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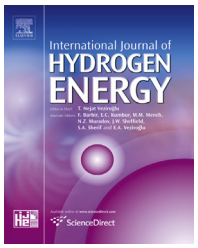

Methanol opportunities for electricity and hydrogen production in bioelectrochemical systems

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ABSTRACT

An anodic syntrophic consortium (exoelectrogenic plus fermentative bacteria) able to use methanol as sole carbon source was developed for the first time in a bioelectrochemical system. In this frame, promising results were obtained in single chamber MFC, comparable to those obtained with readily biodegradable substrates. Regarding MEC operation, the presence of homoacetogenic bacteria led to electron recycling, avoiding net hydrogen production in single chamber MEC. In a double chamber MEC, satisfying results (in terms of coulombic efficiency and cathodic gas recovery) were obtained even though energy recovery still restrained the feasibility of the process. The approach used in this work with methanol opens a new range of possibilities for other complex substrates as electron donors for bioelectrosynthesis.

1. Introduction

The forecast of fossil fuels shortage and the negative impact of its usage on environment drive the need to search for alternate sustainable fuel sources [1]. In this frame, bioelectrochemical applications may facilitate wastewater treatment for reuse and valorization, for example for power or hydrogen generation. These are considered as promising systems and have the potential to occupy a prominent place in future renewable energy generation, bioremediation, and wastewater treatment [2]. The opportunities of bioelectrochemical systems (BES) would lay on their capability of converting chemical energy of non-fermentable and fermentable substrates into electricity or other high added-value products under relatively mild

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conditions and using a wide variety of substrates with inexpensive metals as catalysts. The most common BES nowadays are microbial fuel cells (MFC) aiming at electricity generation and microbial electrolysis cells (MEC) for hydrogen production. The key of BES is the enrichment of the anode in exoelectrogenic bacteria (also known as anode respiring bacteria, ARB) which have the ability to transfer their electrons extracellularly to a solid anode [3]. The anodic oxidation reactions are equivalent in both MFC and MEC, while the reduction reaction occurring on the cathode varies depending on the system. In an MFC, electricity is generated as a result of an overall thermodynamically favorable reaction where oxygen is reduced to water, whereas in MEC, additional energy is required to drive the overall reduction reaction [4].

In determining the type of carbon source for BES, cost and availability impacts the total economy of the technology. Conversion of substrates other than volatile fatty acids (VFA) is essential in view of their practical implementation. ARB can use a limited range of substrates and fermentative bacteria do not have external electron transfer abilities. Nevertheless, the utilization of fermentable substrates (glucose, xylose, sucrose), non-fermentable substrates (acetate, propionate and butyrate) and wastewaters of domestic, swine, brewery, paper recycling, starch and food processing wastewaters for the generation of power or hydrogen through BES has been reported [5–10].

Among all the different carbon sources used, methanol has never been reported to be a successful carbon source for BES. Understanding previous failures and achieving methanol-driven BES is interesting not only for potential methanol utilization but also as a pathway to follow for the utilization of other complex carbon sources. When compared to other alcohols such as ethanol or butanol, methanol is a more economical approach due to its availability from different sources. Biomethanol can currently be obtained from any organic waste source that can be first converted to synthesis gas [11]. Also, unlike ethanol, it does not interfere with human food chain and its purification process is simpler.

Methanol interaction in BES systems is also interesting in the frame of utilizing crude glycerol as carbon source, a target waste product to valorize. Crude glycerol as a raw material for processes such as BES for hydrogen production was reported to be an interesting carbon source [12,13] but Chignell and Liu [14] observed a decrease in hydrogen production yield when methanol was present in this waste stream. Direct utilization of methanol for operation of BES was attempted by Kim et al. [15], studying the feasibility of alcohols (ethanol and methanol) for power generation using double chamber MFC, succeeding with ethanol and reporting non-appreciable electricity generation with methanol. Regarding MEC, direct methanol utilization has never been reported and its effect on hydrogen production is rather unknown. Finally, the utilization of methanol in BES is a challenging task due to its possible inhibitory and toxic effect on ARB at high concentration.

