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Photoelectrode, photovoltaic and photosynthetic microbial fuel cells

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ABSTRACT

This review examines the combination of photoelectric cells (PEC) and microbial fuel cells (MFC), including photosynthetic MFCs. It was found in a number of investigations that photoanodes and photocathodes can be well combined with electrogenic and photo-electrogenic microbes. The progress in this field originates from the idea that MFCs using light to power converting electrodes generate more power than with the dark reaction in an MFC alone or by solar power in a PEC. There are a multitude of possible designs for establishing Photo-MFCs. It is noteworthy that in addition to electric power, also hydrogen, methane and other solar-bioelectrofuels are producible using hybrid MFC-PEC type reactors, which are assembled from artificial and native photosensitive electrodes and electrogenic microbes.

1. Introduction

1.1. General

When standard microbial fuel cells (MFC) are light supported, their power increases above what is possible with the dark reaction alone. Several types of light supported MFCs are described in the literature, yet the total number of papers on this topic is small with ~2% in comparison to what is known about MFCs more broadly. A light enhanced MFC can be based exclusively on biological systems, but often it consists of a non-biotic anode or cathode and a biotic electrode. Even if an MFC is light enhanced it remains an MFC as at least one of the two electrodes is in contact with microbes (Fig. 1).

The combination with light is of particular interest when the aim is to produce hydrogen with microbial help. The standard MFC is unable to generate the power to overcome the overpotential of 0.135 V as needed to produce hydrogen under microbial electrolysis cell conditions [1]. The additional voltage comes from solar power, which is just high enough to cause hydrogen evolution, when a photobioanode and platinum cathode is used [2].

The usual MFC consists of a bioanode, which obtains its power from electrogenic microbes that adhere to anode surfaces and digest nutrients from aqueous solutions. The highest theoretical power calculated by Pocaznoi et al. from their experimental data was found to be 8.98 W/m^2 [3]. However, under real laboratory conditions MFCs do not generate such high values and are clearly lower, generally 1–3 W/m^2. One of the highest recorded powers with a microbial bioanode was 6.9 W/m^2 [4]. In recent years not much progress has been made in improving MFC's power output. Moreover, the scale-up is particularly challenging as many factors need to be studied to improve these MFC reactors. One approach to overcome this low power hurdle is to enhance the MFC with light. In a light enhanced MFC, both light and microbial powers are thought to combine as one adds to the other rising the voltage and power but there is a need for detailed research. Consequently, in such a combined setup more electricity can be produced and new applications become possible. These include more efficient wastewater plants [5], kitchen waste degradation [6] biofuel production [7] and even chemical synthesis [8]. Solar enhanced microbial fuel cells using photosynthetic microorganisms have been reviewed by several authors [9–13]. Apart from pure electricity production, other fuel generation has also become a subject of interest that has been covered by some reviews [14,15]. While cyanobacteria are thought of mostly as anodic microbes, microalgae are described to be functional in cathodes [16–18]. Conversely, the combination of photoelectric cell and microbial fuel cell technologies reviewed here is a newer subject that has hardly been described. It has to be kept in mind that there are many more possible MFC variants, such as for example the plant microbial fuel cell [19] that show that future research is possible and will address new and possibly unexpected special combinations.

This critical review presents and discusses combinations of photoelectrical cells and microbial fuel cells. It starts with an introduction of what a microbial fuel cell is, in order to provide some insight for newcomers to the field of solar bioelectric systems. The review then continues from a microbial fuel cell researcher's perspective with the idea that such bioelectric systems generate more power under solar light irradiation. The focus is then expanded to photoelectric anodes and cathodes that collaborate with microbes in general. Next is a review of photobiological systems based on microalgae and other

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Nomenclature

CB	conduction band
CEM	cation exchange membrane
DSSC	dye sensitized solar cell
E_F	Fermi level
FTO	F-doped tin oxide
HER	hydrogen evolution reaction
ITO	indium tin oxide
MEC	microbial electrolysis cell
MFC	microbial fuel cell
MR-1	manganese reducing (one oxidation state)
N719	ruthenium-dye
NHE	normal hydrogen electrode
NW	nanowire
Omc	outer membrane cytochrome
PEC	photo electric cell
P_{max}	power maximum
VB	valence band

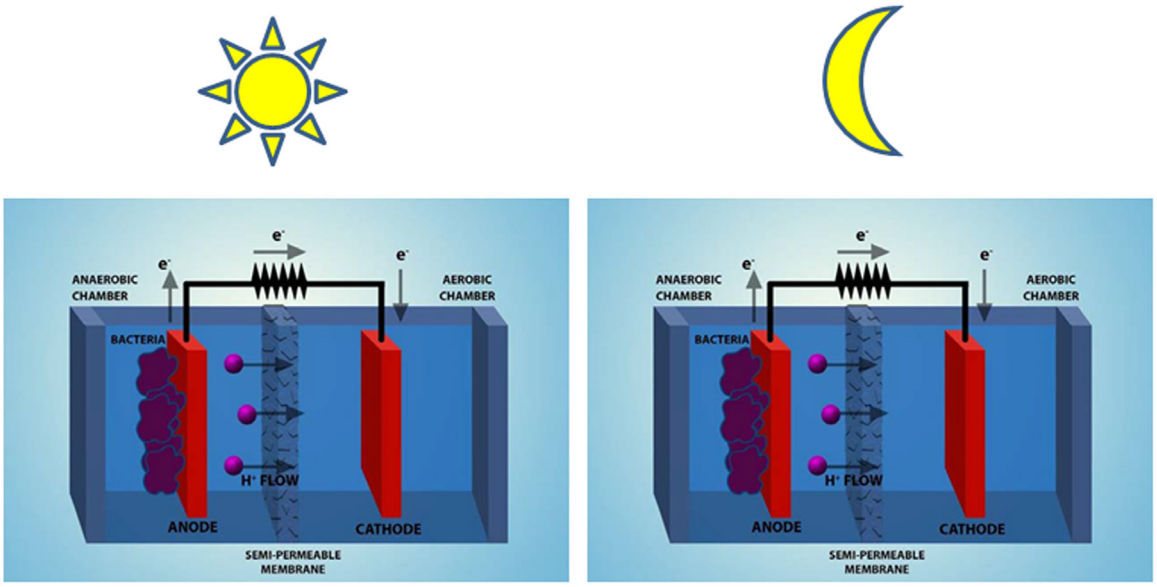

Fig. 1. Dual chambered microbial fuel cell (MFC). Left: irradiated by light on the anode or cathode or altogether (dark and light reactions). Right: MFC without light (only dark reactions) as in standard use. (Adapted from: [24], © creative commons).

photosynthetic microbes, and of MFCs interconnected with dye-sensitized solar cells. Finally, the history and future of Photo-MFC-PEC type reactor research is outlined.

1.2. The solar microbial fuel cell in a nutshell

A microbial fuel cell (MFC) is a bio-battery with an anode (negative pole) and a cathode (positive pole). It is comparable to the galvanic cell that students use in general chemistry laboratories to study the elements' potentials and how batteries work. The difference between MFCs and galvanic cells is that MFCs use microbes rather than chemicals in the anode. These microbes donate electrons instead of ready to use chemicals [20]. The liberated electrons then travel over the external circuit to the cathode as in a galvanic cell (Fig. 1, left side). At the same time an equal amount of protons are generated, which also pass to the cathode through a semi permeable membrane. In the cathode the electrons and protons react with oxygen to form water, the final waste product. A fascinating aspect of MFCs is that there are almost endless possibilities for variations based on their very simple battery setup. Several reviews provide more information on MFCs [21–24]. This review discusses one of these possible setups, the light enhanced MFC (Fig. 1, right side).

