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Fluidized granular activated carbon electrode for efficient microbial electrosynthesis of acetate from carbon dioxide

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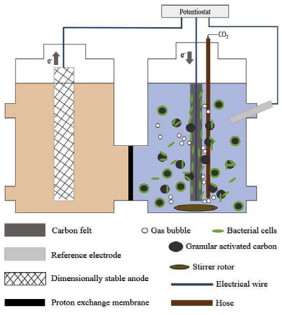
GRAPHICAL ABSTRACT



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ABSTRACT

The electricity-driven bioreduction of carbon dioxide to multi-carbon organic compounds, particularly acetate, has been achieved in microbial electrosynthesis (MES). MES performance can be limited by the amount of cathode surface area available for biofilm formation and slow substrate mass transfer. Here, a fluidized three-dimensional electrode, containing granular activated carbon (GAC) particles, was constructed via MES. The volumetric acetate production rate increased by 2.8 times through MES with 16 g L^{-1} GAC (0.14 g L^{-1} d^{-1}) compared with that of the control (no GAC), and the final acetate concentration reached 3.92 g L^{-1} within 24 days. Electrochemical, scanning electron microscopy, and microbial community analyses suggested that GAC might improve the performance of MES by accelerating direct and indirect (via H_2) electron transfer because GAC could provide a high electrode surface and a favorable mass transport. This study attempted to improve the efficiency of MES and presented promising opportunities for MES scale-up.

1. Introduction

Microbial electrosynthesis (MES) is a promising technology to produce biocommodities from CO_2 with an input of electricity from renewable sources (Lovley, 2011; Lovley and Nevin, 2013; Nevin et al., 2010; Zhang et al., 2013). In this process, electroautotrophic microbes

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can utilize electrons directly or indirectly via H_2 from a cathode to reduce CO_2 (Shin et al., 2017). In comparison with biological photosynthesis and other CO_2 fixation ways, MES has many advantages, such as high transformation efficiency, low cost, and mild reaction conditions (Bajracharya et al., 2017a). MES may also be suitable and effective for the storage of electrical energy, such as solar or wind, in a chemical form (Nevin et al., 2010).

Several pure stains (*Sporomusa, Clostridia and Moorella* sps.) have been reported for metabolic reduction of CO_2 to acetate and other multi-carbon compounds in MES at −0.6 V/Ag/AgCl cathode potential (Aryal et al., 2017; Nevin et al., 2010; Zhang et al., 2013), because of their ability to fix CO_2 via the efficient Wood-Ljungdahl pathway (Nevin et al., 2010). Recently, mixed culture from different sources has also successfully been applied for synthesizing acetate (Marshall et al., 2013; Modestra and Mohan 2017; Jourdin et al., 2015; Patil et al., 2015; Song et al., 2017), butyric acid (Batlle-Vilanova et al., 2017) and isopropanol (Arends et al., 2017). Compared to pure stains, mixed culture offers some merits such as resistance to environmental disturbance, higher biomass and acetate production rate, possibility operate conditions without sterile, and convenient to future applications. However, the mixed culture showed the lower energy recovery efficiency, as the competition of electrons between electrosynthesis and non-electrosynthesis bacteria.

Other important factors for MES, such as electrode material (Bajracharya et al., 2015; Jourdin et al., 2015; Marshall et al., 2013; Song et al., 2018), reactor design (Giddings et al., 2015), membranes (Gildemyn et al., 2017; Xiang et al., 2017), and product separation (Gildemyn et al., 2015; Bajracharya et al., 2017b; Batlle-Vilanova et al., 2017), have been studied. Among these factors, the electrode of MES plays a crucial role in the enhancement of the performance of MES. Many efforts have been devoted to enhancing the bacterial extracellular electrical transfer rate by reducing the activation energy of electron transfer (Nie et al., 2013; Jourdin et al., 2014), incorporating positively charged functional groups (Zhang et al., 2013), and improving biofilm conductivity (Song et al., 2017).

Cathode biomass in a biofilm depends directly on the total effective surface area per volume of a reactor. Limited diffusion and a decreased electron transfer rate occur when biofilms thicken (Borole et al., 2011). As an alternative technique, a three-dimensional electrode process combined with carbon particles has been demonstrated as an effective way to enhance the specific surface area of a working electrode (Fockedey and Lierde, 2002; Xiong et al., 2011; Zhao et al., 2010). Graphite or activated carbon is commonly used as a carbon particle that provides a cost-effective means of creating a high electrode surface area. The maximum acetate concentration of MES remarkably increases when graphite granules are used (Marshall et al., 2013) in a packed bed reactor. However, the irregular shape of carbon particles and the bed porosity can lead to the higher electrical resistance in the MES. In addition, the packed bed could clog with biomass.

