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# Exoelectrogenic Activity of a Green Microalgae, *Chlorella vulgaris*, in a Bio-Photovoltaic Cells (BPVs)

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Bio-photovoltaic cells (BPVs) are a new photo-bio-electrochemical technology for harnessing solar energy using the photosynthetic activity of autotrophic organisms. This is a new technology for the production of sustainable and "clean" energy.
Currently power outputs from BPVs are generally low and suffer from scarce efficiencies. However, a better understanding of the electrochemical interactions between the autotrophic microorganisms and conductive materials will be likely to lead to increased power yields. In the current study, the green microalgae *Chlorella vulgaris* was investigated for exoelectrogenic activity.
To assess the exoelectrogenic activity of *C. vulgaris* a particular bio-photovoltaic cell was designed and built. The most important element is represented by the electrode configuration, based on inexpensive materials, with the anode immersed in the cultural broth and the cathode exposed to the atmosphere. This configuration represents a very interesting simplification for the cell design, furthermore allowing a simple illumination of the algal culture via a light source positioned above the cell, perpendicular to the electrode surface.
This new kind of bioelectrochemical system does not need organic substrate and mediators, and the net production of $CO_2$ is zero.
This device was then characterized by measuring the electrical performance of the BPV. A power density of 14 μW/m2 was recorded, revealing interesting potentialities for green unicellular algae fuelled BPVs.

## 1. Introduction

A continuously growing population has led to increasing energy demand all over the world. The reported current consumption of petroleum is $10^5$ times faster than nature can produce (Satyanarayana et al., 2011). This population explosion combined with a rapid consumption of limited oil reserves (stocks of fossil fuels) is contributing to the increase of atmospheric $CO_2$, resulting in global warming. Climate change is currently recognized as one of the greatest threats to mankind. Hence, both the demand in energy and the ecological consequences have forced to look for substitutes for fossil fuels by using other resources including renewable sources (Satyanarayana et al., 2011). Sustainable alternative energy sources that are available nowadays all have their drawbacks. They are weather dependent (wind, solar power), compete with food/feed production (some biofuels) (Fargione et al, 2008) or involve high investment costs (Huesemann, 2006). While much research is being conducted into a wide range of energy solutions, it does not appear that any one alone will be able to replace fossil fuels in its entirety. As such it is likely that a number of different alternatives will be required, providing energy for a specific task in specialized ways in various situations. The discovery that bacteria can be used to produce electricity from waste and renewable biomass has gained much attention. In this field microbial fuel cells (MFC) represent an emerging technology that utilises heterotrophic bacteria to convert chemical energy stored in organic matter into electricity (Logan et al., 2006).
Similarly to microbial fuel cells, self-sustainable microbial fuel cells that rely on light instead of organics as an energy source are being developed. Considering that sunlight offers an unlimited source of energy, this has become an increasingly popular area of research in recent years.
Microbial photobioelectrochemical cells convert light into electricity by exploiting the photosynthetic activity of phototrophic microorganisms. Photosynthetic reaction centers of green plants, algae, and cyanobacteria, in fact, are nanoscale photovoltaics, that use photosynthetically active radiation (PAR) to

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oxidize water (photolysis). The resulting electrons are employed to synthesize adenosine triphosphate (ATP), and β-nicotinamide adenine dinucleotide phosphate (NADPH). The possibility to harvest electrons, for current generation in a MFC, directly from the photosynthetic electron transfer chain of a photoautotrophic microorganism has remained until now relatively unknown (Pisciotta et al., 2011).
Two different types of microbial photobioelectrochemical cells can be distinguished (Figure 1): type one uses light – via photosynthesis – as the sole energy source. Strictly speaking, this type should rather be referred to as a microbial solar cell than a fuel cell, since no continuous supply of fuel takes place. This kind of cell is called bio-photovoltaic cell (BPV). Type two, the photomicrobial fuel cell (PMFC), uses light to facilitate the generation of electric current from the anaerobic microbial oxidation of organic matter (Rosenbaum and Schrçder, 2010). In the present study, we have tested a novel BPV device to examine *Chlorella vulgaris*, a green microalgae and to demonstrate its light-dependent exoelectrogenic activity.