2. Photoelectrode microbial fuel cell

2.1. Microbial fuel cell with photobioanode

A photobioanode combines microbial and light power in the same electrode. The photobioanode is usually a bifunctional quadratic two-sided electrode [25]. One side, which is usually flat and covered by glass, is exposed to light and on the back or dark side the surface is in contact with electrogenic microbes. Generally, this electrode is a semiconductor as used in solar panels. When this semiconductor anode is irradiated electron holes are created and the microbes in the biofilm donate electrons to the just created electron holes. The idea is that the microbes enable a faster excitation rate for electrons from the valence band (VB) into the semiconductor's conduction band (CB) (Fig. 2). The solar irradiation equally increases the MFC's working potential. The capacity of the biofilm to supply electrons is a potential limitation. Other researchers have shown that the photobioanode can be split into two separate anodes to combine their power, resulting in an enhanced power overall [26].

Initially photobioanodes used in investigations were based on hematite nanowire attached to an FTO glass substrate. The glass protected side was illuminated and on the back side (dark reaction) the hematite layer was in contact with *Shewanella oneidensis* MR-1 bacteria biofilm [25] (Fig. 2). The overexpression of a D-lactate transporter in this microbe was recently performed to enhance electron donation [27]. This kind of photobioanode was tested over extended process times. To do so, the hematite surface exposed to the microbes was covered with a carbon layer, establishing an inert seal against water infiltration but to function as biointerphase surface. Carbon is typically the preferred electrode material for microbial adhesion in MFCs. With this advanced photobioanode the probability of iron leaching into the cultivation was considerably reduced [28]. In a similar approach, a hematite-stainless steel anode combination was produced and used. It improved the electron substitution to the holes in the hematite layer. Through the use of this kind of anode, another feature of photobioanodes became

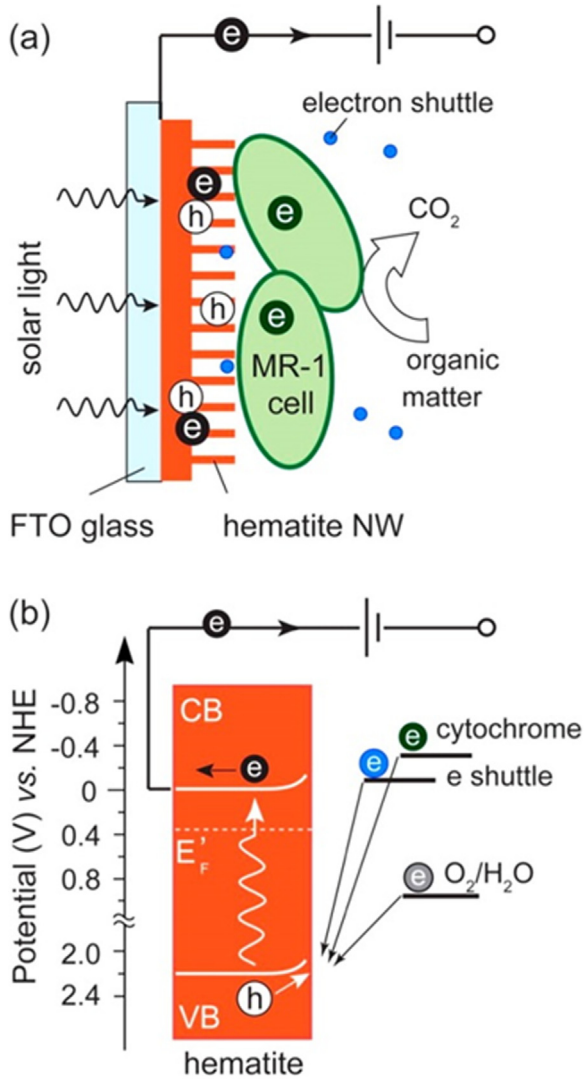

Fig. 2. A) Bifunctional photobioanode in microbial fuel cell. B) Energy diagram, promotion and delivery of electrons (e) from microbes into the semiconductor hematite. Electrons were promoted form the valence band (VB) into the conducting band (CB) at an accelerated speed in combination with electrogens (MR-1). Electron holes (h) were filled with microbial electrons (e). (Reprinted with permission from [25], copyright 2014, American Chemical Society).

apparent. Photobioanodes improved the biofilm thickness by enhancing respiration, caused by illumination, which accelerated the transfer of electrons from the microbes to electrodes, which is a wanted side effect. This is comparable to electrostimulation using a potentiostat [29]. Thicker biofilms are a welcome property because the anode's internal resistance drops as there is a greater source power from the MFC and higher currents are possible [30]. The most interesting aspect in this microbial electrolysis cell is that voltages are high enough to enable microbial electrolysis and hydrogen evolution. The hydrogen evolution reaction (HER) was also examined in more detail by splitting the photobioanode-MFC into a separate MFC and photo electric cell (PEC) in a separate MEC that nevertheless let them work together as shown by Li and coworkers [31]. Here the photoanode was not in contact with microbes or any other medium component. This reduces the danger of the hydrogen generating cathode becoming polluted. The pollution causes a particular problem when using waste containing soluble metals that migrate to the cathode and poison the surface reducing its activity for the HER [29]. Therefore the dual use of separated MFCs and PECs is a concept that has recently attracted more attention [31–33].

Another examined photobioanode material is titanium dioxide (TiO_2). Particles of this stable semiconductor were, for example, doped on macroporous carbon foam on one side of a quadratic surface. The backside of the sponge like carbon remained untouched and provided a large surface for microbial adhesion [34]. There was no clearly defined separation into a light exposed and the dark microbial side as in most other works. The microbes were therefore allowed to pass through the pores into the irradiated zone. How well the microbes survived in direct sun light was not examined in detail, but bacteria are usually destroyed on irradiated TiO_2 surfaces. This photocatalytic effect is described in detail in a comprehensive review [35]. The purpose of the aforementioned setup was to degrade 4-chlorophenols to detoxify polluted water using the principle of the photobioanode, which works more efficiently with microbial electron supply. This light enhanced MFC process improved the degradation 4-chlorophenols from 28% to 41% [34]. The concept of the photobioanode has also attracted interest from researchers who develop solar biosupercapacitors [36,37]. These biosupercapacitors are not directly comparable with microbial fuel cells and are not discussed further in this review. It may however, be of interest to follow this kind of investigation when working with photobioanodes.

2.2. Photocathode in microbial fuel cell to generate more electricity

Intuitively there could be the idea that more electricity is produced with an MFC using solar irradiation than without. This looks obvious until it becomes clear that most semiconductors are not very good conductors. Consequently the questions of what to do arises combining photocathodes and MFCs. Titanium dioxide (TiO_2) was one of the first photo sensitive materials used in photocathode MFCs. It absorbs UV-light in particular and is widely used for this property in sunscreen products. TiO_2 is a cheap mineral, called Rutile, and mined in diverse locations. It is an n-type semiconductor, which becomes a conductor above a certain light intensity. When coated on graphite and used in an MFC, its power improved 1.57 times, generating 12.03 W/m^3 [38]. TiO_2 used in an MFC showed that the band cap of TiO_2 can be reduced [39]. Another material for higher powers using solar light and MFCs is the photocatalytic active lithium-tantalat, which is also known for its water splitting properties [40]. It was used as a photocathode, delivering three times as much power (63 mW/m^3) when irradiated with a 500 W UV/Vis lamb in comparison to the dark reaction [41]. Photocatalytic copper indium sulfide ($CuInS_2$), is also known to be photocatalytically active and can generate hydrogen [42]. This $CuInS_2$ semiconductor was tested in flower like nano-structures. When used as a photocathode in a dual chambered MFC with Nafion membrane the electrical power of 0.108 mW/cm^2 was relatively close to that generated by a Pt/C electrode generated with 0.123 mW/cm^2 in the dark [43]. That it is possible to produce higher electrical powers was also shown by using microbial fuel cells to clean wastewater with a TiO_2 anode combination, which provided 1284 ± 20 $mW\,m^{-2}$ [44].

