

2.1. Basic architecture of MFCs

Although multifarious structures have been built for MFCs yet the basic components and working of all the cells remain consistent. Various components of the MFC produce varying resistance, which collectively account for the cumulative internal resistance of the device. An MFC contains a chamber with anode and cathode separated by a proton exchange membrane (Ghasemi et al., 2012).

2.1.1. Anode

A vital component of MFCs is the anode due to its significance in the growth of microbial cells. It expedites the flow of electrons by the electrochemical reactions of the microbial cells. Carbon is the most prevalent electrode material used in the MFCs. Anodes can be graphite electrodes, carbon nano-tubes, rods and plates (Cheng and Wu, 2013; Erbay et al., 2015; Ahmad et al., 2018; Majid and Ahmad, 2018, 2019). Recently, researchers have worked to revolutionize the anodic material by using nano-technology to increase the efficiency and MFC potential (Zou et al., 2017a,b). An imperative factor of the anode is its congeniality for the microbes in order to facilitate the formation of biofilms. Microbial cells at the anode act as biocatalysts oxidizing the

organic substrate thereby generating electrons and protons (Rahimnejad et al., 2012a,b). The anodic chamber of the MFC contains an anode, microbes and a substrate. The microbial electron transfer can be enhanced by the use of electron mediators (also present in the anode chamber) and intensification of the MFC architecture (Aelterman et al., 2006). Furthermore, a quintessential anode should display low resistance and greater chemical stability along with increased surface area (Huggins et al., 2014; Park et al., 2014). Two types of electron transfer occur between the microbe and the anode; direct extracellular electron transfer (DEET) and indirect extracellular electron transfer (IEET). The electron flux in DEET occurs either through direct contact (cytochrome) or through the formation of various extracellular extensions between the outer membrane of microbial cell and the anode (Xiong et al., 2006). Bacteria *Geobacter* spp. forms a biofilm on the anodic material and grow extracellular pili for the direct electrochemical connection with the electrode (Lovley, 2012). IEET between bacterial cells and anode occurs by the production of redox mediators or the oxidizing of fermentative products formed by the bacterial metabolism such as the generation of hydrogen. The redox mediator involves the endogenous electron mediators (EEM) such as flavins produced by *Shewanella putrefaciens* (Zou et al., 2017b). MFCs dependent upon the IEET generate low power potential as compared with those that rely on DEET (Bonanni et al., 2012; Leang et al., 2013).

2.1.2. Cathode

Cathode in the MFCs are responsible for the oxygen reduction reactions (ORR) (Zhao et al., 2005; Harnisch and Schröder, 2010). The efficiency of MFC power generation depends upon the ORR occurring at the cathode. A high redox potential of the cathode is desirable to catch the protons. The oxygen molecule in the cathode is the usual electron acceptor due to its high oxidation potential (Logan et al., 2006). When the concentration of oxygen at the cathode increases so does the efficiency of electron flux (Larminie and Dicks, 2000). To enhance the cathodic activity for the ORR, it is crucial to apply catalysts at the cathode (Aryal et al., 2017). Platinum is among the preferred cathode material due to its high surface area but its high cost hampers its utilization. To alleviate the issue of expensive cathode material, graphite was utilized by Zhang et al., which also amplified the MFC efficiency due to its large surface area (Zhang et al., 2012a,b). MFC researchers have suggested various economical yet effective cathode catalysts. An effective catalyst significantly reduces the activation energy for the MFCs. These catalysts can be biotic as well as abiotic. Table 1 displays a list of a few abiotic and biotic cathode catalysts from multitudes of

Table 1
List of some abiotic and biotic cathode catalysts utilized in MFCs.

Abiotic catalysts		Biotic catalysts	
Platinum group metal-free catalysts (Fe, N, C, Mn, Co, Ni)	(Santoro et al., 2015, 2018; Kodali et al., 2017a,b)	<i>Marine algae</i>	Reddy et al. (2019)
Carbon xerogel doped Fe-N-GO (CXFeNGO)	Thapa et al. (2019)	<i>Marinobacter</i> sp.	Debuy et al. (2015)
Rhodium-Activated Carbon	Bhowmick et al. (2019)	<i>Roseobacter</i> sp.	Debuy et al. (2015)
Carbon nanotube/polypyrrole nanocomposite	Ghasemi et al. (2016)	<i>Bacillus</i> sp.	Debuy et al. (2015)
Nickel-phthalocyanine/MnOx	Tiwari et al. (2017)	<i>Thiobacillus ferrooxidans</i>	Ulusoy and Dimoglo. (2018)
Cobalt oxide-nanocarbon hybrid	Song et al. (2015)	<i>Pseudoalteromonas</i> sp.	Debuy et al. (2015)
Iron-phthalocyanine/MnOx	Burkitt et al. (2016)	<i>Pseudomonas fluorescens</i>	Zhang et al. (2016)
Nickel oxide/carbon nanotube composite	Huang et al. (2015)	<i>G. metallireducens</i>	Zhang et al. (2017)
Graphene oxide/MgO	Li et al. (2017)	<i>D. desulfuricans</i>	(Mohamed et al., 2017)
Silver nanoparticles	Noori et al. (2016)	<i>Rhodobacteraceae bacterium</i>	Milner et al. (2016)
Manganese dioxide Iron and aminoantipyrine (Fe-AAPyr)	(Jiang et al., 2017) (Santoro et al., 2015a,b)	<i>Nitrosomonas</i> sp.	Liao et al. (2018)
Cu/Co doped octahedral molecular sieve	(Li et al., 2011a,b,c)	<i>Azovibrio restructus</i>	Abbas et al. (2018)
Manganese-Polypyrrole-CNT	Lu et al. (2013)	<i>Pseudomonas putida</i>	(Khater et al., 2017)
Graphene nanosheet	Wen et al. (2012)	<i>Sphingopyxis</i> sp.	Zhang et al. (2017a)
Activated carbon nanofiber	Ghasemi et al. (2011)	<i>Shewanella xiamenensis</i>	(Khater et al., 2017)
Nitrogen doped carbon nanotubes	Li et al. (2011a)	<i>Mycobacterium peregrinum</i>	Teng et al. (2016)
CoMn ₂ O ₄ @GE (Bare graphite electrode)	Liu et al. (2018a,b)	<i>Flavobacterium</i> sp.	Zhang et al. (2019a,b)
Polyaniline Graphene/TiO ₂	(Han et al., 2018)	<i>Chlorobium</i> sp.	Qi et al. (2018)

others.

The cathodic materials can be categorized into abiotic and biotic groups. The use of a variety of cathodic material depends upon the application of MFC. Researchers have utilized an assortment of cathodic materials including; graphite, carbon paper, carbon cloth, Platinum electrode, macroporous hollow fibre cathode, air cathodes, carbon felt cathode, Pt coated carbon paper and graphite felt, among various others (Dong et al., 2012; Pasupuleti et al., 2016; Katuri et al., 2018; Chen et al., 2018; Oliot et al., 2017; Deng et al., 2009). Various researchers have reported the use of biocathodes in MFCs for the oxygen reduction reactions (Watanabe, 2008; Huang et al., 2011; Rahimnejad et al., 2012a,b). Biocathodes enhance the electricity generation and power potential of the MFC thus improving the cathode efficiency. The use of biocathodes in MFCs can lower the aggregate cost of the cell thereby removing the need for using catalysts or electron mediators (Xia et al., 2013). Furthermore, the by-products produced are also eradicated by the metabolic reactions of the microbes (He and Angenent, 2006). Rahimnejad et al., categorized biocathodes into two categories based on terminal electron acceptors; aerobic and anaerobic (Rahimnejad et al., 2015). Oxygen molecules are reduced by the aerobic biocathodes generating a high power output than anaerobic biocathode. Zhang et al., demonstrated the reduction of charge transfer by using biocathodes (Zhang et al., 2012a,b).

