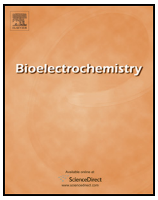
Bioelectrochemistry 122 (2018) 1–10

Contents lists available at ScienceDirect

Bioelectrochemistry

journal homepage: www.elsevier.com/locate/bioelechem



Light-dependent processes on the cathode enhance the electrical outputs of sediment microbial fuel cells

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ARTICLE INFO

Article history:
Received 31 December 2017
Received in revised form 15 February 2018
Accepted 25 February 2018
Available online 27 February 2018

Keywords:
Sediment microbial fuel cells
Light irradiation
Cathode
DNA analysis
Microbiota
Photosynthesis

ABSTRACT

In this study, we explored in details the influence of the light irradiation on the SMFCs electrical outputs. The experiments at both natural and artificial illumination firmly show that during the photoperiods the current grows up. The intensity of the current increase depends on the duration of the photoperiod as well as on the wavelength of the monochromatic light source applied. The highest influence of the light irradiation has been obtained at wavelengths, corresponding to the absorption peaks of essential pigments in the light-harvesting system of oxygenic photosynthesizing microorganisms. The decreased values as well as the discontinued fluctuations of the current as a result of suppressed illumination or substitution of the biocathode with a new one suggest that photosynthesizing microorganisms, co-existing in the cathodic biofilm consortium, contribute to the overall SMFC performance. The microscopic observations confirm the existence of chlorophyll-containing microorganisms on the cathode surface. Though the performed metagenomics DNA analysis has not certified a dominance of photosynthesizing microorganisms, all other results support the hypothesis that the current enhance during the photoperiods is due to the in situ bio-oxygen production on the cathode surface, thus lowering the mass transport limitations for the oxygen reduction reaction.

1. Introduction

Sediment microbial fuel cells (SMFCs) are considered as promising devices for power supplying different electronics and sensors operating at remote areas [1–4]. Though among other bioelectrochemical systems SMFCs mimic at highest extent processes occurring in natural environment, their proof-of-concept was done relatively soon after discovery that some bacteria, occupying marine or freshwater sediments, are able to accomplish direct extracellular electron transfer (EET) [5–8]. In the nature, such bacteria couple their catabolic processes with minerals like Fe_2O_3 or MnO_2 as final electron acceptors, while in MFC they use in similar manner an electrode (anode). The specificity of SMFCs in comparison with the other MFC types is that they use microbial consortia, exploiting as substrates the abundance of organic matter naturally existing in the sediments. Because of the existing opposite gradients of oxygen and sulfides in the sediment depth, the bacterial species colonize the sediment in a manner, which meet in highest extent their specific requirements for preferable nutrients and final electron acceptors. In SMFCs, the so-called exoelectrogenic (or anode-respiring) bacteria form a biofilm on the anode and transfer electrons extracellularly to it directly (through outer-membrane cytochromes or conductive pili) or indirectly (through soluble, redox active secondary metabolites referred as endogenous mediators) [9,10]. The difference between the potentials of the cathode, placed in the oxygenated water layer above the sediment, and the anoxic anode, buried in the sediment, creates an electromotive force of several hundred millivolts, which can be used for electricity generation. The solid-liquid interface between the sediment and water columns naturally separates the anodic and cathodic compartments, omitting the necessity of ion-exchanging membrane and thus considerably reducing the operational cost of the constructed devices.

Usually, a large fluctuation of the electrical outputs is observed after the start-up of SMFCs, which is attributed to rearrangement of the microbial community along the sediment column. After a certain period of time, however, when the redistribution of the microbial community is accomplished, the system reaches a steady-state and the electrical outputs become more stable. In our previous study [11], we explored nine identical freshwater SMFCs for over 20 months and established that after entering a steady-state their performance becomes homoscedastic, i.e. all fuel cells start to respond in a similar way, keeping some

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https://doi.org/10.1016/j.bioelechem.2018.02.009
1567-5394/

difference between absolute values of the measured parameters. Recording precisely the electrical parameters at later stage of experiment, we observed periodical oscillation of OCV and current values, following the day/night cycle. Similar behavior was previously established with Direct Photosynthetic Plant Fuel Cells, utilizing higher aquatic plants (duckweeds) as biocatalysts [12,13]. Connecting both observations, we hypothesized that the main reason for the periodic fluctuation of SMFC electrical outputs is the light irradiation, which may affect the metabolic activity of photosynthetic microorganisms in the system.

The permanently rising mankind energy demands put the attention on development of new, sustainable technologies, particularly for solar energy conversion. One of the modern trends in this direction, which is still in the lab-scale stage of development, is based on coupling of photosynthetic energy conservation and electricity generation in so-called phototrophic microbial fuel cells (photo MFCs). The photo MFCs development began in the 1960s by combination of photosynthetic bacteria and metallic electrocatalysts [14], and later on with exogenous mediators [15]. The increasing attention to the photo MFCs, however, arose in the first decade of this century.