Research to date suggests that light has an influence on the power production of MFCs but the available data show that semiconductors often do not enable higher electrical power as they are bad conductors. Nevertheless, in the situations discussed here, powers increased between 1.5 and 3 times in Photo-MFCs. Yet, when compared to high density power, MFC experiments performed without light produce results that still seem below often cited reference values, for example the 500 W/m^3 that Ringeisen [45] and collaborators found in 2006 and which has become a widely accepted reference value. Another limitation is the reachable surface on an electrode by light beams. This is in contrast to microbial catalysis, which works in the dark where a whole volume of anodes participates in power generation.

2.3. Hydrogen from photocathode-microbial electrolysis cell

A photocathode is a means to increase the working potential in an MFC to a level where the hydrogen evolution reaction becomes spontaneous. According to the available literature, this is the primary idea to

date of this combination. Hydrogen evolution in a "microbial electrolysis cell" (MEC) is a non-spontaneous reaction and not possible with microbial power alone as biological working potentials are typically below 0.5 V. Nevertheless MEC driven hydrogen generation is, in theory, possible well below the power needs of standard water electrolysis using pure water. The overpotential in an MEC equipped with a platinum cathode is only 0.135 V before the reaction becomes spontaneous [1]. The voltage needed for effective hydrogen evolution is somewhat higher at about 0.4 V. However, the biocatalysis supported process is only possible with convenient metabolites such as acetate. When these are not available, the overpotential is larger and can mount, in the worst case, to 1.23 V, which is the overpotential in water electrolysis. MEC based hydrogen generation is therefore a challenge and a review on the state of the art is available [46].

Solar supported microbial electrolysis is of industrial interest as it generates hydrogen with the low applied voltage and obtained hydrogen is, in theory, cheaper than most other comparable processes. More research is needed to explore the question as to whether or not other materials are also of interest for this process. To date, only a small number of articles have been published on light-supported MECs [47].

Diverse photocatalytic materials enable the hydrogen evolution reaction (HER) [48]. A semiconductor with a narrow band gap and specific properties enabling the hydrogen evolution reaction is required (Fig. 3), however, only a small number of electrode materials with such properties have been employed in photocathode-MECs to date.

TiO_2 nanorods are a catalytic surface used for hydrogen evolution in a photocathode-MEC. In this study, TiO_2 particles were deposited on fluorine doped tin oxide (FTO) coated glass. With appropriate light irradiation, 2.2 $\mu L\, h^{-1}\, cm^{-2}$ of hydrogen gas formation was possible [49]. Again, the power was only 6 mW/m^2 due to an internal resistance of 10 kΩ. The light used was generated by a 300 W Xenon lamp. The low power was routed in the poor conductivity, which is a known problem for semiconductors such as TiO_2.

The stability of semiconductor coatings also matters in view of a real-world application, rather than just best performance under laboratory conditions. The stability of the coating was examined for TiO_2 and showed reasonable activity. Its coating was realized on indium tin oxide (ITO) surfaces and carbon on paper. While TiO_2 is rather stable, its coating on other materials poses a critical challenge as it is difficult to ensure its stability. In the formerly described experiment, both coatings remained in place during 200 h of uder the irradiation with a 30 W mercury lamp [50].

A somewhat more effective photocathode material than TiO_2 is cuprous oxide (Cu_2O), which is a p-type semiconductor with a narrower band cap than the wide band-cap TiO_2 (Fig. 3) [51]. Cu_2O was used in an MEC in the form of nanowires deposited on copper foil [52]. The irradiation with white light caused powers 1.25 times higher than with the dark process [53]. This hydrogen evolution reaction was performed

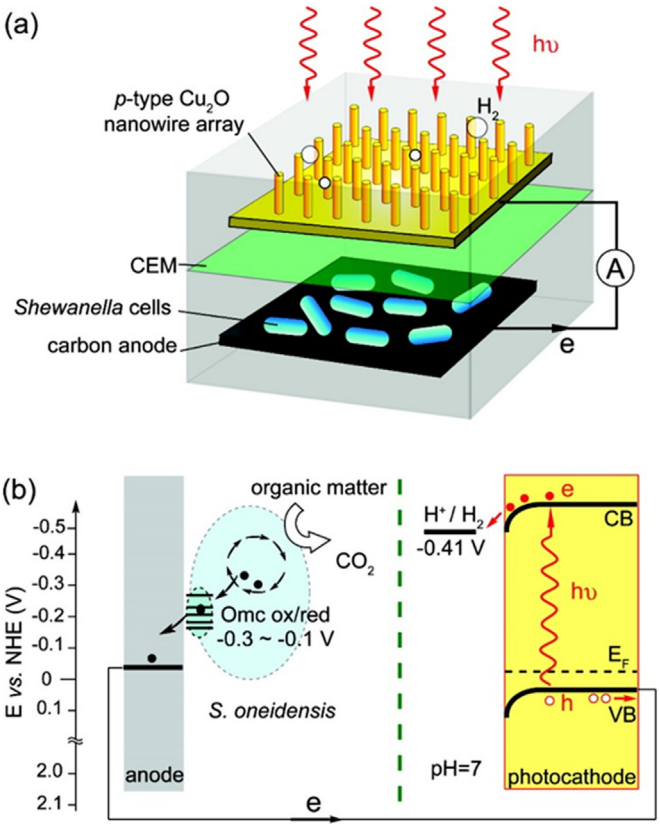

Fig. 4. Cupric oxide (Cu_2O) in photocathode-MFC. A) The dual-chamber light photocathode-MFC becomes a photocathode microbial electrolysis cell. (b) Electrons (black dots) from *Shewanella oneidensis* MR-1 pass to the anode and are transported through the external circuit into the photocathode and were then promoted by light from the valence band (VB) into the conduction band (CB). (Reprinted with permission from [54] Copyright 2010 American Chemical Society).

with moderate irradiation power of 20 mW/cm^2 [54] (Fig. 4). The experimental results confirmed that cuprous oxide is a more efficient photocatalyst than TiO_2 in Photocathode-MECs [55]. However, the disadvantage of Cu_2O over TiO_2 is the higher toxicity for most microbes and it is less robust [56]. Many researchers have tried to reinforce Cu_2O electrodes. To do so, other elements were added to obtain a composite material, which provided stability and did not leach into the electrolyte [57]. This improved stability was realized by spin-coating NiO_x on a Cu_2O cathode, resulting in a Cu_2O/NiO_x composite surface [58]. With the obtained NiO_x film on the electrode surface, it outperformed the unmodified Cu_2O surface in terms of stability clearly. With this kind of

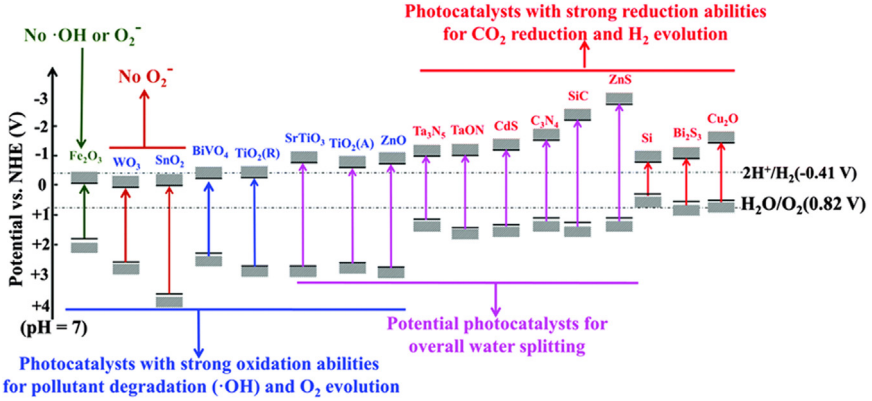

Fig. 3. Photocatalysts with band gaps for possible application in MECs (values for pH = 7 in aqueous solutions). (Reprinted with permission from [55] Copyright © 2016, Royal Society of Chemistry).

