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Fe_3O_4-modified carbon cloth electrode for microbial fuel cells from organic wastewaters

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ABSTRACT

The organic waste of anaerobic biohydrogen fermentation was used as the feedstock for further treatment. The bacterial contained fermentation waste was the introduced to a double-chamber microbial fuel cell (MFC) with Fe_3O_4-modified carbon cloth electrode. The main purpose of this study is to produce biohydrogen, reduce the chemical oxygen demand (COD) of organic waste and recover the electric power during waste treatment. The maximal (hydrogen yield) HY of 1.3 mmol H_2/g TVS (total volatile solids) was obtained, and the hydrogen production rate was 25.4 mmol H_2/L/d. The electricity generation in MFC can be obtained after a short acclimatization period of two days. The power generated was found to depend on the organic matter contained in the waste, and the maximum power density of 10 mW/m^2 (at an open circuit potential of 0.15 V) was obtained. These results pointed to the optimal conditions to enhance the hydrogen yield, energetic yield of MFC, and the COD removal in this newly designed system.

Keywords: Biohydrogen; Carbon cloth; Fe_3O_4; Microbial fuel cell; Chemical oxygen demand; Open circuit

1. Introduction

Organic wastewater is a potential bioenergy source via the use of anaerobic fermentation technology [1,2]. Hydrogen generation from wastewater costs less than other approaches and can be carried out using local feedstock [3,4]. Moreover, a microbial fuel cell (MFC) is a kind of electrochemical cell that uses micro-organisms as the anode catalyst, and directly changes chemical energy into electrical energy [1,2,5]. While such technology has not yet been commercialized, it shows great promise as a method of wastewater treatment, energy recovery, and desalination of brackish water and power sources for environmental sensing devices [1–3,5].

Biological fuel cell development is an interesting and promising innovation that can add to the already existing types of fuel cells. Biological fuel cells can convert the chemical energy of organic matter directly

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into electric energy to conventional fuel cells in mild reaction conditions (ambient temperature, normal pressure, and neutral pH) and platinum is not required [6]. Instead of platinum, the catalyst is either a micro-organism or an enzyme with mediators [6,7]. The biological fuel cell can then convert the chemical energy of organic matter directly into electric energy [1].

Anodes are often made of carbon- or graphite-based materials, e.g. graphite plates/rods/felt, carbon cloth/foam/paper, and reticulated vitreous carbon [8,9]. Among these, carbon paper, cloth, and foams are among the most commonly used anodes, and their use in MFCs has been widely reported [1,9]. Due to the working principles of MFCs, anode materials need to have a porous structure with a large surface area [10]. This will allow for extensive biofilm formation throughout the material, while enabling efficient transport of nutrients and waste at the same time. The material also needs to possess a networked structure that can provide a stable support for biofilm attachment. The importance of surface area for power generation has been previously demonstrated [11].

Among a wide variety of metal oxide nanoparticles, Fe_3O_4 nanoparticles are particularly attractive due to their unique magnetic and electrical properties [12]. Nano-sized magnetic bio-conjugated materials have been used in electrochemical biosensor devices due to their many advantageous properties, such as large surface area, higher bioactivity, excellent conformation stability, and better contact between the biocatalyst and its substrate [8,13].

Much work has been carried out to make new and modified anodes for MFCs and thus address major limitations such as resistance to mass transport and bio-accessible surface area [1,2,14]. Some of these efforts involve the use of transition metal complex and conducting wire to greatly increase the electrode transfer, surface area, and conductivity of a porous matrix [15,16]. Such research used two-tiered structures to maximize the substrate–biofilm–anode interfacial area [9], and a previous study showed that the addition of Fe_3O_4 in anode increases the maximum power density by 22%, and that the capacitance of the anode is also increased after Fe_3O_4 modification [17].

This work is focused on a particular variety of MFCs which can convert various organic matters, such as glucose, acetate, and butyrate in wastewater or sludge waste, into electrical power [1,2]. This consists of fuel cells in which bacteria are directly used to catalyze the conversion of organic matter into electricity without the addition of mediators [6]. The power density produced by this type of cell is low and normally below 50 mW/m^2. Both one and two-chamber MFCs are already studied in literature [1,2,6], and are considered to have more commercial application potential than other kinds of biofuel cells due to their simplicity [18]. Furthermore, commercial Fe_3O_4 powder is used to enhance cell performance, and it has the benefits of being low cost, and non-toxic to micro-organisms. Moreover, different kind of fuels can be fed to this type of cell.