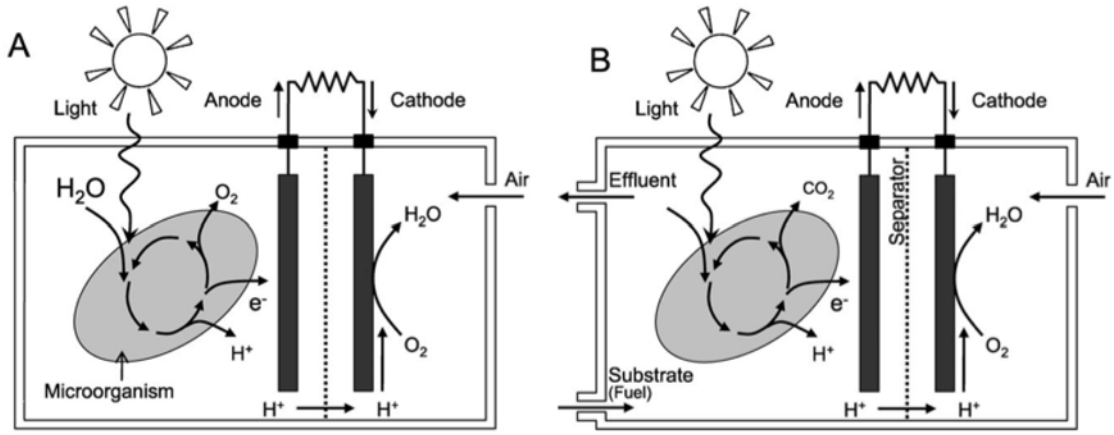


*Figure 1: Principle setup of (A) a bio-photovoltaic cell (BPV) and (B) a photomicrobial fuel cell (PMFC).*

## 2. Materials and methods

### 2.1 BPV design

The BPV cells were constituted by two overlaying cylindrical compartments in PMMA, as shown in Figure 2. The upper compartment (i.e the anodic chamber, diameter 4 cm; height 3.1 cm) was equipped with three sealable openings on the top, necessary for electrochemical measurements and to perform the ancillary operative activities. The lower one (i.e. the cathodic chamber, diameter 4 cm; height 0.5 cm) was open to the air to ensure the presence of atmospheric oxygen required for the cathodic reaction.
Between the two compartments the electrode system was placed. It was a joint disc composed by two 5.075 $cm^2$ arc-welded stainless steel rhombic (diagonal 1.9 mm) meshes (diameter 0.5 mm) intercalated by a proton exchange membrane (PEM) of Nafion 117.

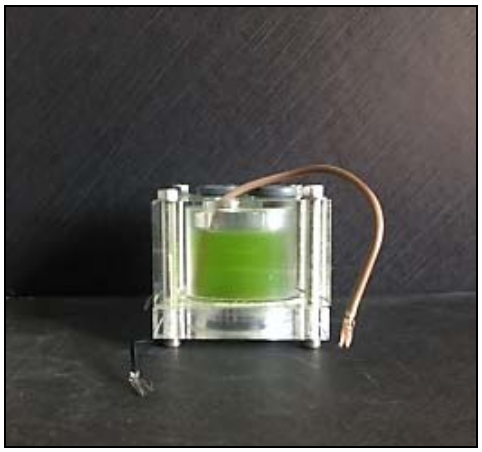

*Figure 2: Biophotovoltaic cell experimental setup*

### 2.2 Photosynthetic Cultures

The freshwater unicellular green alga *Chlorella vulgaris* was cultivated in BG11 medium (Stanier et al., 1971) in 0.5 L plane-flat photobioreactor operating at room temperature under 12 h:12 h light/dark cycles and under constant bubbling with air.