coating Liang [58] produced 5.09 μL h^{-1} cm^{-2} of hydrogen, which is a productivity rate 2.5 times higher than that with TiO_2, but using 0.2 V of applied voltage from a potentiostat in addition to light use. There are not many other composite semi-conducting materials with a even smaller band gap than Cu_2O. But other materials, such as silicon (Si), have an even lower value (Fig. 3). More of such materials are known and many contain Cd and Pb, which are in contrast potentially toxic toward microbes if they leach into the medium. Leachates are also problematic when lost to the environment and some researchers addressed this problem, employing less toxic composite materials such as $CuInS_2$. This composite also provided a small band-gap of 1.45 eV and high excitation coefficients using visible light [59]. MoS_3 is another novel, promising photoactive material, which was obtained by heating MoS_2 and has also been used in conventional MECs [60]. MoS_3 was deposited on silicon nanowires (SINW) and upon irradiation good quantities of hydrogen were obtained [61]. MoS_3 is of applied interest as it is cheap, meaning it could reduce the cost of photocatalytic electrodes, and is probably not very toxic. The lower price is based on the fact that sulfur is cheap and that molybdenum an abundant element in the Earth's crust. In a Photo-MEC, the MoS_3 photocathode was 53% more effective than a comparable TiO_2 electrode [62]. Light caused measurable currents and resulted in a power maxima of ~70 mW/m^2. Conversely, under dark conditions, almost no current was detected resulting in a power maxima of ~10 mW/m^2. MoS_3's photo activity can be adjusted by varying the MoS_2 content, what is of interest in generating electricity rather than hydrogen. [63].

The photocathode-MFC was also designed to solve problems in sewage works. For example, TiO_2 photocathodes degrade azo dyes. Textile coloring dyes are used in large quantities in the textile industry and pollute wastewater effluents. Many of these molecules are stable and difficult to degrade fully using wastewater microbes. Photocathode-MFCs degrade such dyes while also producing electricity, which worked well by doping the TiO_2/Ti anode with Ag using it as biocathode [64]. In a single cell photocathode-MFC the degradation not only resulted in electricity but also in a notable co-generation of hydrogen [65].

3. Photovoltaic microbial fuel cell

3.1. Dye sensitized solar cell supported microbial fuel cell

There are non-transparent and transparent solar panels and both can be combined with MFCs and MECs. To date, MFC researchers have primarily given their focus to the glass based transparent solar panels. The reason is probably due to their low open circuit voltages (0.1 and 0.8 V) that is adjustable to needed voltages in MFCs and MECs to enhance their power [66]. For more information on DSSC research, see Grätzel's review, which also includes a section on the historic background of this subject [67]. Hagfeldt et al. also provide a detailed review [68]. The open circuit potential of a MFC cell hardly surpasses 0.9 V and is often clearly lower [69]. MFCs and DSSC are therefore an interesting tandem system that enables stable current or hydrogen generation (Fig. 5). Such a combination of an MFC with a rutheniumdye DSSC was exposed to a 40 mW/cm^2 lamp by Ajayi. As a result hydrogen evolved with 78% of efficiency [70]. This is a very good performance, but it is noteworthy that acetate was used as the electron and proton source. DSSC voltages equally enable the HER in a bioelectric system with less expensive cathodes to replace costly platinum, which is currently used in many MECs. Chae and coworkers [71] showed the potential of this combination in a DSSC-MEC using a carbon felt cathode. As expected, this cathode underperformed in the dark reaction when less than 0.7 V was applied, but became equally productive as a platinum loaded carbon felt cathode when a voltage above this threshold was applied. The efficiency reached 77% with the carbon felt electrode and was slightly less efficient than the Pt-cathode with 82% [71]. The solar cell (DSSC) surface needed in prospective applications is relatively small in comparison to the size of an MFC [72]. The use of solar cells (DSSC) not only enables the HER under microbial electrolysis conditions, but also produces hydrogen from microbial solutions that are bad proton and electron donors and resemble, to some extent, pure water. More research is needed to show what happens if the microbial activity is insufficient in comparision to excessive solar light. Little is known about the ability of microbial biofilms to sustain and survive the excessive demand for metabolites which provide electrons and protons such as acetate. The microbial electrolysis cell is under these conditions de facto no longer a typical microbial electrolysis cell. Nevertheless, it is expected that microbes contribute to and reduce the overpotential for the HER in DSSC-MECs. Such research was performed with activated sludge where no hydrogen evolved but more biogas was produced [73].

3.2. Microbes within dye sensitized solar cell used as microbial fuel cells

The use of living microbes in a dye sensitized solar cell (DSSC) has been largely untreated. However, the research performed so far has addressed an applied problem [74]. These researchers used wastewater and the DSSC setting to accelerate wastewater purification. Their idea was to use the wastewater as an electrolyte in order to substitute I^-/I_3^-, which is usually employed in DSSCs as a mediator (Fig. 6). Nanostructured plasmonic Ag/AgCl on chiral TiO_2 nanofibers were employed as the photo-anode. The cathode changed its property during the experiment and became covered with copper [74]. While there are only

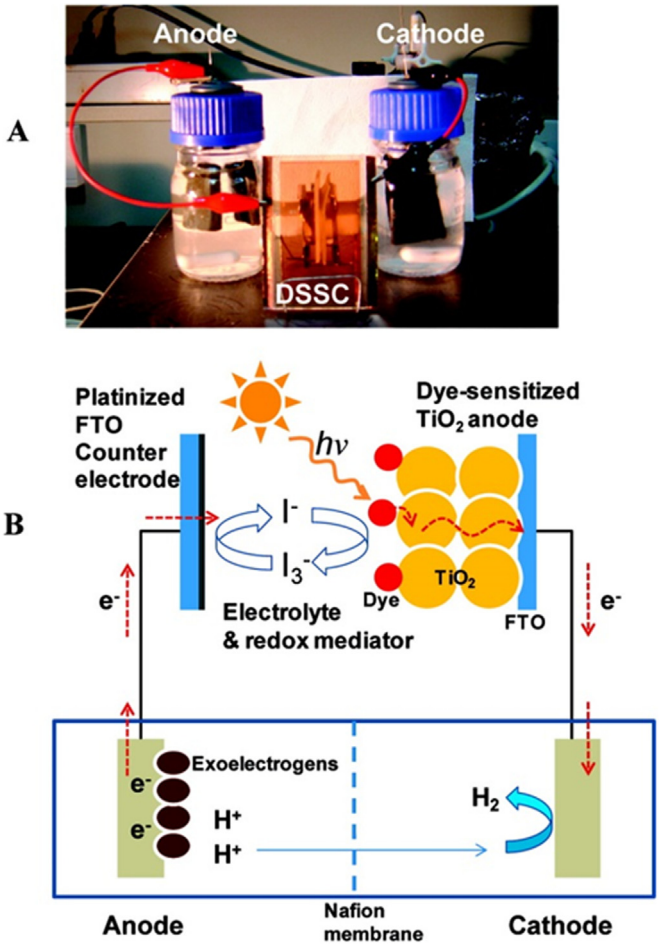

Fig. 5. Dye Sensitized Solar Cell (DSSC) powered microbial electrolysis cell (MEC) for hydrogen generation. A) Photograph with an external DSSC as power source and the MEC in the back. B) Electrons were generated with electrogens and transported to the DSSC and promoted by light into the valence band and then transferred to the cathode in the MEC generating hydrogen (H_2). (Reprinted with permission from [71] Copyright 2009 American Chemical Society).