The objective of this work is to optimize the hydrogen fermentative process from beverage wastewater using batch reactors. Special attention has been paid to clarify the effects of the chemical oxygen demand concentration on power generation, and the role of the oxygen concentration in the cell performance. Likewise, the acclimatization period is also studied, and a simple method is proposed to rapidly generate a micro-organism culture capable of producing electricity from wastewater.

2. Methodology

2.1. Substrate and microorganisms

The initial substrate was beverage wastewater, and was collected from influent to the anaerobic digester tank from a beverage factory located in central Taiwan. After collection, the factory wastewater was immediately transferred to the laboratory and stored at 4°C. The pH, COD, conductivity, and TSS of the beverage wastewater are 6.81 ± 0.26, 1,534.16 ± 22.33 (g/L), 1,124 ± 35.22 (m/S), and 58.9 ± 0.24 (g/L), respectively. The above wastewater was directly used as the substrate for a biohydrogen fermenter with heat-treated Li-Min sewage sludge, and the effluents can be used as the substrate in an MFC without any modification.

A mixed colony was obtained as anaerobic digester sludge from the Li-Min wastewater treatment factory, also located in central Taiwan. The colony was propagated in a biological medium containing 20 mM acetate without any heat treatment process.

2.2. Fe_3O_4-modified carbon cloth electrodes

All the modified electrodes were prepared using drop coating technique. For the Fe_3O_4-modified carbon cloth electrode, a mixture of modified ink was prepared by thorough mixing of Fe_3O_4 powder, carbon ink, and cyclohexanone, and the final weight ratio of the suspension mixture was 1:1:8, respectively. 10.0 mL of this mixture was placed onto the bare carbon cloth electrode (3 × 0.5 cm) and allowed to dry in an oven at 60°C for 30 min. For the fuel cell experiments, both cathode and anode were used with

a geometrical surface area of 3.0 cm^2. When not in use, the electrode was kept in a dry condition at room temperature.

2.3. Biohydrogen production

This experiment used Li-Min sewage sludge for 95℃ and 1 h heat treatment to acclimate H_2 production. Its VSS content was 3.22 g/L, and the COD concentration was controlled to 10, 20, and 30 g/L, with a total sugar concentration of 5 g/L. It was much lower than that seen in domestic sludge, and also can be used as the background value. For the purpose of finding the optimal conditions, we used different digestion days of thermophilic aerobic-digested sludge as the substrate and added Endo nutrient formulation for cell culturing in a 37℃ incubator to produce biohydrogen, and thus the best digestion days for optimizing gas production were found. A batch system was used for hydrogen production, and the culture ratio is shown in Table 1.

2.4. MFC system

The MFC experiments were carried out in batch mode using a self-made glass fuel cell model, which was composed of two 250 mL volume-bottom flasks pressed together laterally. The main purpose of this system is to remove the organic material and help produce electricity using micro-organisms. A Nafion 117 cation exchange membrane (180 μm thick, 4.4 cm diameter, Dupont Ltd) was clamped between the windows separating the anode and cathode compartments. Both anode and cathode were Fe_3O_4-modified carbon cloth electrodes (3× 0.5 cm, local company in Taiwan). The cathodic compartment was first filled with 200 mL of a 0.1 M KCl solution with 0.1 M potassium ferricyanide. Another compartment inoculated with organic wastewater from the effluents of biohydrogen fermenter [19]. These batch experiments were operated at 25℃, and 90% of the media was replaced in both cathode and anode for each test. During normal operation, the anode and cathode were connected by means of wires and a resistance. Cell voltage (V) and electrode potentials were measured continuously using a digital multimeter with a 10 Ω external resistor.

2.5. Analytical methods

All chemicals and solvents used in this study were of analytical grade (Seelze, Germany). All chemical solutions were prepared using deionized water (18.3 MΩ) from a Barnstead water purification system, which was also used to clean the samples. The analytical procedures of Standard Methods were used to determine pH, ORP, alkalinity, and VSS concentration of liquid content [20]. Ethanol and VFA were analyzed with a gas chromatograph with a flame ionization detector (Shimadze GC-14, Japan). Biogas volume was determined by a gas meter (Ritter, Germany), and gas composition was analyzed with a gas chromatograph with a thermal conductivity detector (China Chromatograph 8700T, Taiwan). The morphology of the samples was observed and measured by a field emission scanning electron microscope (SEM, HITACHI S4800, Japan). Current and potential measurements in the MFC experiments were carried out using a digital multimeter (Integra 2700 series equipped with 7700 multiplexer, Keithley Instruments, Inc., Cleveland, USA) interfaced to a personal computer. For the determination of the power output, a variable resistance (0–5 kΩ) was used as the external load.