2.1.3. Membrane/barrier

A physical membrane (barrier or separator) creates a separation between the anodic and the cathodic compartments in an MFC. Cations pass through the membrane resulting in current generation. Membranes are classified into a diverse range of groups base on their capability to filter including; selective size barriers, salt bridges and ion exchange separators (Li et al., 2011b). Furthermore, they are divided into cation exchange membranes, anion exchange membranes, ultrafiltration membranes, bipolar membrane, microfiltration membrane, glass fibres, nylon fibres, porous fabrics among various others. However, these membranes are not cost-effective. Researchers have also explored a variety of low cost substances to be utilized as separators. These comprise biodegradable shopping bags, laboratory gloves, clay ware, natural rubber, eggshells etc. (Winfield et al., 2014). In certain MFCs membranes are not necessary since these fuel cells contain ionised liquid solutions. The ions may eliminate the need to utilize membrane to separate the anode and cathode (Lee and Nirmalakhandan, 2011). In such cases, both the electrodes should be of different material resulting in electrochemical separation or placed at an appropriate distance to avoid short circuit. Utilizing a membrane-less MFC is cost-effective

since it alleviates the use expensive membranes but at the same time it creates competition for anode due to the diffused oxygen from the cathode region (Wang et al., 2013). A wide variety of MFCs utilize atypical and unconventional materials that serve the dual purpose of functioning as the MFC architecture as well as ion exchange membrane. Such prototypes have been manufactured using 3D technology (Philamore et al., 2015). Complete reactors are formed from these materials that are porous and possess high durability such as nylon infused membrane, microporous filtration membrane and photocopy paper (Freguia et al., 2010; Winfield et al., 2015).

2.1.4. Microbial-entities in MFCs

As mentioned earlier, Micheal C. Potter in 1911 was the first researcher to report the utilization of microbes; *Escherichia coli* and *Saccharomyces* sp., which disintegrate organic compounds to obtain energy. He displayed in his research findings the liberation of electric current with the change in anolyte by the microbes. Microbes utilized in MFCs can be found at numerous dwellings including activated sludge, wastewater and various sediments (Strik et al., 2011; Lu et al., 2012; Yan et al., 2012). Microbes transfer electrons to the anode through the extra cellular electron transfer mechanism after metabolising the organic substrate (Paitier et al., 2017). These exoelectrogenic microbes generate electrons to the electrode (anode) thus causing current to flow through the system towards the cathode. Majority of electrogenic microorganisms belong to the proteobacteria community (Zhang et al., 2018). However, electrogens from other microbial groups have also been reported widely (Yang et al., 2019). Up till now, no microbial community has been declared as the nonpareil. Furthermore, various researches have shown that not only electrochemically active microbes but non-electrogens have been found to facilitate the generation of electricity through a symbiotic relation of latter with previous one (Fazli et al., 2018).

2.1.5. Substrates in MFC

A decisive factor for the potency of current generation by MFC is the type of substrate used in the cell. An assortment of substrates is utilized depending upon the nature and requirements of the MFC. These range from pure compound to organic substrates, to wastewater and activated sludge. Pant et al. have discussed various types of substrates used in MFCs and their current densities in comprehensive detail in their review (Pant et al., 2010). One of the basic and simple substrate used in MFCs is acetate. Acetate has been shown to generate high current than various other substrates. It has been found to generate a current density of 0.8 mA/cm² at maximum power (Logan et al., 2007). Dumas et al.

used sodium fumarate as a substrate in MFC with pure culture of *G. sulfurreducens* along with stainless steel cathode and obtained a comparatively high current density of 2.05 mA/cm² at maximum power (Dumas et al., 2008). Some other common substrates used are starch, glucose, malt extract and lactate (Bratkova et al., 2019; Hassan et al., 2019). The type of substrate used are based on several other factors including microbes at the anode, electrode material, nature and type of MFC. Many types of wastewaters are also used as a substrate in MFC. They can vary based on the origin or their source such as synthetic wastewater, brewery wastewater obtained, which contain food-derivative organic compounds, starch-processing wastewater, which is an energy-rich resource and dye wastewater obtained as an effluent from various textile industries (Haldar et al., 2019; Nandy et al., 2019; Salar-Garcia and Ortiz-Martínez, 2019; Werkneh et al., 2019). Other wastewater sources include domestic, chocolate industry, food industry, meat processing, paper manufacturing and urban wastewaters (Corbella et al., 2019; Haavisto et al., 2019; Radeef and Ismail, 2019; Rathour et al., 2019; Subha et al., 2019). Solar radiation has also been found to be an imperative source of energy for the fuel cells thus arose the concept of “living solar cells” by Rosenbaum et al. (2005a,b). MFCs utilizing sunlight will be discussed later in this review. The MFCs not only remove pollutants from the substrate (wastewater) but also utilize them for current generation.

2.2. Bioelectrogenesis

The generation of electricity by MFCs is carried out in a series of steps (Kim et al., 2007; Patil et al., 2009). Initially the microbes metabolise the substrate present in the anodic compartment (Chae et al., 2009). Following electrogens catabolism, the electrons generated by microbes flow towards the anode. The electrons thus generated flow through the external circuit towards the cathode due to the potential gradient (Park et al., 2017). The electron acceptors present at the cathode are reduced. Protons are also formed at the anode that transfer towards the cathode through the membrane (Jana et al., 2010; Rahimnejad et al., 2011). These series of steps involved in current generation are responsible for the entire performance of MFC. The environmental factors including pH, redox potential, temperature and ionic strength influence the performance of the MFCs by affecting the above-mentioned processes (Liu and Li, 2007). An optimal pH supports the microbial growth, thus facilitating a maximal current and power output. Furthermore, it was observed by Puig et al. that a controlled pH also reduces internal resistance of an MFC (Puig et al., 2010). However, an elevated pH decreases the ORR, thus decreasing current production. Temperature fluctuations strongly effect the microbial species in MFCs and their activation energies (Oliveira et al., 2013). Power density tends to increase with the rise in temperature as it supports microbial metabolism (Larrosa-Guerrero et al., 2010). Furthermore, resistance also tends to decrease with increasing the temperature of MFC. A higher redox potential effectively regulates electron transfer along with facilitating microbial growth (Adelaja et al., 2015).

The active biocatalysts (microorganisms) are present at the anode that oxidize the carbon sources of the substrate (organic) resulting in the production of electrons and protons. The electrons that are liberated by the microbes are transferred to the anode through either DEET or IEEET modes (Marsili et al., 2008; Choi and Sang, 2016). The electron transfer can be through electron mediators, cytochrome-c membrane proteins, conductive pili or bacterial nanowires (Liu et al., 2004; Prasad et al., 2007; Logan, 2009; Schaetzle et al., 2009). Oxygen is also present at the anode, which might cause hindrance in the proper functioning of the microbial cells to produce electricity. Thus, it is favourable to provide anaerobic environment at the anodic chamber. Two fundamental reactions occur at the anode and cathode that form the basis of electron flow and electricity generation.