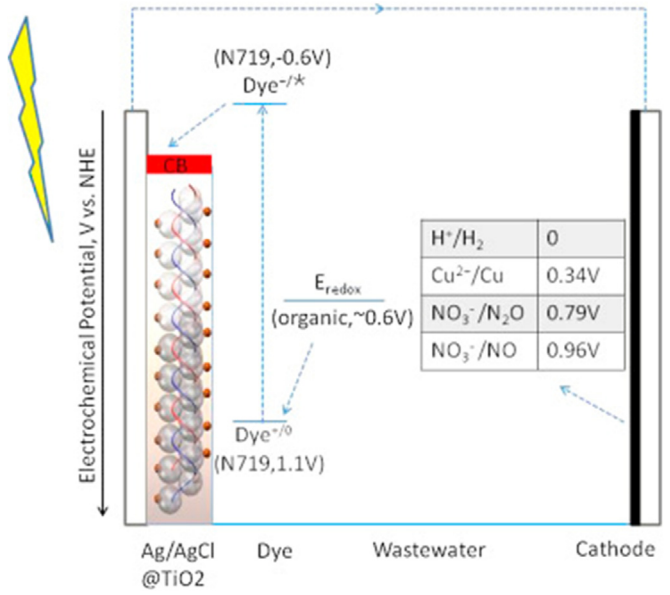

Fig. 6. DSSC inspired Photo-MFC: The anode (left) is made from plasmonic Ag/AgCl@ chiral TiO_2 nanofibers. The electrolyte in the cell was wastewater. And the cathode was thought to release hydrogen [74] (Reprinted with permission, Copyright © 2014 Elsevier B.V. all rights reserved).

few reports on the use of wastewater and contained microbes, there is more known about the use of biological sensitizers. Most are about plants, although some deal with components extracted from microbes [75,76].

4. Photosynthetic microbial fuel cell

4.1. Microalgae-microbial fuel cells

Microalgae are equally microbes, however algae use in an MFC looks exceptional, and therefore these MFCs are called Microalgae-MFCs, both here and elsewhere [77]. There are two major axes of algae use under investigation by a number of researchers. The first is microalgae mass as a valuable substrate for generating bioelectricity in the dark reaction in an MFC with electrogenic microbes, which is comprehensively described in a recent review [16]. The more interesting way of using microalgae is as a biocatalyst in the MFC's cathode. There it produces oxygen, biomass and chemicals. The even more exciting use of microalgae in MFCs is to combine both kinds of microalgae-MFCs enabling a cycling microalgae-MFC (Fig. 7).

The primary reason for using microalgae in an MFC is to generate metabolic oxygen and release it into the aqueous media of the cathode to generate electricity. Microalgae in MFC cathodes are of particular interest as it replaces oxygen bubbling. The algae free non-biotic aqueous oxygen cathode in MFCs is often cited as a limiting component in an MFC and better solutions, where no stirring is needed, for example, have been looked for [78]. Also buffer and membrane free microalgae MFC use have also been examined in this context [79]. Up to now, the most popular solution in this respect is the air-oxygen cathode (non-algae based) [80]. However, it remains unclear if this will be the winning solution in the future as exact oxygen dosing is important in order to avoid the destruction of the anodic electrogens such as *Geobacter*, which are very sensitive to oxygen.

Finally, from an integrative perspective, the microalgae-MFC enables low cost aeration while producing biomass, and, with the appropriate algae, chemical products as well. If this can be accomplished it would translate into reduced operational costs for electricity generation [81].

One of the most compelling arguments for the microalgae-MFC is that all nutrients can be reused in the same MFC (Fig. 7). This means that a microalgae-MFC could transform CO_2 into fuel and other alkanes, while the MFC functions independently and indefinitely. Repurchasing fertilizers (Nitrogen, Phosphorous, Potassium and other nutrients) is not required because the remaining salts are reused as fertilizers, see also the review by Lee et al. [17].

Another key question for microalgae-MFCs is the availability of cheap CO_2. Although CO_2 is accumulating in the atmosphere, its concentration is very low and the recovery from the air is an energy intensive task. Yet the MFCs' anode is a source of CO_2, which is a possible rich source of this gas as most MFCs are not very coulomb efficient. There is a range of biotechnological processes that can be realized in the MFCs' anode and the exhaust of concentrated non-toxic CO_2 gases can be guided to the cathode.

Bioethanol production from corn, sugar cane and wine making waste are examples of processes that release good quantities of CO_2. Powell and coworkers studied the capture of CO_2 from such bioethanol plants with microalgae. In their study the CO_2 was guided from the

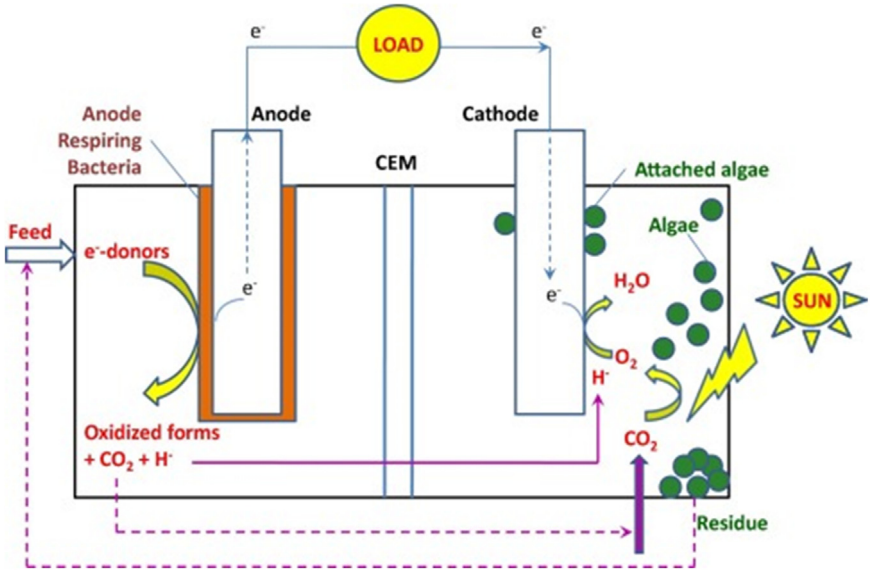

Fig. 7. Microalgae–microbial fuel cell. Here shown as a circular system. Reuse of cathodic residues (right side) in the anode (left side); it functions by design for unlimited time and only needs to be supplemented by H_2O, CO_2 and light to generate electricity and chemicals [17] (Reprinted with permission, Copyright © 2015 Elsevier B.V. all rights reserved).

anode into a cathode containing microalgae. The evolving oxygen was reduced in-situ with anodic electrons and protons [82]. The success of this process is partly guaranteed as the CO_2 feed is richer than needed because this yeast MFC generates relatively low quantities of electrons. This is because electricity generation is not realized at the expense of ethanol production, which is harvested as an energy vector. In fact electrons very likely originate from side reactions. This is the case when working with *Saccharomyces cerevisiae w*here just generated ethanol is conserved by the Crabtree effect. Here the oxidation and reduction are in equilibrium and even the presence of oxygen does not change this [83]. This Carbtree effect was also observed in an MFC, as shown with a 10-l scale triple stack MFC. The inertness for further ethanol oxidation remains as long as glucose concentrations are high enough [84]. Another potentially large-scale source of biogenic CO_2 are municipal wastewater treatment plants. Here in particular the not yet realized large scale anaerobic MFC is a potential source of enriched CO_2 gas exhaust useful for a microalgae-cathode to generate electricity.

Yet, the microalgae mass could be used as seasonal energy storage that is digestible in the MFC to generate electricity. Based on the reusability of algae mass, the reactor enhance from a conceptional point of view energy production in wastewater treatment plants [77,85].

All in all, the current challenge is the capacity of the microalgae-MFC to function as a self-sustained entity.

The alga based oxygen supply works quite effectively, as has been shown with *Scenedesmus obliquus*. Here the microalgae-cathode outperformed mechanical aeration with 32% efficiency [86]. A problem are also here cations that accumulate over time in the catholyte which need to be removed to maintain the cathode functional [87]. In addition, these cations should be recycled. In conclusion, the microalgae cathode is not yet proven as an equally good or better cathode than the far better known air-oxygen cathode [88].