Hence, in the present investigation, we have evaluated the performance of methanol in BES for bioelectricity and biohydrogen production with syntrophic consortia developed using ARB and anaerobic sludge. To the best of our knowledge, this is the first successful attempt of methanol utilization as a sole carbon source in BES.

2. Materials and methods

2.1. Microbial fuel and electrolysis cells

MFC were 28 mL methacrylate vessels provided with a lateral aperture (3.8 cm diameter), where a PTFE diffusion layer stuck to the cathode permitted oxygen diffusion into the cell while preventing water leakage [16,17]. The anode was a titanium wire connected to a graphite fiber brush (20 mm diameter × 30 mm length; 0.21 m^2 specific surface area) made with fibers of diameter 7.2 μm (type PANEX33 160K, ZOLTEK). It was thermally treated at 450 °C for 30 min to enhance biomass adhesion and inoculated from an already working MFC [18]. The cathode consisted of graphite fiber cloth (3.8 cm diameter, 7 cm^2 total exposed area) coated with platinum (5 mg Pt/cm^2, ElectroChem Inc.). The two electrodes, spaced 2.5 cm apart, were connected through a 1000Ω external resistance.

MEC were homologous to MFC, but the cathode was not exposed to air and the cell had a glass cylinder at the top, tightly sealed with a PTFE rubber cap that enabled gas collection. The gas produced was further collected in a gas-tight bag (Ritter, Cali-5-bond) connected to the glass cylinder. Both electrodes were connected to a power source (HQ Power, PS-23023) applying a potential of 0.8 V. Current production was measured by quantifying the voltage drop across a 12 Ω external resistance serially connected to the circuit. The cell was easily converted to a double chamber MEC by coupling an identical module and placing an anion exchange membrane in between (AMI-7001S, Membranes International INC). The membrane was soaked overnight in a 10% sodium chloride solution. Under this configuration the distance between electrodes increased to 7 cm.

The cells operated with methanol as sole carbon source in fed batch mode unless otherwise stated. The medium contained per liter: 1.6 g methanol, 172 mL PBS stock solution, 2.925 g $KHCO_3$ and 12.5 mL mineral media. The medium was completely replaced with fresh one when voltage response decreased below 20 mV. MEC were sparged with nitrogen for 10 min after feeding to guarantee anaerobic conditions. The PBS stock solution contained per liter: 70 g Na_2HPO_4 and 12 g KH_2PO_4. Mineral media solution contained per liter: 1 g EDTA, 0.164 g $CoCl_2 \cdot 6H_2O$, 0.228 g $CaCl_2 \cdot 2H_2O$, 0.02 g H_3BO_3, 0.04 g $Na_2MoO_4 \cdot 2H_2O$, 0.002 g Na_2SeO_3, 0.02 g $Na_2WO_4 \cdot 2H2O$, 0.04 g $NiCl_2 \cdot 6H_2O$, 2.32 g $MgCl_2$, 1.18 g $MnCl_2 \cdot 4H_2O$, 0.1 g $ZnCl_2$, 0.02 g $CuSO_4 \cdot 5H_2O$ and 0.02 g $AlK(SO_4)_2$. Cobalt (II) chloride was added to the system to enhance the growth of acetogens versus methanogens [19]. A 50 mM 2-bromoethanesulfonate concentration was used according to the work of Parameswaran et al. [20], where it was stated that such concentration would selectively inhibit methanogenic bacteria. 2-bromoethanesulfonate had been previously stated to inhibit methanogenic activity [21,22] and to be more effective than other chemical inhibitors or changes in system conditions such as pH and temperature [23]. In the double chamber MEC configuration the catholyte was a 100 mM PBS solution. Cells were kept at room temperature during all the operational period.

Voltage evolution was monitored by means of a 16-bit data acquisition card (Advantech PCI-1716) connected to a personal computer with a software developed in LabWindows CVI 2013 for data acquisition.