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Hybrid MFC-MEC systems: principles and applications

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Microbial electrolysis cell (MEC) and microbial fuel cell (MFC) are emerging bioelectrochemical technologies, intensively investigated during the last two decades. These two types of systems are originally developed for simultaneous wastewater treatment and hydrogen production or electric energy generation respectively, using microorganisms as biocatalysts. A different and attractive approach to improve the feasibility of these systems is to integrate MFCs with MEC. Such hybrid systems are still at an early stage of development. They have the ability to overcome the limitations of stand alone bioelectrochemical systems. The principle and application of hybrid MFC-MEC systems and their constructional elements are reviewed and discussed.

Keywords: bioelectrochemical systems, hybrid MFC-MEC system, hydrogen production, energy generation.

INTRODUCTION

Microbial electrolysis cell (MEC) and microbial fuel cell (MFC) are bioelectrochemical systems (BES) and both of them use microorganisms. Microbial electrolysis cell is a technology for hydrogen production closely related to microbial fuel cells (MFCs). Whilst MFC's produce an electric current from the microbial decomposition of organic compounds, MECs partially reverse the process to generate hydrogen or methane from organic material by applying electric current [1]. Simultaneously with the production of hydrogen or electric current, respectively, these systems purify waste water.

A new and successful way to improve the feasibility of MFCs is to integrate MFCs with other technologies to produce hydrogen fuel [2] or other products [3, 4], the so-called MFC hybrid systems. The classification and relationships of various MFC hybrid systems are present in Table 1 [5]. They have the ability to overcome the limitations of standalone BES [6, 7].

Since the open circuit voltage of an MFC could reach as high as 0.80 V, the extra energy needed for an MEC can be supplied by a MFC. In such MEC-MFC-coupled system, hydrogen can entirely be harvested from the substrate in the microbial cells [8].

For the first time Sun *et al*. [8] reported on the development of a coupled MFC/MEC system for the production of biohydrogen from acetate. In this system consisting of coupled MFC and MEC the electricity needed to run the electrolysis was supplied by the MFC with an air cathode.

Many reviews of individual MFC [9-19] and MEC [20-29], respectively, have been published in recent years focusing on different topics: electrode materials, biocathodes, electrocatalysts, membrane materials, microorganisms, reactor configurations, wastewater treatment, mechanisms of electron transfer, perspectives, applications, etc.

However, there is a lack of a review on MFC-MEC hybrid systems. In this study the principle and application of hybrid MFC-MEC systems and their constructional elements are reviewed and discussed.

HYBRID SYSTEM MFC-MEC

Structure and operating principle of hybrid system MFC-MEC

Sun *et al*. [8] demonstrated the possibility of using a single-chamber MFC to directly power a two-chamber MEC (Fig. 1). In this coupled system, hydrogen was produced from acetate without external electric power supply. They also found that the input voltage of the MEC can be adjusted by external resistance in a series circuit [30]. In order to improve the voltage supply, one or two additional MFCs were introduced into the MFC-MEC coupled system [31].

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Table 1. The classification and relationships of various MFC hybrid systems

MFC hybrid systems							
Chemical processes		Biological processes			Physical processes		
Electro-Fenton processes	Photochemical processes	Traditional biological treatment processes	Plant/ Constructed wetlands	Microbial electrolysis cell	Desorption/ Capacitive deionization	MDS-based technologies	Membrane bioreactors
+MFC		+MFC			+MFC		

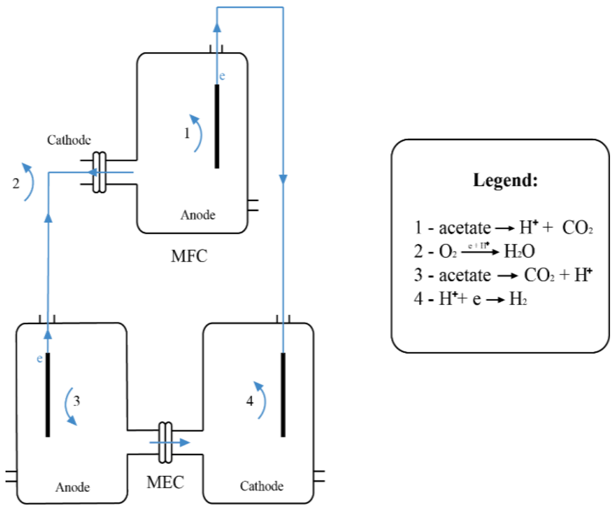

Fig. 1. Laboratory-scale prototype of the MEC–MFC-coupled system [30].

The hydrogen production was significantly enhanced by connecting MFCs in series, while opposite results was observed with parallel connection. Therefore, connecting several MFCs in series could be an efficient way to improve the voltage supply in such coupled system [25].

Multiple MFCs in series and in parallel as the power source were investigated, and the former arrangement was proven to be more appropriate. For example, it was reported that the H_2 production with MFCs installed in series in a MEC-MFC system was much higher than that with MFCs in parallel [31]. With three 350-mL MFCs in series powering a two-chamber MEC, a H_2 production rate of $0.48 m^3$ H_2 $m^{-3}d^{-1}$ was achieved [32]. However, it is problematic to use several MFCs in series due to the voltage reversal phenomenon when the anodic and cathodic polarities switch on its own, reducing the voltage output and even causing irreversible damage to any bioanodes in the system [33, 34]. A new way to combine MFC with MEC is to use capacitors in parallel charged by multiple MFCs. After charging, the capacitors are discharged continuously to supply power. The H_2 production in a coupled system increased from 0.31 m^3 m^{-3} d^{-1} without capacitors to 0.72 m^3 m^{-3} d^{-1} with capacitors [35].