4.2. Electrogenic microalgae-MFC

Electrogenic microalgae are rare species and were just recently discovered to be of interest in Photobiological-MFCs. Ongoing discovery oriented explorative research is being conducted in this novel field of MFC research. Electrogenic microalgae are used in the anode as electron donators like any other electrogenic bacteria. The anodic use of such microalgae is a surprising possibility as they also produce oxygen. This causes a problem for the Photobiological-MFC as oxygen is an electron sink. O_2 is generated by the same microalgae and its coulombic efficiency is in danger of being reduced as oxygen leads to the aforementioned self-consumption of electrons. Therefore, it does not seem like a good idea to produce electricity with electrogenic microalgae. One of these electrogenic microalgae is *Chlorella pyrenoidosa*, which generated a P_{max} of 30.15 mW/m^2 in a Photobiological-MFC using a potassium ferricyanide solution as catholyte [89]. To verify that electrons originated from *C. pyrenoidosa*, the light intensity was varied and current variations resulted. The currents were in the micro ampere range and absolute values. The effectiveness of these eletrogenic microalgae is, however, not easy to assess.

To advance the discovery of electrogenic microalgae, researchers developed a sediment type Photo-MFC for screening. It was filled with benthic soil samples from marine and other environments in New Zealand and the Antarctic [90]. Electrogenic microalgae, as well as cyanobacteria, became attached to the anode under light irradiation. The benthic *Paulschulzia pseudovolvox* algae was isolated and examined for electrogenic properties, which became measurable after one month of cultivation. The open circuit potential rose under the presence of light (Fig. 8) but electric power maxima were rather small. However, this analysis was only based on absolute data. The results can be compared to almost isolating *Chlorella vulgaris*, which is nonelectrogenic with only 14 μW/m^2 [91]. This value is several magnitudes below cyanobacteria species found equally in these benthic samples [92].

4.3. Microbial fuel cells with photosynthetic bacteria

Photosynthetic bacteria in MFCs are used in the anode but possibly also in the cathode. The most interesting feature is that photosynthetic bacteria function with carbon electrodes and no modification to them is needed. This is in contrast to inorganic material based photoelectrodes, where the stability and poisoning of the surfaces are issues. The use of photosynthetic bacteria in MFCs has not been widely investigated. This could, however, change, as there are many photosynthetic bacteria, including the *Cyanobacteria* and, *Heliobacteria* [93]. Many are electrogenic such as *Cyanobacteria*, which generate electricity upon light irradiation [94]. In many instances the photosynthetic bacteria were found to be part of a co-culture with heterotrophic bacteria.

A key issue with such consortia is whether they are preferable for the anode or the cathode because photosynthesis generates oxygen and therefore they are equally useful in the MFC cathode as in the anode. But as previously mentioned, the electrogenic faculty of cyanobacteria is a good reason to consider them electron donators in the anode. Xing and coworkers investigated such a consortium of photosynthetic microbes, illuminating the anodes while feeding them glucose. The power increased by 8–10% in comparison to the dark reaction. Using acetate, the power density increased even by 34%. This is a well-known boost effect known for electrogenic microbes, which reveals that a convenient nutrient spikes electron transfer also in a Photobacteria-MFC. A microbiome analysis showed that *Rhodopseudomonas palustris* was the dominant photosynthetic bacterium and the dissimilatory iron reducing *Geobacter sulfurreducens* [95,96]. Another photosynthetic microbe is *Rhodopseudomonas palustris* G11. It was isolated from activated sludge and then cultivated as a pure culture in the dark. It accumulated polyphosphates and poly-β-hydroxybutirate and these microbes were then transferred to photo-MFCs to produce electricity by digesting accumulated polyphosphates and poly-β-hydroxylbutyrate [97]. The release of the stored energy only caused low powers, however the process was enhanced using light to stimulate power generation by a factor of 2 reaching up to 0.15 mW/m^2.

Another photo bacterium is *Synechocystis sp*., which was examined by Liu et al., [98]. The photosynthetic electron donation capacity of this bacterium was assessed on a microchip allowing electrical and microscopic observations simultaneously. These experiments were performed under an important external resistance of 770 kΩ as the electric phenomenon was expected to be weak. The use of *Synechocystis* sp. resulted in a current of 0.12 μA/cm^2. This weak electric effectiveness contrasted with the comparatively powerful *Shewanella oeidensis* MR-1, which generated a 12.5 times higher current (1.5 μA/cm^2). Yet by all accounts, the most striking observation was that the synergistic co-generation of the current by the co-cultivation of the two microbes led to a

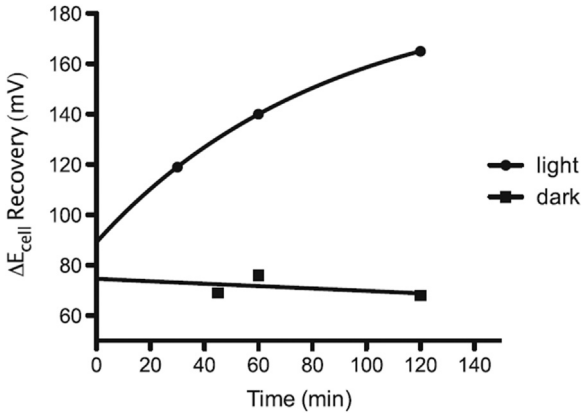

Fig. 8. Examination of the electrogenic *Paulschulzia pseudovolvox* under open circuit potential conditions. With light, the potential (ΔE_{cell}) rose and no change was observed in dark conditions [90] (Reprinted with permission, Copyright © 2013, Springer Science +Business Media Dordrecht).

surprisingly elevated current of 8 μA/cm^2 [98]. It was already known that co-cultures eventually outperform pure MFC cultivations for photosynthetic microbial mixtures *Chlamydomonas* and *Geobacter* [99]. Badalamenti also found that the co-culture of phototrophic *Chlorobium* and the non-phototrophic *Geobacter* was a prerequisite for measurable photosynthetic currents [100]. To understand the full potential of phototrophic co-cultures, more research is needed.

4.4. Light quality for microalgae and photobacteria microbial fuel cells

In comparison to non-biotic photoelectrodes, microbes, in most cases, are less resistant under light irradiation than most photomaterials. This is not only true for applied powers but also specific wavelengths. In a first assumption the wavelengths should correspond fully or partly to the solar light spectrum with comparable intensity as it reaches the Earth's surface. In fact many kinds of light sources were used in microalgae MFC investigations. Several studies show that light quality is a very important factor for microalgae. This is certainly also the case for photoactive bacteria but almost no data was found concerning their use in MFCs. Here, the more general literature provides indications about the appropriateness of light sources for photosynthetic bacteria. For microalgae, more data is available about effective power generation under light influence in Photo-MFCs. In almost all cases microalgae were exposed to light of specific visible light bands. Although the whole visible spectrum could be used, the use of specific light bands is of interest as they trigged or suppressed pigment generation, the concentration of which increased or limited the MFC's performance [101].

As previously mentioned, the light intensity influenced microalgae's growth rate. But there are other factors, such as their attachment to the cathode and the planktonic density, that need to be considered to understand the light intensities' impact on current production. Most of these challenges are very much in line with data from heterotrophic microalgae cultivation in photo-bioreactors. An important fact is that inadequate light quality limited algae growth, which will impact power generation [102]. This restriction was in many, if not in all, cases reached much earlier than with non-biotic photo electrode materials because the later are more robust. The light sources described for microalgae-MFC investigations are often not very powerful. This means their irradiation energy is well below the average solar power of 136 mW/cm^2 that reaches the Earth's surface [103]. However, reported data are often not comparable among each other as there are no field specific standards, which is not only a problem in Photobiological-MFC research but a general issue with MFCs [104]. Therefore, most researchers referenced experimental results to blank runs. The following discussion is conducted based on the premise that data in itself is conclusive, while comparisons across the field are, in most cases, only of a qualitative nature.

