

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/m² [3]. However, under real laboratory conditions MFCs do not generate such high values and are clearly lower, generally 1–3 W/m². One of the highest recorded powers with a microbial bioanode was 6.9 W/m² [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 photo-electrical 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

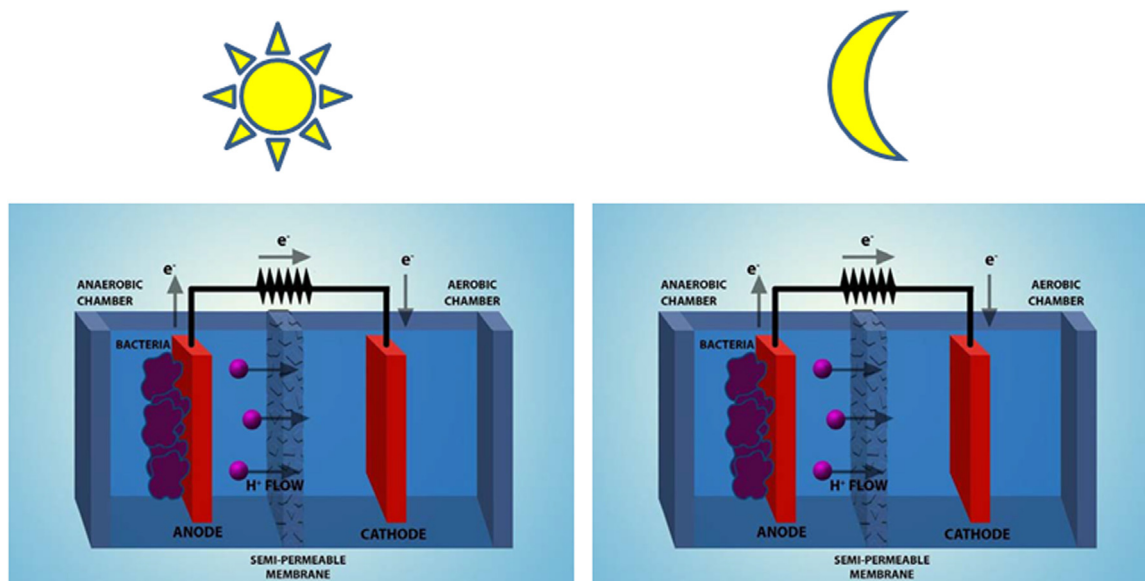


Fig. 1. Dual chambered microbial fuel cell (MFC). Left: irradiated by light on the anode or cathode or altogether (dark and light reactions). Right: MFC without light (only dark reactions) as in standard use. (Adapted from: [24], © creative commons).

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 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

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