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Short communication

Electricity generation of microbial fuel cell with waterproof breathable membrane cathode

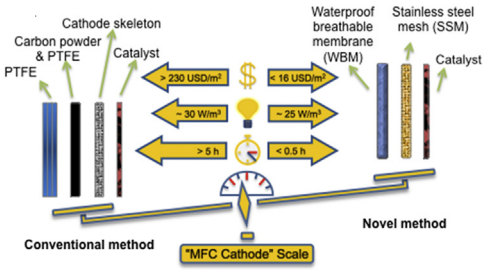
Defeng Xing [a, b, *], Yu Tang [a, b], Xiaoxue Mei [a, b], Bingfeng Liu [a, b]

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[b] School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- A fast and inexpensive method of making cathode was developed.
- Cathode was fabricated via assembling stainless steel mesh with waterproof breathable membrane.
- SSM/Pt@WBM showed better stability than Pt@SSM/WBM after long-term operation.

GRAPHICAL ABSTRACT



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ABSTRACT

Simplification of fabrication and reduction of capital cost are important for scale-up and application of microbial electrochemical systems (MES). A fast and inexpensive method of making cathode was developed via assembling stainless steel mesh (SSM) with waterproof breathable membrane (WBM). Three assemble types of cathodes were fabricated; Pt@SSM/WBM (SSM as cathode skeleton, WBM as diffusion layer, platinum (Pt) catalyst applied on SSM), SSM/Pt@WBM and Pt@WBM. SSM/Pt@WBM cathode showed relatively preferable with long-term stability and favorable power output (24.7 W/m^3). Compared to conventional cathode fabrication, air-cathode was made for 0.5 h. The results indicated that the novel fabrication method could remarkably reduce capital cost and simplify fabrication procedures with a comparable power output, making MFC more prospective for future application.

1. Introduction

Microbial fuel cells (MFCs) are devices that use bacteria as catalyst to oxidize a wide range of biodegradable matters with simultaneous bioenergy generation and have become one promising technology for wastewater treatment [1,2]. To date, the main query and discussion on this attractive technology for future application focuses on increase of electron transfer and reduction of the capital cost [3,4]. Single-chamber air-cathode MFC, using readily available air as sustainable oxidant, has gradually become the preferential choice due to its practicability, sustainability and high power density [5–8].

Components of conventional cathode fabrication including carbon cloth (CC), platinum catalyst, polytetrafluoroethylene (PTFE), Nafion binder are widely used in an air-cathode MFC system regardless of extremely high expense [9]. To reduce the capital cost

* Corresponding author. School of Municipal and Environmental Engineering, Harbin Institute of Technology, 73 Huanghe Road, Nangang District, Harbin, Heilongjiang Province 150090, China.
E-mail addresses: dxing@hit.edu.cn (D. Xing), 996832407@qq.com (Y. Tang), 835421853@qq.com (X. Mei), lbf@hit.edu.cn (B. Liu).

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for future application, some cost-effective substitutes of catalyst, diffusion layer, cathode and anode materials etc. were investigated. Non-noble metal, metal oxides and carbon could be used as an alternative to platinum (Pt) catalyst in MFCs [10]. The carbon cloth as base material of the cathode has advantages of good conductivity, air permeability and excellent corrosion resistance, but imposes cost on MFC systems. In recent years, substitutes such as carbon felt, carbon mesh, stainless steel mesh (SSM), graphite brush, etc. have been tested and shown great performance as electrode materials [11–15].

Fabricating cathode is one of the most important process for constructing MFC, and it is as well in continual trial and improvement. An ultrafiltration hydrophilic tubular membrane coated with graphite and Co-tetra-methylphenylporphyrin (CoTMPP) was used as cathode instead of the conventional cathode structure in the previous study [16]. Similarly, anion (AEM) and cation (CEM) exchange membranes were tried as supporting material with the same catalyst [17]. Using carbon mesh instead of carbon cloth, cathodes with other diffusion layers such as poly (dimethylsiloxane) (PDMS), Goretex cloth etc. were as well tested [12,18]. These cathode fabrication methods differed greatly from the conventional way, saving capital cost and simultaneously showing favorable power generation. However, the materials used in the procedures were still not quite cheap, and the skeleton materials (e.g. AEM, CEM and carbon mesh) were not firm enough for supporting large cathode when scaling up MFC. Serving as electrode material, SSM showed not only similar superiority as CC but also had strong structure, which was considered rather important for further scaling up.

As previously described, another approach for making cathode was investigated by applying polydimethylsiloxane (PDMS) (diffusion layer) onto SSM with series of operation and showed competitive performance [19]. An one-step method was developed by applying polypyrrole/anthraquinone-2-sulfonate (PPy/AQS) onto SSM via electropolymerization [20]. In spite of low cost and acceptable performance, the complexity of methods with multiple steps was still exposed in these studies as another prospective challenge. In this study, a fast, uncomplicated and inexpensive method for making cathode was developed by assembling SSM with waterproof breathable membrane (WBM). The electrochemical performances of assemble and conventional fabrication methods were compared.