In the following section a number of research results are highlighted, demonstrating the importance of the quality of the light in use. For example, Juang [105] and coworkers examined the impact of four different fluorescent lamps on microalgae consortia with two dominant genera. When doubling the irradiation power of a 6 W lamp with a 12 W lamp, a minor power increase 0.1 mW/m^2 (~5%) resulted. By further increasing the fluorescent light's power using a 18 W and 26 W lamp, a power drop set in and the MFC lost up to 50% of its power [105] (Fig. 9). A side effect of the more intense light here was a temperature rise in the microalgae cultivation. Higher temperatures favor microalgae growth to some extent. An irradiation threshold for maximal power generation with a microalgae-MFC was observed when using a

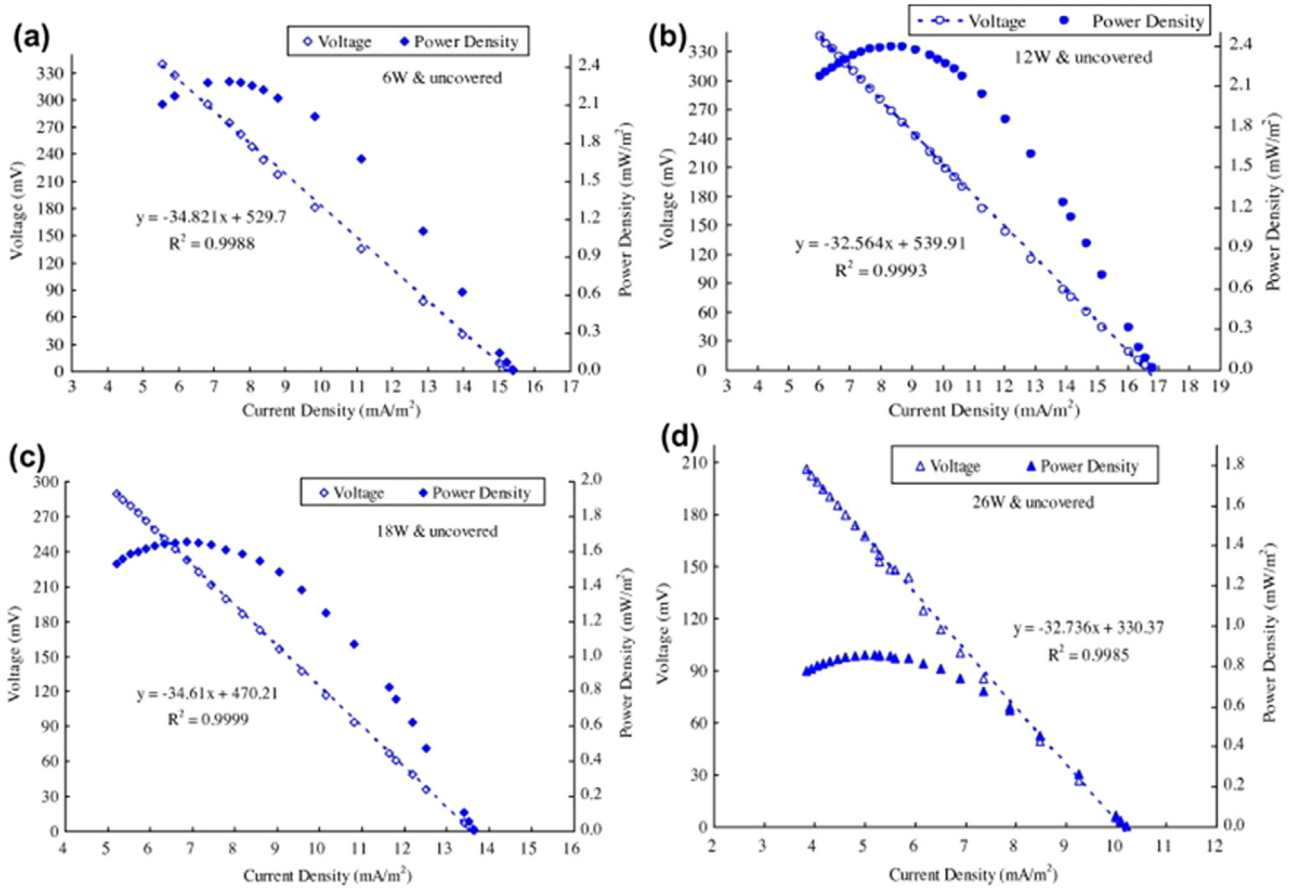

Fig. 9. Light intensity and related power maxima with microalgae-MFC. Changing from a 6 W lamp (a) to a 12 W lamp (b) the power increased slightly. But with higher intensities power maxima declined (c and d) [105] (Reprinted with permission Copyright © 2015 Elsevier B.V. all rights reserved).

pure microalgae culture with *Desmodesmus* sp. A8 [106]. In this investigation the quantity of dissolved oxygen was closely monitored to ensure sufficient high concentration. The MFC powers followed here the light intensity, again reaching an optimum before declining. In general, moderate light intensity enabled well performing MFCs, and, if dosed appropriately, MFC-power reached an optimum. *Chlorella vulgaris* was used relatively often for light enhanced MFCs [107,108] and when employed with low power fluorescent light it showed a steady increase from 26 μE/(m^2 s) to 96 μE/(m^2 s), improving power by a factor of 6–62.7 mW/m^2 [109].

LED lamps are another low power light source and of particular interest as the light's color (band width) is easily changed. Lan and coworkers [110] investigated the potential of LED light with MFCs. A LED irradiated microalgae-MFC generated more power with red than with blue light when *Chalmydomonas reinhardtii* was used [110]. The obtained power depended on the light's intensity, which increased from 300 lx to 900 lx, achieving MFC power of 12.94 mW/m^2. In all this work the microalgae-MFC generated, on average, far less power than a standard cathode. Although the concept is compelling, more research is needed to understand how the existing shortcomings can be altered to produce higher power.

5. The photosynthetic microbial fuel cell for fuel and chemical production

Photosynthesis is used here as a metaphor for out of the box thinking. Photo microbial fuel cells are useful in a much broader sense.

A solar panel not only enables electricity generation but also the production of goods. In this respect cars, houses and consumer goods can be produced by solar light. It is then a kind of artificial photosynthesis. This idea has also reached microbial fuel cells with the possibility of generating substances such as bulk chemicals, fuels and specialties from CO_2 and water, powered with solar light, which was detailed in an editorial by Schröder [111] (Fig. 10). Methanisation by bioelectrocatalysis is an example of such a solar process. This method which is already running on a lab scale using a potentiostate [112]. There are also carbon-carbon bond forming microbes, which convert CO_2 into acetic acid and other compounds. These microbes receive electrons directly from the cathode and no intermediate hydrogen is generated [8]. The prospect of generating longer hydrocarbon chains with this technology using solar light is compelling.

6. Historical background and future perspectives

The history and future of Photo-MFCs is described here from an MFC perspective. PEC type systems are not comprehensively covered in this review. Microbial fuel cells are often perceived as a very recent development. However, there is Potter's foundational work about MFCs published in 1911 [113] and forgotten until Davis and Yarbrough rediscovered it in 1962 [114]. 20 years later, in the 1980s, Bennetto conducted a series of investigations [115]. These researchers used none-electrogenic bacteria requiring mediators, which limited the usefulness of those MFCs. The discovery of electrogenic microbes in the 1990s, such as *Shewanella oneidensis* MR-1 [116] and *Geobacter metallireducens* [117], changed the future of MFCs as direct electron transfer became possible. This has led to a notable increase in research efforts and also in publications (since 2003). But MFCs continued to be known as notoriously weak electricity generators, which led to the idea of enhancing MFC power by photosynthetic bacteria [118]. A next other approach to enhance power was to combine an MFC with a PEC as reported by Chiao et al. in 2006 [119]. Beside photosynthetic bacteria, the use of algae as oxygen suppliers in the cathode was another rather compelling setup [82], which due to its simplicity attracted a number of researchers. With the increase of activities in MFC research, the microbial electrolysis cell also came into the spotlight, generating hydrogen instead of electricity with the same setup [120]. This led to the integration of photobioanodes and photocathodes [23,25,54] which became a rather interesting concept for producing hydrogen.