At anode: Organic substrate + H₂O → CO₂ + H⁺ + e⁻

At cathode: O₂ + 4H⁺ + 4e⁻ → 2H₂O

Microbes generate the reducing particles when they metabolise the substrate present in the fuel. These reducing particles are carried by redox components, which are later accepted by terminal electron acceptors (Srikanth and Mohan, 2012). When the liberated electrons reach the cathode after flowing through the external circuit they react with the oxygen along with the protons thus forming water (Aelterman et al., 2006). Electricity is generated which is utilized by an external resistor present between the anode and cathode in the external circuit. It is important to point out that the anode releases an equal amount of electrons and protons. The transfer of protons towards the cathodic chamber is through diffusion, which is a slow process causing internal resistance in the fuel cell. This is a limiting factor resulting in a slow reaction rate of MFC. According to Liang et al. (2007), an MFC faces several types of internal resistances based upon their source and MFC architecture. They further discussed anodic, cathodic and ohmic resistances. Fan and Li have characterised them as ohmic, charge transfer and diffusion resistances. In their review, they have explained the sources of these resistances. Ohmic resistance arises due to the electrolyte and PEM. Diffusion resistance occurs in the electrodes, thus called anodic and cathodic resistance (Fan and Li, 2016). The efficiency of proton transfer between the anode and the cathode depends upon the nature of proton exchange membrane and specific configuration of the reactor. A membrane potential called the proton motive force is formed across the membrane. This potential in turn produces a potential difference between the microbial cell membrane and the anode causing the delivery of electrons to the external circuit and protons to the cathode (Zhang et al., 2017). The negative anodic potential and the positive cathodic potential creates a potential difference called the electron motive force, which causes the electrons to move in the circuit towards the cathode (Zhao et al., 2018). Thus generating bioelectricity, which is harnessed through an external load.

2.3. Applications of MFCs

MFCs have been used for multifarious applications since their inception. A few main applications are mentioned in this review (Fig. 3). The main application of MFC is the generation of bioelectricity (Sadabad and Gholikandi, 2018). A variety of electrogenic microbes including bacteria and fungi have been utilized extensively for the

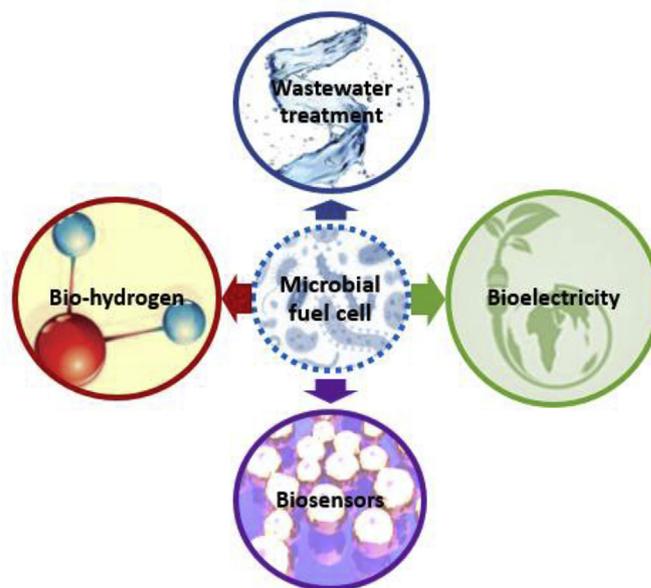


Fig. 3. Different applications of microbial fuel cells in multiple fields.

production of electricity-generating microbial fuel cells (Miran et al., 2017; Sekrecka-Belniak and Toczyłowska-Mamińska, 2018). The electricity potential depends upon a number of factors including; microbial strains, nature of substrate, electrodes material, configuration and type of fuel cell. Although extensive research has been performed on MFCs yet more studies are required to increase the efficiency and stability for adequate electricity generation. A recent and intriguing study was conducted by Ozdemir et al., who generated electricity from human urine containing tetrahydrocannabinol utilizing a microbial fuel cell with voltage generation up to 0.27 V (Ozdemir et al., 2019). It was presented by Koo et al. that the addition of supporting material at the cathode would drastically improve the electricity generation potential of the fuel cell. Koo et al. used reduced graphene oxide for elevated power density by MFC (Koo et al., 2019). Another application of MFCs usually occurring alongside bioelectricity production is the treatment of wastewater (Hiegemann et al., 2018; Yadav et al., 2018). Organic substrate i.e. wastewater from various sources is metabolized by microbes at the anode to generate electrons. The metabolism of these substrates also results in their treatment i.e. they are degraded by the microorganisms with the liberation of carbon dioxide. Liu et al. conducted the pioneer wastewater treatment study in 2004, which was followed by numerous such researches (Liu et al., 2004). Long et al. developed parallel circuit MFCs for the removal and subsequent degradation of azo dyes from water (Long et al., 2017). Instead of producing electricity, MFCs can also be utilized to produce biohydrogen (Montpart et al., 2015; Wan et al., 2015). Rathinam et al. have harnessed thermophiles to catalyse various substrates at wide operating conditions to produce biohydrogen in MFCs (Rathinam et al., 2019). Furthermore, the hydrogen produced by MFCs is renewable, which can be stored and used later. The potential at the anode is elevated for the production of hydrogen gas.

2.4. Limitations of MFCs

Power generation from MFCs has recently been considerably high and adequate to supply current to small lab-scale systems (Mohammadifar and Choi, 2019; Prasad and Tripathi, 2019). However, certain limitations and challenges are faced by such fuel cell technology. The foremost challenge is to overcome the internal resistance of the cell caused mainly by the proton exchange membrane (Shreeram et al., 2018; Wu et al., 2018). Furthermore, the high cost of the electrodes utilized in some cells such as those manufactured from gold, platinum and other expensive materials is a huge limiting factor hindering its economical usage (Kodali et al., 2017a,b; Jarosz et al., 2018; Sadeghifar and Rashid-Nadimi, 2018). The efficiency of energy extraction from wastewater is still low and requires more research to increase it. The highest electrical output achieved in 2018 by treating agricultural wastewater through MFC was 27 W/m³ as reported by Ceconet et al. (2018). In 2019, Zhang et al. were successful in producing in-situ electricity by the degradation of organic pollutants with the electrical output reaching up to 106 W/m³ (L. Zhang et al., 2019). However, the high power density achieved depends upon high initial concentration of the organic pollutants. The start-up time or the activation energy required by the MFC also limits its productivity. Another principal impediment to effective fuel cell working is that the energy is not enough for continuous operation of the external load attached. Low temperature is also a limit for the competent working of fuel cell since the microbial reactions are lethargic (Zhang et al., 2017). One crucial restraint is the instability of the microbial cells (Pareek et al., 2019). After their extraction and isolation from indigenous environments, the microbes may not retain enduring stability.