After sterilization of BPVs, the anodic chamber was loaded with 25 mL of *C. vulgaris* suspension in BG11 medium (initial biomass concentration equal to 8.0 g/L). BPVs operated at room temperature under 12 h:12 h light/dark cycles exposed to a 25 W fluorescent lamp (215 µmol photons $m^{-2}$ $s^{-1}$). Agitation during all the experiments was ensured by an orbital shaker (Stuart SSM1) maintained at 80 rpm.

### 2.3 Electrochemical Analysis

Open circuit voltage (OCV) was measured at 1.5 min intervals using a digital data acquisition system (VMP, BioLogic, Knoxville, TN).

To determine the polarization curve and hence calculate the power curve, pseudo steady-state voltages were measured at variable external loads (from 20 MΩ to 4 Ω) under constant operating conditions.

In a polarization curve the voltage as a function of the current is represented. The measured current was normalized based on the anode surface area as current density.

Changing the resistance (load) of the external circuit, the voltage is measured and the current is calculated according to Ohms law Eq (1):

$$I = \frac{E}{R_{ext}} \tag{1}$$

A power curve, which describes the trend of the power as a function of the current, is obtained from the polarization curve, according to the Eq. (2)

$$P = I^2 R_{ext} \tag{2}$$

An apparent internal resistance ($R_{int}$) was calculated from the linear region of the polarization curves using the Eq. (3) (Logan, 2008).

$$R_{\text{int}} = -\frac{\Delta E}{\Delta I} \tag{3}$$

For measuring the anode potential an Ag/AgCl reference electrode was inserted into the anode chamber at distance of 0.3 cm to the anode surface.

## 3. Results and discussion.

### 3.1 Positive Light Response

BPVs after loading with *C. vulgaris* (8.0 g/L) suspension were exposed to circadian cycles and OCV was recorded.

During operation at 12 h:12 h light/dark cycles, BPVs containing the photosynthetic microorganism displayed a substantially positive light response (Figure 3). During each light/dark cycle, after the beginning of illumination an increase of the cell OCV of about 60 mV throughout the whole illuminated phase was recorded. During the following dark phase the OCV partially decreases of about 40 mV.

BPV loaded with BG11 in the absence of any photosynthetic cultures showed no light response (Figure 3).

Since the OCV positive response is immediate, no biofilm is supposed to be required to electrons transfer to the anode. As well it's hard to suppose the presence of endogenous electrons shuttles, being the cultural medium freshly replete at the beginning of the experiments. Therefore is reasonable that electrons transfer mechanism occurred through direct contact of microalgal cells with the anode surface. The immediate and relatively slow increase of OCV during the illuminated phase and its evident synchronism with the light\dark cycles leads to the exclusion of a respiratory transfer chain origin of the reduced equivalent involved in the OCV establishment. In fact, if any reduced equivalent came from the catabolism

of endogenous energy substrate produced during the dark phase of photosynthesis, a delay between photoperiod and OCV response should be noticed.
For the first six days the OCV trend was characterized by a higher diurnal increase. This result indicate that this period was necessary for the acclimation of *C. vulgaris* to the cultural conditions inside the BPVs. Once *C. vulgaris* reached the homeostatic state the OCV regularly oscillated between about 140 and 200 mV.