Increasing the initial acetate concentration and solution conductivity in MEC is also beneficial to H_2 production [31, 32]. The increase in phosphate buffer concentration improved the feed solution conductivity, resulting in an increase in the H_2 production rate from (2.9 ± 0.2) mL L^{-1} d^{-1} to (7.9 ± 0.3) mL L^{-1} d^{-1} with a Coulombic efficiency of (31.9 ± 7.2) %. Varying the relative reactor sizes of MFCs to MECs could also enhance MFC-MEC performances [35]. More investigations are needed to improve MFC-MEC efficiency and to further reduce costs.

MFCs have also been used to power CO_2 reduction in the cathode of MECs, which further shows the promising perspective of MFCs as power sources for MECs [36].

Microorganisms

The identity of the specific microorganisms determines the products and the efficiency of the MEC and MFC. Depending on the organisms presented at the anode, MECs can also produce methane by a related mechanism [10]. Biowaste and wastewater provide immediate profits and the greatest likelihood for success of these bioelectrochemical systems. Electrogenic microorganisms consuming an energy source (such as acetic acid) release electrons and protons, creating an electrical potential of up to 0.3 V. In a conventional MFC, this voltage is used to generate electrical power. In a MEC, additional voltage is supplied to the cell by an outside power source. The combined voltage is sufficient to reduce protons, producing hydrogen gas. The efficiency of hydrogen production also depends on which organic substances are used. Various organic matters such as cellulose, glucose, glycerol, acetic acid, sewage sludge and various wastewaters can be used in MEC and MFC to produce hydrogen and electric energy, respectively.

The most investigated microbial cultures for application in MECs and MFCs are *Archaea*, the single-celled cyanobacterium *Cyanothece* 51142 [37], Dechlorinating bacteria (*Dehalococcoides* spp. and *Desulfitobacterium* spp.), methanogens and homoacetogen microorganisms [38], and *Shewanella putrefaciens* [39-42], *Pseudomonas aeruginosa, Enterococcus faecium* [43], *Rhodoferax ferrireducens* [44], respectively.

ADVANTAGES VERSUS STAND-ALONE SYSTEMS

The hybrid systems are more promising compared with stand-alone systems.

A hybrid energy system usually consists of two or more energy sources or methods used together, *via* suitable energy conversion techniques, to provide fuel savings, energy recovery and increase overall system efficiency [45].

Some of the prior studies on hybrid schemes of fuel cell systems by Abdullah *et al*. had demonstrated the feasibility and superiority of hybrid systems compared to stand-alone systems for various applications other than effluent or waste water treatment [46, 47]. Some of the notable advantages are:

(1) more stable and sustainable voltage generated;

(2) better overall treatment efficiency;

(3) energy saving potential [48].

MFCs are capable of recovering the potential energy present in wastewater and converting it directly into electricity [49]. Using MFCs may help offset wastewater treatment operating costs and make advanced wastewater treatment more affordable for both developing and industrialized nations [50].

There are both advantages and disadvantages associated with hybrid system [4]. Generally, hybrid systems are more stable and sustainable in terms of voltage generation and treatment efficiency compared to stand-alone systems. Bio-energy generated can help to offset the treatment operating costs of the overall system. In terms of energy balance, bio-energy generated from the hybrid system must be at least equal or greater than the energy used to operate the overall system.

Although MFC-hybrid systems are more promising than stand-alone MFCs, much more research is needed to overcome significant hurdles for practical deployment.

PERSPECTIVES FOR HYBRID SYSTEM MFC-MEC APPLICATION

The performance of the MEC and the MFC was influenced by each other. This MEC-MFC-coupled system has a potential for biohydrogen production from wastes, and provides an effective way for *in-situ* utilization of the power generated from MFCs.

Apart from H_2 production, MFC-MEC hybrid systems were also used to recover cobalt particles [51], Cu^{2+} and Ni^{2+} ions [52], Cr^{4+} and Pb^{2+} ions [53] and two groups of metal mixtures [54] from wastewater with contaminant degradation [55, 56]. The nutrient removal/recovery from wastewater was also reported in MFC-MEC hybrid systems.

The integration of MFC with MEC also promoted the process of ANAMMOX (anaerobic ammonium oxidation) without the requirement of an external carbon source [57].

Recently, CO_2 reduction in an MFC-MEC system has been reported [52, 58]. When powered by an MFC with 18.5 Wm^{-2} maximum power density, it was shown that the MFC-MEC hybrid system reduced CO_2 to CO at a rate of 0.06 mmol m^{-2} h^{-1} [52].

The major obstacles for the real-world applications of MFC-MECs include the low voltage output of MFCs, high internal resistance and high operating costs. The long-term stability of such a hybrid system is also a concern because a slight change of operating conditions can lead to system instability.

CONCLUSION

Hybrid MFC-MEC system is a new and successful way to integrate MFCs with MEC to produce hydrogen fuel or other products. It is more promising compared with stand-alone systems. Connecting several MFCs in series could be an efficient way to improve this system. With three MFCs in series powering a two-chamber MEC, a H_2 production rate of 0.48 m^3 H_2 $m^{-3}d^{-1}$ was achieved. By using capacitors for intermediate energy storage the H_2 production rate in a coupled system increased from 0.31 m^3 m^{-3} d^{-1} to 0.72 m^3 m^{-3} d^{-1}. There are many factors affecting the hydrogen production: electrode materials, membrane materials, microorganisms, reactor configurations, etc., which should be further improved in order to industrial application of the hybrid MFC-MEC systems.

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