3. Photosynthetic MFCs

According to an estimation only 1% of energy from sunlight if converted into electricity successfully can produce energy ten times the

current energy utilized by the world (Service, 2005). More focus has been devoted to non-photosynthetic MFCs for the generation of electricity. However, recently a transformation has been observed in the scientific community towards more sustainable energy production. The use of photosynthetic MFC that utilize microbial entities capable of converting sunlight into chemical energy is thus gaining popularity (Fig. 4). These microbes contain certain specialized light harvesting complexes; photosystem I and photosystem II that function as the units of photosynthesis. These light harvesting units are the same that are present in higher plant leaves that perform the function of photosynthesis. The structure and function of photosystem I and II is discussed in more detail in the next section. Their utilization in MFCs is highly sustainable in terms of bioenergy generation. However, not all photosynthetic MFCs utilize the whole living microbial cell rather sub-cellular components are also used for the process of photosynthesis. Various sub-cellular components used in photosynthetic MFCs include chloroplasts, thylakoid membranes and extracted photosystems (Tyszkiewicz et al., 1982; Mimeault and Carpentier, 1989; Gunther et al., 2013). The biological entities are immobilized on the photo-electrochemical fuel cells resulting in photosynthetic MFCs. Due to several limitations faced by conventional MFCs, explained previously in Section 2.4, photosynthetic MFCs technology is being explored to increase the stability of such devices.

3.1. Sub-cellular photo MFC

Such fuel cells utilize anoxygenic photosynthetic entities attached onto the electron acceptor. Janzen and Seibert conducted the earliest known study on photosynthetic microbial fuel cell in 1980. They used photosynthetic reaction centre from *Rhodobacter sphaeroides*, a purple nonsulfur bacteria (Janzen and Seibert, 1980). The photosynthetic centres were attached on the electrodes which when irradiated produced current. Efrati et al. used extracted PS-I and PS-II from *Mastigocladus laminsus*, incorporated on the ITO anode that exhibited photo-induced redox reaction (Efrati et al., 2013). PS-I extracted from thylakoid structures of baby spinach was immobilized on Au leaf anode by Ciesielski et al. using sodium ascorbate as a feedstock and dichloroindophenol as electron transporter (Ciesielski et al., 2008). Gerter et al. saw an impressive current density by incorporating photosynthetic protein PS-I on electrode, which generated 1500 mA/m² under dry conditions (Gerster et al., 2012). Most photosynthetic MFCs use microbes that are devoid of PS-II reaction systems hence an exogenous electron donor and acceptor is obligate.

3.2. Whole cell photo MFC

Whole-cell autotrophic microbes are also used to generate electricity. Since sub-cellular photo MFCs utilize only a part or a sub-entity for photosynthetic function they are less potent in terms of sustainability. Whole-cell photo MFCs are capable of self-repair and generate current under light and dark conditions. Rosenbaum et al. were able to produce 182.5 mA/m² current density by using *Rhodobacter sphaeroides* suspension and lactate (Rosenbaum et al., 2005a,b). A mixed consortium of phototrophic microbes was incorporated on biocathode by Cao et al., which produced 750 mA/m² current density (Cao et al., 2009). *Shewanella oneidensis* was utilized in photosynthetic MFC by initially modifying them and deposition of biofilm on graphite (Johnson et al., 2010). Cho et al. achieved remarkable electrical output of 790 mW/m² using *R. sphaeroides* cells when illuminated with light (Cho et al., 2008). *Rhodospseudomonas palustris* produced a current of 5.9 mW/m³ by metabolising *Arthrospira maxima*, a cyanobacterium (Inglesby et al., 2012). In another study, Rosenbaum et al. used green algae, *Chlamydomonas reinhardtii* in acetate to produce H₂ under aerobic conditions (Rosenbaum et al., 2005a,b). Photo MFCs are also able to produce photosynthetic biohydrogen, which displays their advantage as energy generating systems. The biohydrogen can be

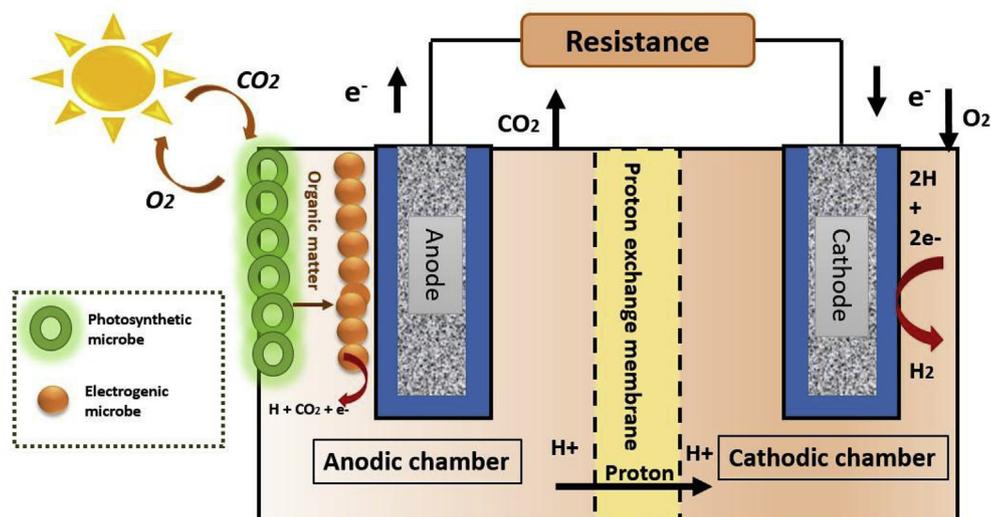


Fig. 4. Photosynthetic microbial fuel cell illustrating production of organic matter by photosynthetic microbes, which acts as a fuel and is oxidized by electrogenic microbes in the anodic chamber.

converted into bioelectricity to overcome the problem of hydrogen handling and recovery.

At times photosynthetic autotrophic microbes are mixed with heterotrophic bacteria to produce a synergistic relationship (Pillot et al., 2019; Rashid et al., 2019). In one such relationship, the photosynthetic microbes; cyanobacteria or some other bacterial group provides organic content to the heterotrophic bacteria. A better green electrical output was observed in such systems as compared to other systems with a single type of microbe. However, the current density was higher under dark conditions than light. The integration of photosynthesis with MFC technology has opened several neoteric possibilities for sustainable bioenergy generation.

4. Plant microbial fuel cells

Plant MFCs (PMFCs) are a derivative of the benthic microbial fuel cell also known as sediment microbial fuel cell. Benthic or sediment MFCs work on the principle of potential difference between sediment in the seabed and the oxygen rich water near the surface. In PMFCs, the roots exude various organic substrates, which are catalysed by the microbes present on the surface of anode generating electricity (Fig. 5). The plant root exudates serve as fuel where the anode is fixed in a matrix while the cathode is present in the fresh water upper zone. A continuous supply of organic exudates is provided by the plant roots providing advantage over conventional MFCs in terms of sustainability. Strik et al. were the pioneers to produce PMFC that used living plants and bacteria to convert solar energy into green electricity (Strik et al., 2008).

Mostly aquatic plants are preferred for PMFC including rice plant, *Anisogramma anomala*, *Glyceria maxima* and *Arundo donax* among others (Schampelaire et al., 2008; Helder et al., 2010; Takanezawa et al., 2010; Timmers et al., 2010). Various exudates from plant roots include different secretions and gases, which comprise of carbohydrates and amino acids highly amenable to microbial degradation (Flint et al., 2012; Jin et al., 2018). Studies on PMFCs have exhibited glucose to be the most effective substrate for maximum power generation (Zhang et al., 2017c). High power densities by glucose substrate were achieved in various researches with power densities, 220 mW/m² and 156 mW/m² (Min and Logan, 2004; Chae et al., 2009). Electrons are also donated to the anode by soils instead of root exudates. Electrons are generated in the anodic zone via anaerobic respiration. Various factors effecting the conversion efficiency of PMFCs have been displayed in Fig. 6.