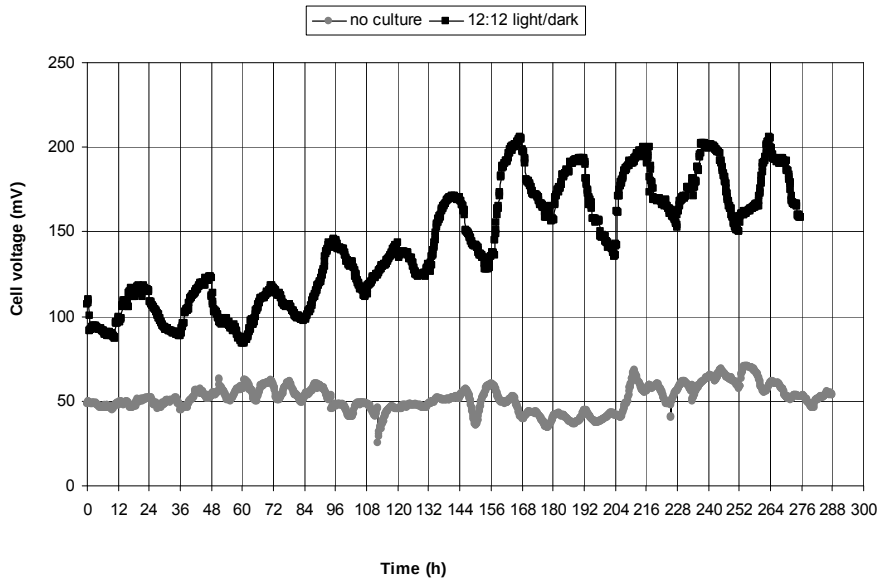


*Figure 3: OCV trend for a 12h:12h photoperiod*

### 3.2 BPV Performance

BPV performances were evaluated by means of the polarization curve. As reported in Figure 4, varying the external resistances from 20 MΩ to 5 Ω, the voltages decrease from 151 mV to 0.1 V, while the current densities increase from 0 mA/m$^2$ to 0.48 mA/m$^2$.

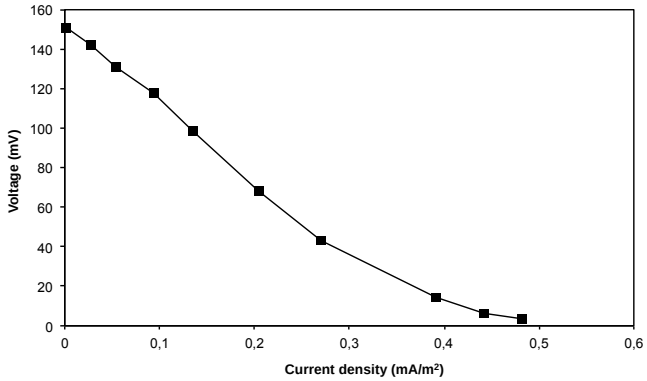


*Figure 4: The polarization curve of BPV*

Basing on the maximum power transfer theorem, a value of 396 Ω internal resistance was calculated. This value appears relatively high if compared to the value obtained for microbial fuel cells, (about 60-70 Ω, Logan et al., 2006). However a reduction of the cell internal resistance could be obtained through a better assemblage of the electrodes system, especially regarding the contact between Nafion and air cathode (increasing the contact area), thus increasing the cell performances. The effect of activation and concentration overpotentials are visible respectively at low and high current values.
Two power curves were generated to characterize the performance of the device (Figure 5a e 5b). Similarly to the positive photo responses observed previously during light cycling (Figure 3), increased power density outputs were observed over a range of external resistances during illumination, while the power generated in the cell in the dark is negligible.