In comparison with a packed bed reactor, a fluidized bed reactor has many advantages, such as simple construction, excellent particle mixing effect, no biomass blockage, and a large contact rate between particles and substrates (Tisa et al., 2014). In this study, the fluidized granular activated carbon (GAC) particles as a moving electrode was constructed and its impact on the performance of mixed culture-driven MES was explored. The MES performances with and without the presence of fluidized GAC particles were compared, and the effect of fluidized GAC additive amount on the acetate production rate in the MES was also investigated.

2. Materials and methods

2.1. Materials

GAC with a specific surface area of 900 $m^2\,g^{-1}$ and an average pore diameter of 2.2 nm (Shanghai Activated Carbon Co., Ltd., China) was washed several times with distilled water to remove impurities. After the last wash, GAC was dried at 105 °C for 1 day to achieve a constant weight prior to the experiment.

2.2. Source of microorganisms and MES experiment

An H-type double-chamber reactor made of glass and characterized by an internal volume of 280 ml in both anode and cathode compartments was used in MES. The anode and cathode compartments were separated with a proton exchange membrane (Nafion 117, Dupont Co., USA). In all of the reactors, a titanium mesh with iridium and ruthenium coating (50 mm × 25 mm × 1 mm, length × width × thickness, Baoji Longsheng Nonferrous Metal Co., Ltd., China) was used as a dimensionally stable anode. Carbon felt (50 mm × 50 mm × 5 mm, length × width × thickness) was utilized as a cathode in all of the reactors. In addition, 4, 8, 12, and 16 $g\,L^{-1}$ GAC were added to the cathode chambers of MES-G4, MES-G8, MES-G12, and MES-G16, whereas MES-G0 without GAC was used as the control group. An Ag/AgCl reference electrode was inserted into the bottle close to the cathode. The cathode compartment was filled with growth medium (Song et al., 2017), and the medium used in the anode compartment consisted of 50 $ml\,L^{-1}$ PETC salt solution, 6 $g\,L^{-1}$ NaCl, and 2 $g\,L^{-1}$ KCl. The enrichment of this mixed culture from a previously reported procedure (Song et al., 2017) was used as a microbial inoculum for MES, and 5% (V/V) of the enriched culture was inoculated anoxically into the cathode chamber of all of the MES systems in this study. Then, the cathode chamber was bubbled with a hydrogen-containing gas mixture (CO_2:H_2; 20:80) to promote biofilm growth on the cathode and GAC. A magnetic stirrer was installed in the cathode to ensure mixing uniformity. After 7 days of pre-incubation, a fresh growth medium was used to replace the medium, and the gas phase was switched to 100% CO_2. The cathode of the reactor was equipped with a potentiostat (CHI1000C, Shanghai Chenhua Instrument Co., Ltd.) at −1.05 V (vs Ag/AgCl) for 24 days. No supplemental nutrient was used in the experiment. All of the reactors were maintained at room temperature (25 ± 2 °C).

2.3. Analysis methods

Organic acids were examined with a high-performance liquid chromatograph (HPLC; Agilent Technologies 1260, USA) (Nevin et al., 2008). The surface morphology of the cathode was observed with a scanning electron microscope (SEM; JSM-5900, Japan). Before SEM analysis was conducted, the samples were fixed in 2.5% glutaraldehyde at 4 °C for 4 h, washed thrice in phosphate buffer (0.1 $mol\,L^{-1}$, pH 6.8), dehydrated in a series of ethanol solution (50%, 70%, 80%, 90%, and 100%), and vacuum dried. Finally, SEM was carried out after the samples were coated with Au/Pt. A precision multimeter and data acquisition system (Keithley Instruments 2700, USA) was used to continuously monitor the current. Linear sweep voltammetry (LSV) was performed using a potentiostat (CHI660D, Shanghai Chenhua Instrument Co., Ltd.). The cathode, the anode, and Ag/AgCl were utilized as a working electrode, a counter electrode, and a reference electrode, respectively, and their scanning potential ranged from −400 mV to −1100 mV at a scan rate of 1 $mV\,s^{-1}$. Coulombic efficiency (CE) was calculated as follows: $CE = C_P/C_T \times 100\%$, where C_T is the total coulomb consumption calculated by integrating the area under the current–time curve (i-t curve); C_P is the coulomb in the product, and its calculation formula is $C_P = b \times n \times F$, where b is the number of electrons in the product (8 $eq\,mol^{-1}$); n is the number of moles of the product; and F is the Faraday constant (96,485 $C\,mol^{-1}$).

2.4. Microbial community

Samples were collected from an inoculum, planktonic cells, and a biofilm on the cathode in MES-G0. Most of the planktonic cells were