Electrodes materials with high surface area are favoured for PMFCs

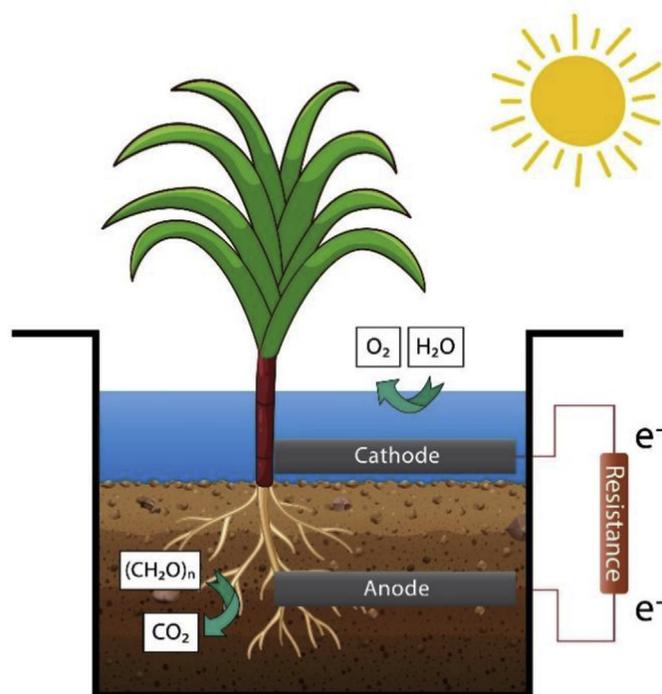


Fig. 5. Plant microbial fuel cell with microbes on anode catalysing the root exudates.

as they increase the association between the microbes and the electrode. Graphite is thus the most preferred electrode material due to its high surface area (Helder et al., 2010). Furthermore, treated electrodes (anode and cathode) efficiently increase the power generation of PMFCs (Tang et al., 2011). In such cases catalysts are utilized at the electrode which might include ferricyanide, thionine, methyl viologen etc. (Timmers et al., 2010). Furthermore, biocatalysts can also be used to enhance the working of PMFCs. Working of PMFCs require formation of biofilm on the anode of the cell. Several bacterial and fungal species have been studied that show electrogenic activity in PMFCs biofilm. Kaku et al. have explored the potential of *Natronocella acetinitrilica* on the anode of PMFCs (Kaku et al., 2008). Furthermore, alpha-proteobacteria have also been studied on the cathode of PMFCs. Various researchers have also exhibited that not all microbes functioning in

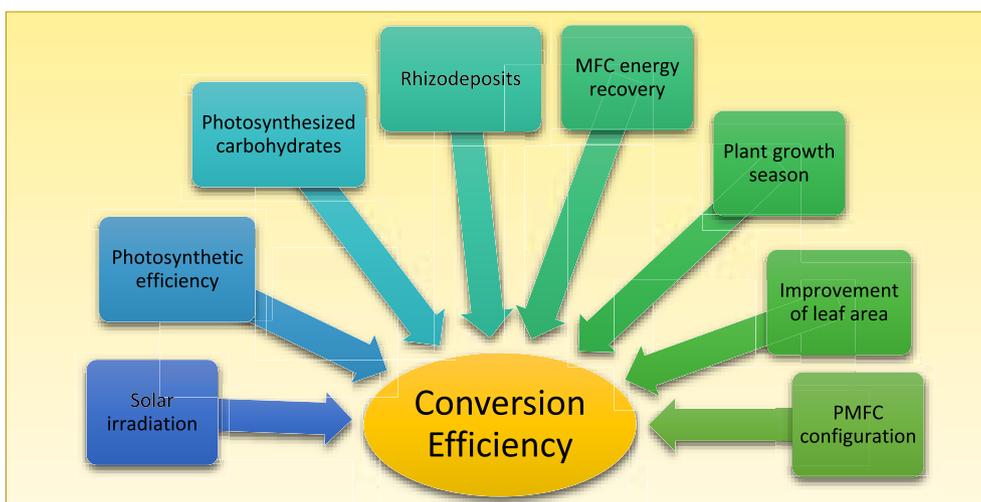


Fig. 6. Factors effecting the conversion efficiency of PMFCs.

PMFCs may necessarily be electrogenic in nature (Sorokin et al., 2007). Two types of bacteria are present on the cathode; aerobic and anaerobic. Inoculum type has a significant influence on the PMFC efficiency. In a study conducted by da Rosa, bacterial inoculum from rice field soil displayed greater potential to form biofilm and subsequently exhibit current generation activity in PMFC (Cabezas da Rosa, 2010). PMFCs have shown great potential in both current generation i.e. the production of green electricity and being an efficacious greenhouse gas removal facility simultaneously. Few studies utilizing plants in microbial fuel cells are listed in Table 2. Strik et al. have proposed an interesting and impressive concept in their review article, which states the use of PMFCs as an integration into the landscape, thus producing “green” cities (Strik et al., 2011). They suggested the use of “green roofs” which will have several beneficial implications including increase in the aesthetic value of the city, lowering of temperature and air quality recuperation, apart from production of green energy.

5. Biophotovoltaic cells

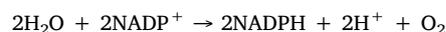
The nexus of photovoltaic and bio-electrochemical cells gives rise to bio-photovoltaic systems. In previous sections, we have discussed the use of photosynthetic entities in MFCs to produce bio-energy. In this section, the concept of bio-photovoltaic cells (BPVs) will be explained and differentiated from other light harvesting bio-electrochemical systems. The main characteristic of BPVs is the utilization of oxygenic photosynthetic bio entities only, which breakdown water when illuminated (Fig. 7). The electrons thus produced are transferred to the anode via IEEET or DEET mechanism. Systems other than BPVs may or may not be able to separate charge from water. The bio entities involved in BPVs light harvesting system may be sub-cellular proteins; photosynthetic reaction centres or whole cell systems of blue green algae or photosynthetic bacteria. A chief difference between an MFC and a BPV is that, though both are bioelectrochemical systems, BPVs are specifically photo-driven systems. Furthermore, MFCs require a carbon source to operate while light energy and water as an electrolyte is enough for BPVs. MFCs contain heterotrophic microbes at the anode and BPVs have photosynthetic microorganisms.

According to McCormick et al. only 37 studies on BPV were conducted from 1964 to 2008. However, in the last decade more than 100 articles were published in various scientific journals (McCormick et al., 2015).