In the first review on photo MFCs, seven different approaches for integration of photosynthesis with MFC technology have been described and discussed [16]. One of them is connected with the synergism between phototrophic microorganisms and mixed heterotrophic bacteria in sediments. However, as the authors of this excellent review underlined, there are considerable differences in the data reported for sediment-type photo MFCs in respect to the electric current response to illumination. He et al. [17] examined freshwater sediment-type photo MFC and established that after several months of operation the well-adapted microbial community produced electric current, exhibiting an inverse relationship with illumination. The authors of this study hypothesize that during the dark periods current increases because of the oxidation of organic compounds accumulated during the light reactions, while the decrease of current production during long-time illumination is due to the presence of dissolved oxygen produced by photosynthetic microorganisms. In this case, the inhibition of the anodic reaction by dissolved oxygen seems reasonable as far in the used construction the anode is put on the bottom of the reactor and covered with a thin (0.5 cm) sediment layer. Thus, the oxic zone should expand downward in the sediment, allowing the anode bacteria to utilize oxygen as an electron acceptor, rather than the anode of the MFC. Recently, we observed a similar behavior of flat-plate transparent reactors, in which the sediment layer is only 1.5 cm thick and the thickness of the anode is 1 cm, so the distance between the sediment surface and the anode is only 2.5 mm from both sides. After proliferation of green-colored microorganisms in the vicinity of the anode zone, the current began to increase during dark periods and to decrease during photoperiods (unpublished data). After long-term operation of the same SMFCs, a voltage reversal, similar to that reported by He et al. [17], was also observed, indicating that possibly the photosynthetic microorganisms near the MFC anode produce more oxygen than those around the cathode, and thus the anode functioned as a cathode and vice versa. Suppression of anodic current generation by photosynthetically produced oxygen was also reported by Darus et al. [18], who examined the effect of illumination on a mixed phototrophic culture enriched from a freshwater pond in flat-plate photoreactors. In opposite, testing marine microbiota in a sediment-type photo MFC, Malik et al. [19] observed long-term light-dependent current generation, which is assigned by the authors to the production and consumption of oxygen by photosynthetic microorganisms, occupying the cathode, during the light and dark phases of photosynthesis, respectively. Positive light response of photo MFCs, using two photosynthetic cultures - strictly planktonic cyanobacteria and natural fresh-water biofilm, was also reported by Zou et al. [20].

In a few studies the influence of monochromatic light on the photo MFCs current generation was also examined. By using light filters, He et al. [17] illuminated their sediment phototrophic MFC reactor with red and blue light and determined the same effect like with the polychromatic light – increase of current during dark periods and decrease at the photoperiods. Applying green microalgae as a biocatalyst in double-chamber photo MFCs illuminated with monochromatic blue and red LED lights, Lan et al. [21] established an enhanced performance in terms of maximum power and exchange current density with increasing the light intensity. The better performance obtained under red LED light illumination was attributed to the acceleration of cell growth when cultivated in the range of wavelength between 650 and 750 nm.

The brief overview of data, reported in the literature, clearly shows that the light illumination may influence in opposite ways the current generation of different MFCs depending on many factors as their construction, used biocatalysts (mono or mix culture), operation conditions (anoxic or oxic), etc.

The aim of this study was to elucidate in more details the influence of the light irradiation on the SMFC performance. For this purpose, we carried out experiments at temperature-controlled conditions, illuminating the explored SMFCs with polychromatic as well as monochromatic light with different wavelengths. Based on findings that the light irradiation affects definitely the cathodic reaction, we further isolate and identify the microorganism species in the SMFC cathodic biofilm. A hypothesis about the influence of the photosynthetic processes on the mechanism of the cathodic reaction is proposed.

2. Materials and methods

2.1. SMFC construction and operation

Freshwater SMFCs, presented in a previous paper [11], were further examined in this study. The SMFCs were constructed by filling transparent polyethylene vessels (height 23 cm, diameter 9 cm) with sediments and water, collected from river Struma, near the town of Blagoevgrad, Bulgaria. The sediment layer height was ca. 15 cm and the water column above the sediment was ca. 4 cm. Plane graphite disks (diameter 8 cm, thickness 1.5 cm) were used for cathodes and anodes. The anodes were buried in the sediment layer 5 cm above the bottom of the vessel and the cathodes were immersed few millimeters under the water surface at a distance of ca. 14 cm from the anodes. In the beginning of current experiments, the explored SMFCs have been operated autotrophically for more than five years, without addition of any nutrients, but only water for compensation of the evaporation.

In the initial stage of experiments the SMFCs were exposed to the natural sunlight illumination in the lab and the OCV or voltage under constant load (510 Ω) together with the irradiance intensity, measured by OPT101 photodiode (Texas Instruments, USA) in close vicinity of the explored SMFCs, were recorded in five minutes intervals using digital multimeter DMM2700 (Keithley Instruments Inc., US) for periods from one to two weeks.

In other set of experiments, in order to eliminate the natural fluctuations in the sunlight intensity and in the ambient temperature the fuel cells were placed inside a thermostat (POL-EKO ST 1 B60) with precisely controlled temperature (±0.1 °C). Two 107 lm, cool white LEDs (CREE XPEWHT-L1-0000-00D01) were used as a light source. To avoid a local heating in vicinity of the irradiated SMFCs, the LEDs were installed outside the thermostat and optical fibers were used to carry the light to the fuel cells (Suppl. Fig. S1). The SMFC voltage under constant load (510 Ω) was recorded in consecutive light/dark cycles ranging from 1 to 12 h at controlled temperature 25.0 ± 0.1 °C. The generated current was estimated by using the Ohm's law. The SMFCs were also illuminated with series of monochromatic LEDs covering a wide range of the visible light spectrum from 447 nm to 665 nm. The effect of the light irradiation on the cathodic reaction was examined by covering the SMFC cathode with aluminum foil or replacing with a new graphite electrode.

The performance of the used cathodes was also examined by means of linear voltammetry at applied scan rate 1 mV/s. The potential was swept in negative direction starting from measured open circuit