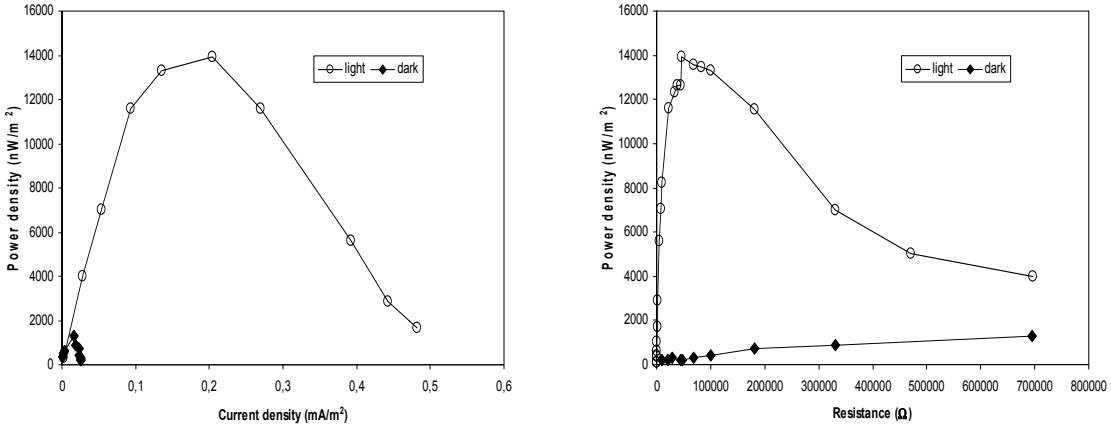


*Figure 5: Power curve (a) as a function of current density; (b) as a function of external load*

A maximum power of 14 μW/m$^2$ was recorded for BPV under illumination (Figure 6), corresponding to a current density of 0.20 mA/m$^2$ and to a voltage of 68.2 mV. Although substantially lower than that reported for MFC in recent years (Fan et al., 2007; Logan and Regan, 2006; Zuo et al., 2008), this power value is comparable with what reported for the first generation of MFCs (Logan and Regan, 2006).
BPVs in the current study are different from conventional MFCs in several key aspects. First, BPVs are 100% light powered and do not require an organic substrate as an energy source. Second, the net production of $CO_2$ in BPVs is zero. Third, the BPVs do not require a buffer or exogenous electron shuttles for their operation.

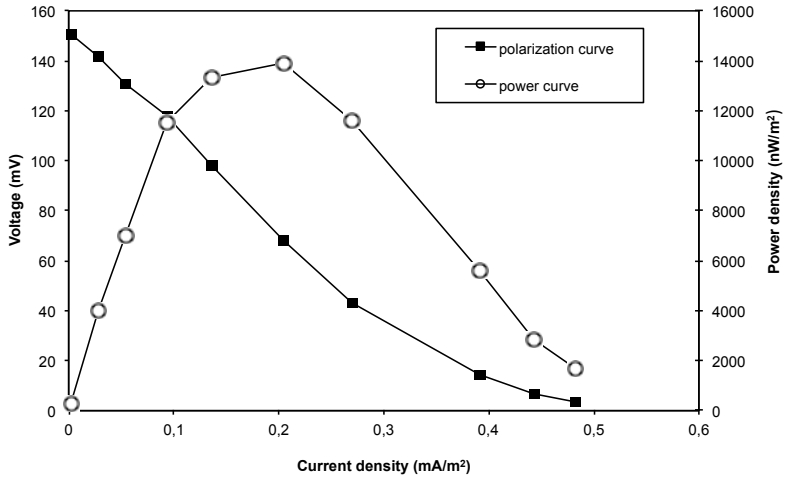


*Figure 6: Power density and polarization curve*

## 4. Conclusion

In this study a new approach to convert chemical energy into electricity through biocatalytic activity was proposed. Exoelectrogenic process of eukaryotes are almost unknown, in particular regarding photoautotrophic microorganisms. An original biophotovoltaic cell made possible to use the green microalga *Chlorella vulgaris* as biocatalyst for current generation. A BPVs positive light response was demonstrated and attributed to exoelectrogenic electrons transfer mechanism. The proposed low cost device, allowed the achievement of an average power density of 14 μW/m$^2$ and an internal resistance of 396 Ω, without using mediators and modified electrodes (Zou et al., 2010). Increasing performances are

expected maintaining the electrodes close assembled, thus reducing the internal BPV resistance value. Furthermore, the use of air-cathode resulted in a simplified cell design.

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