5.1. Photosynthetic reaction centres in BPVs

In this section, we will briefly explicate the concept and working of

photosynthetic reaction centres. The process of photosynthesis is integral in various autotrophic organisms including plants. The light reactions of photosynthesis occur through the photosynthetic reaction centres; photosystem I and photosystem II (Kramer et al., 2004) (Fig. 8). The thylakoid membranes inside chloroplasts are the chief sites containing the photosynthetic reaction centres where photosynthesis occurs (Shimoni et al., 2005). Although cyanobacteria does not contain chloroplasts, they contain the photosynthetic apparatus necessary to carry out photosynthesis. Chloroplasts contain light-absorbing molecules called chlorophylls; chlorophyll a and chlorophyll b while photosynthetic bacteria contains bacteriophyll. Other than these, secondary pigments are also present including carotenoids and phycobilins. These pigments absorb light in various ranges. Photosystem I contains chlorophyll a or P700 while photosystem II contains chlorophyll b or P680 (The numbers, P700 and P680 refer to the range in which they absorb light) (Barber, 2014). Both photosynthetic reaction centres work in the form of a Z scheme of electron transport. When a photon of light falls on PS-I, the electrons become excited and thus move to a higher energy level (Yamori and Shikanai, 2016). The excited electron moves through a series of electron carriers and is accepted by NADP⁺. The electron carriers include phyloquinone, iron sulphur protein complex, ferredoxin and lastly NADP⁺. After accepting electrons, NADP⁺ is converted to NADPH (Minagawa, 2016). Since the P700 is oxidized after losing electrons, it becomes unstable resulting in an electron gap. This gap is overcome by the P680 or chlorophyll b when it is hit by light. The electrons in P680 become excited and move through another chain of electron carriers eventually reaching P700 (Hartmann et al., 2018). The chain of electron carriers include; pheophytin, plastoquinone, cytochrome bf complex, plastocyanin and lastly P700 (Barber, 2016). This process also results in an unstable P680. However, the P680 can gain electrons through its oxygen evolving complex (OEC) by photolysing water to generate electrons (Shevela and Björn, 2017). The Z scheme of electron transport through P700 and P680 is illustrated in Fig. 8. The net reaction of water photolysis and conversion of NADP⁺ to NADPH is given below.



BPVs utilize both PS-I and PS-II to generate energy from light. These cells use oxygenic PS-II reaction centres.

5.2. Performance of BPVs

Like other bioelectrochemical cells, BPVs are also made by using either sub-cellular components or whole cells capable of photosynthesis. In 2005, Touloupakis et al. constructed a biosensor for the

Table 2
Architecture, components and electrical outputs of some PMFCs.

Plant	Cell configuration	Anode	Cathode	Anolyte	Catholyte	Electrical Output	Reference
<i>Acomis calamus</i>	Plant SMFC	Carbon felt	Carbon felt	Fresh water sediment	Water	0.1902 V ^a	Liu et al. (2019)
<i>Oryza sativa</i>	Single chamber PVC pipe	Carbon felt anode	Air cathode	Soil	-	41.41 mW/m ²	Khudzari et al. (2019)
<i>Typha orientalis</i>	Constructed wetland MFC	Nano zero valent Iron	Nano zero valent Iron	Hoagland's trace elements and quartz sand	Hoagland's trace elements and quartz sand	26 mW/m ²	Wang et al. (2019)
<i>Acomis tatarinowii</i>	Plant sediment MFC	Graphite felt plate	Pt coated graphite felt plate	Silica sand	Water	21 mW/m ²	Liu et al. (2018a,b)
<i>Epipremum aureum</i>	Plastic container	Carbon fibre brush	Carbon fibre cloth	Cow dung, garden soil, artificial microbial growth media	Artificial microbial growth media	620 mW/m ²	Sarma and Mohanty, 2018
<i>Alisha plantago-aquatica</i>	Plastic container	Galvanized steel plates	Graphite plates	Soil + water	Soil + water	0.072 mW/m ²	Rusyn and Hamkalo (2018)
<i>Arundo donax</i>	Constructed wetland MFC	Graphite felt	Graphite felt	Quartz sand matrix	Quartz sand matrix	12.82 mW/m ²	Zhou et al. (2018)
<i>Vetiveria zizanioides</i>	Double chambered earthen pots	Graphite fibre	Graphite wire	Garden soil + water	-	68 mW/m ²	Regmi et al. (2018)
<i>Chlorophytum comosum</i>	Garden pots	Graphite	Graphite	Soil + water	Soil + water	18 mW/m ²	Azri et al., 2018
<i>Puccinellia distans</i>	Single chamber PVC pipe	Carbon felt anode	Air cathode	Potting mix	-	83.7 mW/m ²	Khudzari et al. (2018)
<i>Spartina anglica</i>	Flat porous plate	Three layers of graphite felt	Graphite felt	Nitrate-less ammonium rich plant growth medium	Aerobic wastewater	120 mA/m ²	Wetser et al. (2015)
<i>Canna indica</i>	Polymethyl methacrylate cylinder	Graphite disk	Annular carbon cloth	Tap water	Tap water	1015 mA/m ²	Lu et al. (2015a,b)

^a Electrical output mentioned only in voltage.

detection of herbicides and pollutants by utilizing thylakoids from *Spinacia oleracea* and *Senecio vulgaris* on a graphite electrode (Touloupakis et al., 2005). Lam et al. was successful in generating 11 mA/m² current by using a suspension of thylakoid membranes on a gold anode (Lam et al., 2006). PS-II extracted from *Thermosynechococcus elongatus* on gold electrodes was studied by Badura et al. to produce bio-hydrogen. Furthermore, a current of 14 μA/cm² was generated upon illumination (Badura et al., 2006). Thylakoid membranes from baby spinach were fixed on polypyrrole in between two electrodes that served as a bio-chemical sensor for herbicide (Lin et al., 2006). Kato et al. fixed PS-II reaction centre from *Thermosynechococcus elongatus* on anode and generated 16 mA/m² current density from water photolysis (Kato et al., 2012). Calkins et al. generated 250 mA/m² current from Thylakoids from *Spinacia oleracea* immobilized on multi-walled carbon nanotubes (Calkins et al., 2013).

BPVs have advantage over conventional photoelectrochemical cells that they produce current in dark as well through respiratory breakdown of organic compounds produced during the light reactions (McCormick et al., 2011). Cyanobacteria, *Spirulina platensis* was attached on anode in a membrane-less fuel cell to generate 17.5 mA/m² (Fu et al., 2010). Thorne et al. grew a biofilm of *Chlorella vulgaris* on FTO coated glass to produce current density of 110 mA/m² (Thorne et al., 2011). A suspension of *Synechocystis* PCC 6714 was incorporated in a photoelectrochemical cell producing 78.75 mA/m² (Xie et al., 2011). In a two chambered cell, *Synechocystis* PCC6803 was utilized which produced a maximum power density of 6.7 mW/m³ without any net CO₂ production (Madiraju et al., 2012). Raman and Lan observed the effect of various electrodes distances on power density of BPV by using *Chlamydomonas reinhardtii* transformation F5 (Raman and Lan, 2012). They elucidated that shorter distance between electrodes produces high power density since the internal resistance decreases. A mixed consortium of electrogenic microbes was used by Chandra et al. who demonstrated that electrons generated by light reaction were in greater number than electrons generated by dark reaction (Chandra et al., 2012). Subhash et al. utilized domestic wastewater to produce bioelectricity through mixed photosynthetic consortium. The electrogenic activity was observed to be higher during daytime than night (Subhash et al., 2013). McCormick et al. were successful in producing current density of 61.4 mA/m² by a suspension of *Synechocystis* PCC6803 deposited on ITO glass electrode (McCormick et al., 2013). Samsonoff et al. immobilized *Synechococcus bacillaris* (CCAP WH5701) on gold electrode explicated that denser biofilms were grown on surfaces closer to the electrode (Samsonoff et al., 2014). Microfluidic BPVs have also been fabricated by Bombelli et al. that use the soft lithography technique while the cells are settled down at the anode through gravitational force to produce impressive densities of current (Bombelli et al., 2015). Fast growing algae, *Synechococcus elongates* (UMACC 105) was used to generate bioelectricity from BPV on ITO and reduced graphene oxide electrodes (Ng et al., 2018). Various other electrode materials have been utilized in BPVs such as titanium oxide/reduced graphene oxide composite was used in BPV with *Chlorella vulgaris* cells. This combination of electrode material displayed impressive durability and generating 34.66 mW/m² bioelectricity (Senthilkumar et al., 2018). BPVs show great efficiencies for bioenergy generation in light as well as dark conditions. BPV technology is still in infancy stage and is open to several new options for optimisation to increase energy efficiency using various electrode materials and varying cell configuration.