3. Results and discussion

3.1. Biohydrogen production

The experiment was performed with a 100 ml batch reactor filled with 30 ml of beverage wastewater, and the initial beverage wastewater concentration was 20.0 g COD/L. The reactor was purged with helium for 15 min and capped tightly with silicon rubber and aluminum caps to avoid gas leakage. Reactors were then placed in an incubator at 37 ± 1℃.

Table 1
The culture ratio of bio-hydrogen production

Seed	H_2 microflora acclimated from Li-Min sewage sludge	
Substrate	Beverage wastewater	30 mL
Nutrients	Endo formula (concentrated two times)	30 mL
Initial pH	5.5	
Temperature	37℃	
Working volume	60 mL	60 mL

Fig. 1 shows the hydrogen production from beverage wastewaters in batch reactors at 10, 20, and 30 g COD/L concentrations at pH 5.5 and temperature 37 ± 1℃. Hydrogen production was detected and a maximum of 37.3 ml of H_2 was found after 10 d. Hydrogen production increased as initial COD concentration increased (10–30 g/L), producing a maximum accumulated production of 41.3 ml of H_2 after 14 d for the case of the highest initial COD concentration studied (30 g COD/L).

For the biohydrogen batch test, wastewater was used to mix the H_2 microflora, and the batch monitoring test was stopped when biomethane was detected in the GC analysis. The optimal condition was selected at 20 g COD/L with a maximal HY of 1.3 mmol H_2/g TVS and 25.4 mmol H_2/L/d of the hydrogen production rate (HPR) (as shown in Table 2). The biohydrogen production rate is significantly higher than that obtained in the previous studies [21,22]. In order to start the whole process, one batch of the wastewater was first placed in a closed tank without aeration for five days to produce biohydrogen. No wastewater was fed to the system during this conditioning period, so the only substrate available for micro-organisms was that coming from the endogenous metabolism.

The COD degradation was found during the microbial cell operation, suggesting utilization of the carbon source by the biocatalyst for metabolic activity [23]. The COD removal efficiency increased slightly with the increasing organic loading. This is because the organic loading used in this study is lower than that in previous research [24]. The maximum COD removal of 51.4% was obtained in the MFC process.

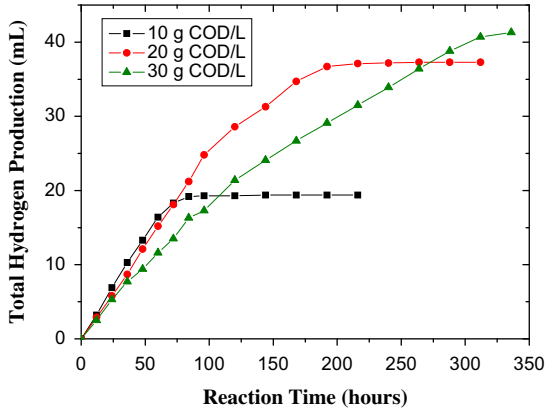

Fig. 1. Hydrogen production using feedstocks with various COD values.

3.2. Electricity production from MFC

The morphology of the carbon cloth, carbon ink with Fe_3O_4, and bacteria on modified electrodes was observed using SEM, with the results showing that the nanostructure of carbon fiber has a diameter of around 10–20 μm (Fig. 2(a)). The carbon fiber can be clearly observed in a low-resolution morphology in each condition. The images of the Fe_3O_4/carbon ink-based carbon fiber (Fig. 2(b) and (c)) also show that the samples have a similar diameter range of 10–20 μm, and the carbon ink can help to connect the carbon fiber and thus enhance conduction. In Fig. 2(c), bacteria can be found on the Fe_3O_4/carbon ink-based carbon cloth. This sample was taken after five days' operation. Fig. 2(c) shows the interface between the microbial cells and the Fe_3O_4-coated surface, which could facilitate efficient electron transfer from the micro-organisms to the electrodes.

Electricity generation in the MFCs was initially examined using the batch cycle operation at an external resistor of 10 Ω [25]. A reproducible cycle of current density was obtained with the Fe_3O_4-modified MFCs after two weeks of microbial cultivation (Fig. 3), indicating the biofilm formation and the bacterial adhesion reached a steady state on the anode electrodes during this experiment. The potential difference across the external resistance reached a maximum of more than 16 mV, approximately 12 h after the start of the experiment, falling to about 50% of its maximum value after 48 h. The current generation was clearly affected by the modifying materials of the anodes. The Fe_3O_4-modified MFC produced a higher current of 0.32 A, which is almost two times greater than that of the bare carbon cloth-MFC. These results demonstrate that the Fe_3O_4 modification of the anode can improve the current generation in MFCs.