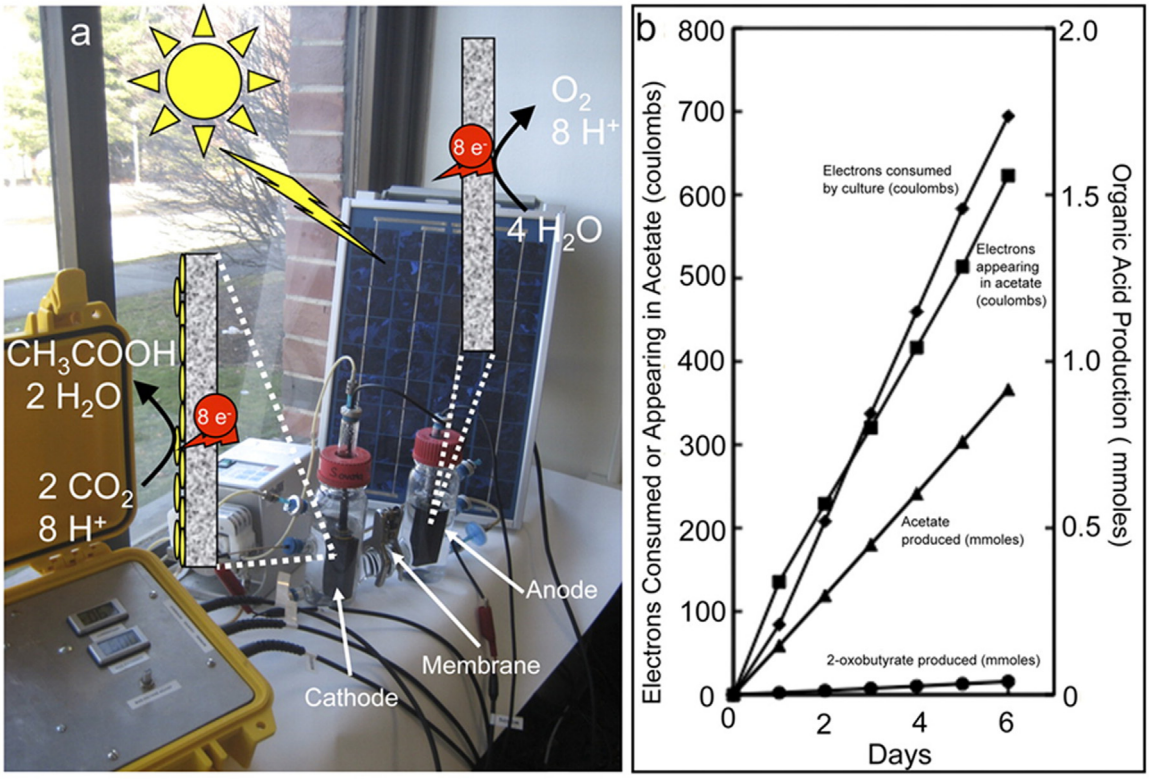

Fig. 10. Light enhanced MFC with solar panel as power supply. *S. ovata* were supplied with electrons, protons and power to generate acetic acid. The solar panel here was from silicon. The anode contained an aqueous solution but hosted microbes for electron and proton generation. (Copyright © 2010 Nevin et al. [8]).

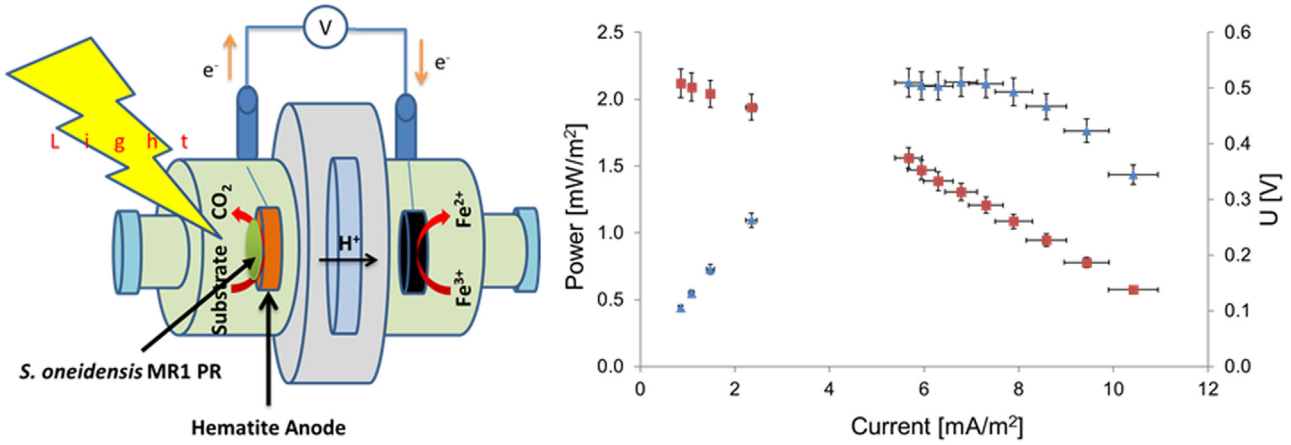

Fig. 11. Left: MFC-PEC hybrid reactor polarized containing *Shewanella oneidensis* MR-1 PR (proteorhodopsin) as biofilm on hematite anode exposed to solar light. Right: Voltage-current and power curves using this biofilm-hematite anode. The anolyte was supplemented with 10 μM retinal to enable light induced proton pumping by membrane bound PR.

The future of light-supported bioelectric systems is beside basic research also about the integration of already known components to such systems. On the biological side, discovery and engineering research for new photobiological bacteria with electrogenic properties is being conducted. There are easy to use newly developed detection systems to discover photosynthetic electrogenic bacteria [86]. The use of genetically engineered enhanced light-sensitive electrogens was examined by Gralnick using a *Shewanella oneidensis* MR-1 PR with proteorhodopsin in the outer cell membrane [121]. These microbes showed in connection with the semiconductor hematite a current cap when polarized. This resulted also in 1.5 times higher current after this cap than with unmodified *Shewanella oneidensis* MR-1 as reference. And a 1.73 times higher current using solar light than in the dark reaction with the modified *Shewanella* (Fig. 11) [122]. More research will be conducted with directly irradiated biofilm MFC-PEC hybrids. The development of new semiconductors with rather small band gaps is another desirable objective as it will lead to the expected increase of powers in MFC-PEC type reactors.

7. Conclusions

Combining photoelectric cells and microbial fuel cells facilitates the hydrogen evolution reaction. In theory, light-enhanced microbial fuel cells generate more electrical power than it is possible with the usual MFCs. However, to date, electricity production is not outperforming the dark process and remains an unresolved challenge where more research is required. Many photoelectrode designs were effectively combined with microbes, and synergistic effects are possible. The algae cathode has been the most thoroughly researched so far and is of considerable interest as it corresponds to the idea of a cycling renewable energy source. In addition to electricity, it also produces biomass that is later combusted in the same setup to generate electricity. It does not require fertilizer, but rather CO_2, water and light. The systems was also used for dye degradation and waste water cleaning while generating electricity. The combination of solar photovoltaic cells with standard microbial fuel cells was also possible where dye-sensitized solar cells in particular have attracted interest. And finally, Photo-MFCs should also be used in bioelectrofuel generation - a very novel research direction.

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