2. Materials and methods

2.1. MFC configuration and operation

Single-chamber air-cathode MFCs (cylindrical chamber, 28 ml) with different types of cathode (7 cm^2 of surface area) were constructed. The cathodes were fabricated via assembling stainless steel mesh (SSM, type SUS304) with building-used waterproof breathable membrane (WBM) that was thermally laminated by two outer layers of polypropylene and an inner layer of microporous polyolefin membrane) (BREAWARF, Ningbo SHANQUAN Building Material Co., Ltd., CHN) (detailed description in Supporting Information). For the first type of cathode, SSM (mesh of No. 40, 60 and 80) spread with Pt catalyst (0.5 mg/cm^2) was assembled with WBM as diffusion layer (designated as Pt@SSM40/WBM, Pt@SSM60/WBM and Pt@SSM80/WBM). For the second type of cathode, WBM spread with Pt catalyst was assembled with SSM (mesh of No. 40) as the current collector (SSM40/Pt@WBM). For third type of cathode, Pt catalyst was directly spread on WBM without SSM (Pt@WBM) (Figure S1 and Figure S2 in Supporting Information). For control tests, the cathodes were made with one carbon/PTFE layer and three diffusion layers of PTFE based on carbon cloth (CC, type B, E-TEK, 30% wet-proofed) (Pt@CC/PTFE) and SSM (Pt@SSM40/PTFE) spread with 0.5 mg/cm^2 Pt catalyst as previous descriptions [9,21,22]. All the anodes were identically made of titanium-core graphite brushes (2.5 cm length × 2.5 cm outer diameter) as previous described [15].

All MFCs were fed with nutrient solution, which contained 2 g sodium acetate, 11.55 g $Na_2HPO_4 \cdot 12H_2O$, 2.77 g $NaH_2PO_4 \cdot 2H_2O$, 0.31 g NH_4Cl and 0.13 g KCl (per liter of DI water). The activated sludge from the secondary sedimentation tank of a local wastewater treatment plant (Harbin, China) was mixed with 2 g/L sodium acetate in volume ratio of 1:5, and was then added into the reactors as inoculum. All MFCs were enriched and operated with an external resistor of 1000 Ω in fed-batch mode in a temperature-controlled room at 30 °C.

2.2. Calculation and analyses

The voltage across a 1000 Ω resistor in external circuit of the MFC was monitored at 30 min intervals using multichannel data acquisition system (Model 2700 with 7702 module, Keithly Instruments Inc., USA) connected to a personal computer via PCI interface. Then the current and power were calculated as previous description [7]. Polarization and power density curves were measured by changing external resistors from 2000 to 75 Ω.

3. Results and discussion

3.1. Electrochemical performance and stability

Cathodes fabricated according to the method by eliminating carbon/PTFE layer, replacing diffusion layers with WBM, and brushing catalyst on SSM (Pt@SSM/WBM) were based on SSM with mesh number of 40 (Pt@SSM40/WBM), 60 (Pt@SSM60/WBM) and 80 (Pt@SSM80/WBM), respectively (Fig. 1). In contrast to Pt@SSM40/PTFE, Pt@SSM40/WBM showed a slightly lower power density of ~27.0 W/m^3, while power densities of Pt@SSM60/WBM (~35.4 W/m^3) and Pt@SSM80/WBM (~36.7 W/m^3) were respectively 16.1% and 20.3% higher than that of Pt@SSM40/PTFE (Fig. 1a). For two control groups, the power density of MFC (~927.5 mW/m^2, ~30.5 W/m^3) with Pt@SSM40/PTFE cathode was similar with that obtained by MFC with Pt@CC/PTFE cathode (~912.3 mW/m^2, ~30.0 W/m^3 (Fig. 1a), which were still acceptable in comparison with previous studies [14,23]. The maximum power density of Pt@SSM80/WBM was slightly lower than that obtained in the MFCs with cathode coating of PDMS (47 W/m^3) [19], presumably due to different operation conditions and configuration of MFCs. Pt@SSM80/WBM and Pt@SSM60/WBM showed higher voltage outputs versus current densities with open circuit voltage (OCV) of 775 mV and 747 mV (Fig. 1b). Other cathodes obtained slightly different voltage curves with OCV of 723–736 mV except Pt@WBM with OCV of 719 mV. The chemical oxygen demand (COD) removal of all MFCs ranged from 93.8% to 96.6% and no large difference could be observed among them (Figure S3 in Supporting Information).

Although Pt@SSM40/PTFE groups showed favorable power generation in the early period, its power output stability unstoppably became increasingly serious as time went by. During long term operation, the MFCs (SSM40 Later) could merely produce a maximum power density of 6.5 W/m^3 power at later stage, which was only one quarter of that produced by the same reactors (27.0 W/m^3, SSM40 Early) (Figure S4 in Supporting Information), and the variation on power generation over time happened similarly to Pt@SSM60/WBM and Pt@SSM80/WBM as well. In order to overcome the instability weakness on account of choosing SSM as improper catalyst carrier, some tiny transformation was made