The polarization curves were used to confirm the above findings. Although the Fe_3O_4-modified MFCs showed a slight difference in open circuit voltage (V_{oc}), the maximum power density of the Fe_3O_4-MFC improved significantly when compared with the bare carbon cloth-MFC (Fig. 4). Specifically, the Fe_3O_4-modified MFC achieved a maximum power density of 0.055 W/m^2 at the current of 31.6 mV. The COD loading is lower than that found in previous research, and results in the lower power density [24]. As expected, the carbon ink MFC-generated power density of only 0.012 W/m^2 at the current density of 11.6 mV. In addition, the carbon ink MFC-exhibited an overshoot in power production, likely caused by inefficient electricity generation during the polarization test.

Table 2
Comparison of bio-hydrogen production and COD removal efficiency

Feedstock (g COD/L)	Total biogas (mL)	H_2 concentration (%)	H_2 (mL)	HPR (mmol H_2/L/d)	HY (mmol H_2/g TVS)	COD removal efficiency (%)
10	46.2	42	19.4	13.2	0.7	44.6
20	86.7	43	37.3	25.4	1.3	46.3
30	105.9	39	41.3	28.1	1.4	51.8

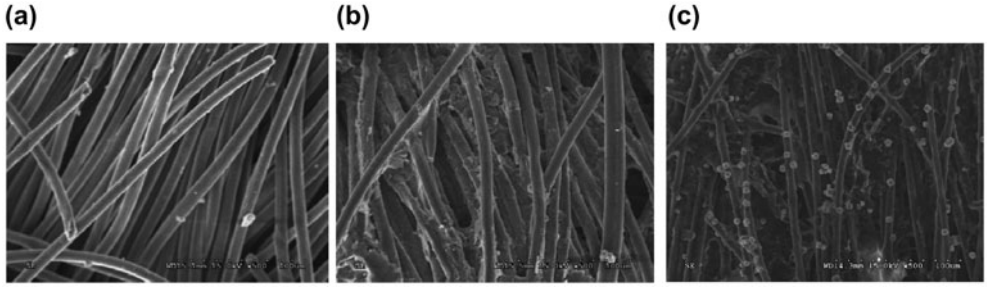

Fig. 2. SEM morphologies of carbon cloth (a), carbon ink with Fe_3O_4 (b), and bacteria (c) on modified electrodes.

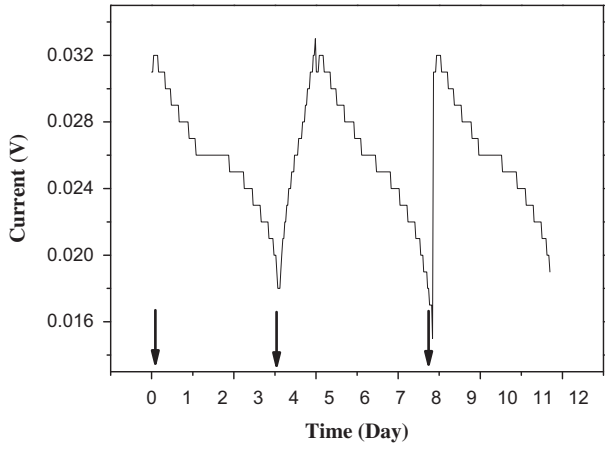

Fig. 3. Cell current as a function of time with an external resistance of 10 Ω.

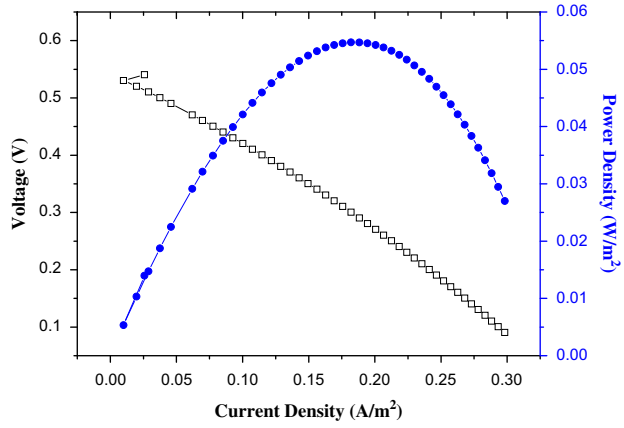

Fig. 4. Polarization curves and power density curves for Fe_3O_4-modified MFC.

4. Conclusion

In summary, carbon ink with an Fe_3O_4 structure was successfully used to modify the anode in a MFC, and significantly improved the MFC performance compared with unmodified carbon cloth and carbon ink anode. The superior electrochemical performance can be ascribed to the synergetic effect of its unique structures, higher surface area, and high conduction in carbon ink, which could provide more active sites for interfacial electrochemical reactions and better biocompatibility.

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