5.3. BPVs in space

An interesting application of BPVs is its use in space missions. Phototrophs including green algae and cyanobacteria were examined in space and exposed to solar UV, temperature variabilities, vacuum conditions in space and cosmic radiation in the EXPOSE-E mission for 18 months by European Space Agency (Cockell et al., 2011). Two algae;

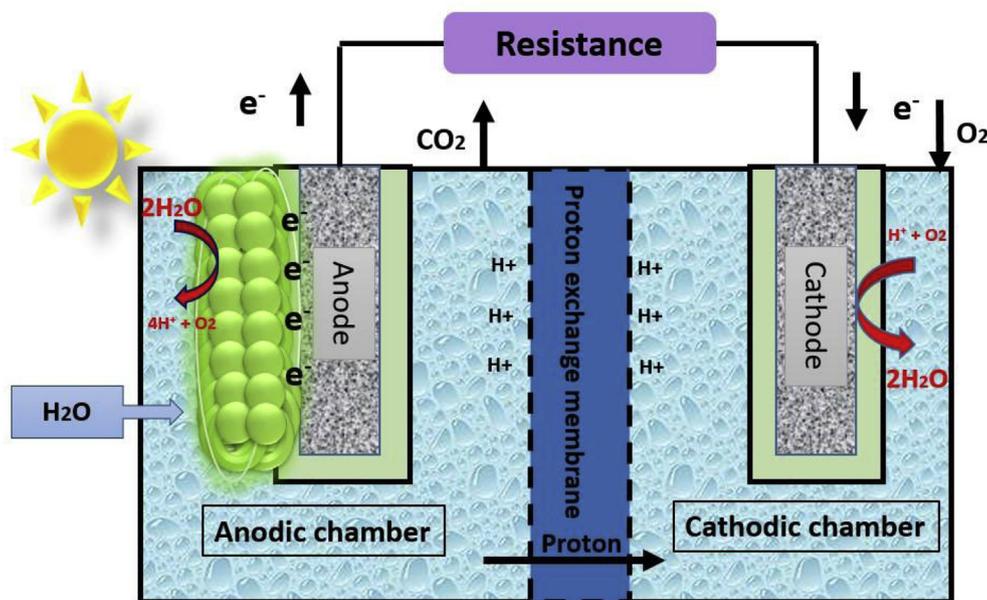


Fig. 7. Pictorial display of biophotovoltaic cell exhibiting the use of sunlight by autotrophic/photosynthetic microbes in the presence of water as substrate to produce bioenergy.

Chlorella and *Rosenvingiella* spp. and a cyanobacterium; *Gloeocapsa* sp. survived the space exposed conditions. Microbial cells were also exposed to extreme UV radiation, which might be even detrimental, yet some autotrophic communities survived. The resilient and tolerant nature of photosynthetic microbes under extreme environmental conditions aid them in their survival such as the protection of cells by surface layers. Phototrophs can thus be efficiently utilized to produce oxygen in life support systems in space missions. Other than oxygen, microalgae can also be utilized as a food production and supply to various space missions (Chacón-Lee and González-Mariño et al., 2010). Other functions of microalgae systems in space include; waste transformation, carbon dioxide reduction and regeneration of air, water and food. Such systems display extensive promise as life support systems in space missions owing to its regenerative capabilities, sustainability and stability.

5.4. Hybrid BPVs

A new hybrid BPV cell system is being researched upon, which

utilizes seawater, one of the most abundant renewable resource, as an electrolyte for such cells. This technology is attributable to BPVs only. This technique, though requires more investigation, can be utilized in the future for the production of fresh water along with energy generation by desalinating seawater. Such a technology opens up a new era for entirely sustainable electricity generation from a nexus of seawater, sunlight and oxygen without the need for supplementary fuel. Mainly, BPVs can utilize any water as an electrolyte and undergo water-splitting reaction to convert it into hydrogen and oxygen at the anode. Such cells might not need any external power source to operate and rely on sunlight only to convert water into energy. Water-splitting technology of BPVs has also been utilized in 2016 for the production of hydrogen fuel. Pinhassi et al. (2016) introduced thylakoids extracted from spinach in BPV to produce a current density of 0.5 mA/cm along with the production of hydrogen fuel. Zhang et al. (2017b) constructed a BPV utilizing seawater as an electrolyte. When illuminated by solar light the cell produced 21.4 μW/cm² after water splitting at the TiO₂ semiconductor anode.

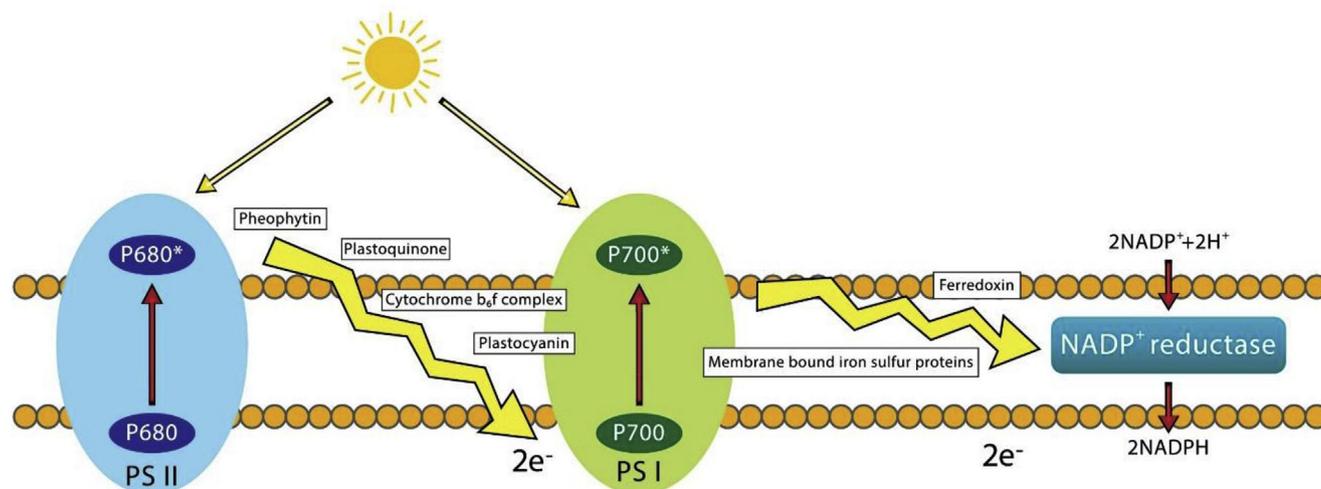


Fig. 8. Z scheme of electron transport chain through P700 and P680 photoreaction centres.

Table 3
Parameters to evaluate bioelectrochemical cell performance.

Equation	Use	Variables involved
$I = E_{\text{cell}} / (A_{\text{mean}} \times R_{\text{ext}})$	Current density	I: current density, E_{cell} : cell potential, A_{mean} : membrane area, R_{ext} : external resistance.
$P_{\text{max}} = I_{\text{mp}} \times V_{\text{mp}}$	Maximum power output	P_{max} : power output, I_{mp} : current at maximal power, V_{mp} : voltage at maximal power.
$C_E = Ms \int_0^{t_s} Idt / F v_{\text{an}} \Delta C$	Columbic efficiency	C_E : Columbic efficiency, Ms: molecular weight of substrate, F: Faraday's constant, V_{an} : liquid volume in the anodic part, ΔC : change in concentration of substrate over batch cycle over time period t.
$\eta = P_{\text{max}} / P_{\text{in}}$	Solar to electrical conversion efficiency	η : solar to electrical energy efficiency, P_{max} : maximum power output, P_{in} : incident power.
$FF = I_{\text{mp}} \times V_{\text{mp}} / I_{\text{sc}} \times V_{\text{oc}}$	Fill factor	FF: fill factor, I_{sc} : short circuit current, V_{oc} : open circuit voltage.
$EE = CE \times PE$	Energy efficiency	EE: energy efficiency, CE: columbic efficiency, PE: potential efficiency.
$E_{\text{device}} = OCV - IR$	Total energy loss	E_{device} : total energy loss, OCV: open circuit voltage, IR: internal resistance.
$Re = l / (A \times K)$	Electrolyte resistance	Re: Electrolyte resistance, l: electrode distance, A: cross sectional area through which ionic conduction occurs, K: specific conductivity of the electrolyte.
$CE = Pe \times Rp \times Ra \times Er$	Conversion efficiency of PMFC	CE: conversion efficiency, Pe: photosynthetic efficiency, Rp: photosynthesized carbohydrates, Ra: rhizodeposit availability for microorganisms, Er: microbial fuel cell energy recovery.

6. Electrical potential of biological fuel cells

Prodigious efforts have been done by researchers to increase the power density, current and stability of MFCs to make their practical application lucrative. Various parameters and equations used to calculate the efficiency and output of bioelectrochemical cells are listed in Table 3. Recently microscale MFCs have been developed which have shown to produce a very high power density of 450 A/m² (Ren et al., 2014). Furthermore, these MFCs behaved as supercapacitors with increased stability. A power density of 1.78 W/m² has been achieved by Rashid et al. by utilizing activated sludge accompanying algae biomass (Rashid et al., 2013). An impressive power density of 788 mW/m² was achieved by using activated sludge as a biocatalyst (Park and Zeikus, 2003). It has been found in various studies that the configuration and architecture of MFCs have a great influence on the electrical performance of fuel cells. Jadhav et al. developed a dual chambered cell with a power density of 6.5 W/m³ (Jadhav et al., 2014). An overflow type MFC reactor was built by Li et al. which produced 18.2 W/m³ power density (Li et al., 2009). A stacked sandwich type fuel cell by Zhang and Agelidaki has been reported to produce 0.294 W/m² power density (Zhang and Angelidaki, 2012). 17.85 mW/m² maximum power was achieved by a clay ware cell with an air cathode (Ghadge and Ghangrekar, 2015). An upflow reactor by Thung et al. utilized a tubular cylinder with carbon flake cathode producing a power density of 44.4 mW/m² (Thung et al., 2015). Furthermore, stacking has also been performed to increase the MFC performance. A stacked MFC system produced 22.8 mW/m² (An et al., 2014). Mathuriya developed an interesting wastewater treatment system with multiple anode chambers producing a continuous 359.6 mW/cm² power density (Mathuriya, 2017). Dong et al. developed a 90 L MFC system which operated for 6 months and produced an impressive amount of power i.e. 0.056 kW h/m³ (Dong et al., 2015). It was observed that in a SMFC the granule size is a crucial factor determining the current density. Arends et al. used small sized carbon felt granules (0.25–0.5 mm) in a plant based SMFC and obtained 77.7 mA/m² current density (Arends et al., 2012). Villaseñor et al. were able to achieve a high power density of 20.76 mW/m² (Villaseñor et al., 2013). They developed a horizontal subsurface flow constructed wetland MFC (CW-MFC), which utilized wastewater as a substrate. A low organic loading in the MFC resulted in a high oxidation of wastewater organic content facilitating electric current. A higher power density of 55.05 mW/m² was achieved by Liu et al., from CW-MFC (Liu et al., 2014). They optimised the CW-MFC by using various cathode materials. Granular activated carbon cathode provided the highest power density due to its large surface area. Helder et al. obtained a soaring 222 mW/m² power density from *Spartina anglica* based PMFC (Helder et al., 2010). Chiranjeevi et al. obtained 163 mW/m² power density from PMFC pot reactor by using *Pennisetum sentaceum* (Chiranjeevi et al., 2012). Chiao et al. built a micro photosynthetic MFC with a power density of 0.023 mW/m² (Chiao et al., 2006). A maximum

power density of 800 mW/m² was achieved by Yagishita et al. from a cellular biophotovoltaic cell (Yagishita et al., 1998) followed by 289 mW/m² by a *Synechococcus* sp. based BPV (Tsujimura et al., 2001). In another study, Yagishita et al. obtained 288 mW/m² from *Synechocystis* sp. using glucose as feedstock (Yagishita et al., 1997).

7. Conclusion and future perspectives

Microbial fuel cell technology has precedence over other renewable energy generating systems in that it not only generates green electricity but also produces a range of other fuels including bio-hydrogen and various other chemicals. Contrastingly, solar cell technology only generates electricity from solar energy conversion (Iqbal et al., 2019). MFC systems are capable of self-repairing since they utilize living cells rendering them more sustainable. These cells are environmental friendly and do not produce toxic pollutants. Bioelectrochemical fuel cells are excellent bioremediants and can remove various noxious contaminants. The photoMFCs and PMFCs also aid in improving air quality due to their ability to perform photosynthesis. Furthermore, PMFCs can also increase the aesthetic value by their incorporation into the landscape. Bioelectrochemical fuel cells can be fabricated in various configurations with utilization of several materials for electrodes. Each configuration generates varying power densities that can be further optimised by the use of high surface area electrodes. However, the electrical outputs of such systems are still not high enough to reach larger scale industrial applications although the amount of power densities of MFCs have increased considerably in the recent years. MFCs can be further optimised by using microscale cells that not only reduce internal resistance of the cell but are also portable and can scale up power efficiencies of other systems as well when used in combination. MFCs is a promising technology since it can function at extreme temperatures such as when using thermophilic microbes. The potential and resilient nature of microbes in fuel cells have also been exhibited by the study conducted in space under extreme conditions. To increase the potential and efficiencies of MFCs, various cost-effective electrode materials should be utilized and more focus should be transferred towards photosynthetic microbes that can obtain their own food and do not require much external input for functioning. However, with the current trend in green energy generation, there is an exponential increase in bioelectrochemical technology research indicating great advancements in this domain in the future.

Conflict of interest

None.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Mahwash Mahar Gul: Conceptualization, Data curation, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Khuram Shahzad Ahmad:** Conceptualization, Data curation, Investigation, Supervision, Visualization, Writing - original draft, Writing - review & editing.

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