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Improvement of microbial fuel cell cathodes using cost-effective polyvinylidene fluoride

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HIGHLIGHTS

- Polyvinylidene fluoride (PVDF) was tested as a new and effective diffusion layer for cathode.
- PVDF cathode produced higher power density and CE than PTFE cathode.
- Cathode with 4 PVDF DLs had an improved three-phase interface and produced the largest MPD.

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ABSTRACT

In this study polyvinylidene fluoride (PVDF) is investigated as an alternative to polytetrafluoroethylene (PTFE) for air-cathode diffusion layers (DLs) in microbial fuel cells (MFCs) for the improvement of MFC power generation. It is found that the cathode fabricated with PVDF achieves a higher maximum power density (MPD) than a PTFE cathode. Successive PVDF or PVDF/carbon black DLs are applied on the base layers in order to optimize cathode performance. The results show significant improvements in such performances as the coulombic efficiency (CE), MPD, and water loss. In electrochemical tests, the cathode coated with four PVDF DLs has the largest current response at a given applied potential, yielding the highest MPD of 0.123 mW cm^{-2} (normalized to the projected cathode surface area) and largest CE (10.7%) in the MFC test. Carbon black is added to the DLs in order to test its effect on the MFC power generation. Cathodes made from pure PVDF DLs perform better than those containing PVDF/carbon black DLs in electrochemical and MFC tests. In addition, a smaller MFC (28 mL) produces a much higher MPD than a larger MFC (700 mL), resulting in an increase in the CE.

1. Introduction

As a promising environmentally friendly technology, microbial fuel cells (MFCs) have attracted increasing attention in areas of wastewater treatment and electricity generation [1–4]. Various oxidants, such as ferricyanide [5,6] and permanganate [7], have been applied as electron acceptors in MFCs. However, oxygen is considered to be the most suitable electron acceptor in wastewater treatment because of its free availability, sustainability, and non-pollutive properties. Therefore, due to their simple structure and direct use of oxygen in ambient air, devices such as air-cathode MFCs have the greatest potential in practical applications involving wastewater treatment [8].

The air-cathode can affect the power production of an MFC due to the poor kinetics of oxygen reduction at the cathode catalytic sites under typical MFC operating conditions (ambient temperature and neutral pH) [9]. Moreover, oxygen transport through the cathode is restricted because of the porous structure of the cathode and low solubility and diffusivity of oxygen in water. The cathodic performance and cathode surface area have been proven to be the two most important factors affecting maximum power densities (MPDs) in many MFCs [10–14]. On the other hand, the expense of the cathode accounts for a large part of the complete MFC cost, which hinders the practical application of MFC technologies. Therefore, exploiting cost-effective cathodic materials and designing efficient cathodes for improving MFC performance are two main challenges still to be met.

Currently, most air-cathodes are made on a base of carbon cloth, using polytetrafluoroethylene (PTFE) as diffusion layers (DLs) on the air-facing side of the cathodes to control oxygen intrusion and

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eliminate water loss [1,9]. By this approach, the performances of MFCs, in terms of increasing coulombic efficiencies (CEs) and MPDs as well as reducing water losses through the cathodes, can be greatly improved [9,15,16]. However, a high temperature of 370 °C must be supplied to meet the requirements of cathode fabrication with PTFE, which leads to a large waste of energy [9].

An alternative material with similar chemical and physical properties to PTFE is expected to further improve the power production and reduce the expense of cathodes. Polyvinylidene fluoride (PVDF) is a highly non-reactive and pure thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. It is universally used in the fields of chemistry, semiconductors, medicine, defense technology, and lithium ion batteries [17,18]. The electron cloud in the monomer molecules of PVDF distributes symmetrically, making PVDF highly hydrophobic and waterproof. More importantly, the PVDF has a lower melting point, which should make it possible to reduce the temperature during the cathode fabrication process. To test this hypothesis, we examined the use of this new polymer in cathodes and investigated their performances in terms of water loss and power generation. We varied the amount of PVDF applied on the carbon-supporting material to optimize cathode performance. To our knowledge, this is the first report using PVDF in DLs of air-cathodes for MFCs.

2. Materials and methods

2.1. Cathodes fabrication

The newly developed cathodes applied carbon cloth (CC, HCP331N, Hesen, China) as the supporting material. The fabrication procedure was modified from Cheng's method [9]. The PVDF/carbon base layer was prepared by applying a mixture of carbon black powder (Alfa Aesar, USA) and PVDF solution (10 μL 18 wt % PVDF per mg of carbon black power) onto the air-facing side of carbon cloth, air-drying at room temperature for 2 h, followed by heating at 250 °C for 20 min. Carbon loading in the base layer was 1.56 mg cm^{-2}. Multiple PVDF layers containing PVDF solution (18 wt %) were coated on top of base layer (0.9 mg cm^{-2} of PVDF for every coating), followed by air-drying at room temperature and heating at 250 °C for 5 min. The cathode DLs were fabricated by applying PVDF layers for 2, 4, 6, 8 times, producing the cathodes of L2, L4, L6 and L8. PVDF/carbon black layers (one to four layers) were applied on top of the previous PVDF/carbon base layer on carbon cloth at the same mass loading as the base layer, producing another four cathodes of C-L1, C-L2, C-L3 and C-L4. After each layer has been applied, the cathodes were air-dried and heated at 250 °C for 5 min. Carbon cloth cathodes with four PTFE DLs were also prepared following previously described method [9]. When the fabrication of DLs finished, Pt catalyst (0.2 mg cm^{-2}, 40% Pt Hesen, China) was then applied to the water-facing side of all cathodes as previously described [19].

2.2. MFC construction and operation

Cylindrical Plexiglas tube single-chamber MFCs (height: 12 cm, diameter: 9 cm, working volume: 700 mL) with air-cathodes were used in this study. Graphite felt (5 cm × 5 cm × 0.5 cm, Beijing Sanye Carbon Co., Ltd) was used as the anode electrode. After being soaked in acetone for 4 h and rinsed with deionized water, the graphite felt was heated at 400 °C for 1 h. These anodes were fixed by titanium wire in the center of the anode chambers, orienting parallel to cathodes. The cathodes with 4 cm in diameter were clamped by flanges. Titanium sheet was used to connect the circuit. The L2 cathode was also examined in a smaller single chamber cubic-shaped MFC (anode chamber with 4 cm in length and 3 cm in diameter) to compare the power production performance with the larger MFC (700 mL).

Each MFC reactor was inoculated using mixed cultures enriched from cracked cereals, which were dominated by *Clostridium pasteurianum* [6]. The MFCs were initially inoculated with a mixture (1:4 in volume) of inoculum and nutrient medium before stable voltages were obtained. When biofilm formed on the anode surface, the solution was switched to only nutrient medium. Nutrient medium (per liter) contained: sucrose, 1000 mg; NH_4HCO_3, 500 mg; Na_2CO_3, 2000 mg; $NaH_2PO_4\cdot 2H_2O$, 3978 mg; $Na_2HPO_4\cdot 12H_2O$, 8771 mg; K_2HPO_4, 125 mg; $MgCl_2\cdot 6H_2O$, 100 mg; trace minerals (12.5 mL L^{-1}) and vitamins (5 mL L^{-1}) [20]. The initial COD and pH of the anolyte were 1122 mg L^{-1} and 7.70, respectively. MFCs were operated in fed-batch mode at 35 °C.

2.3. Analytics and calculation

Voltage (E) across the external resistor (1000 Ω, except as noted) in the MFC circuit was continuously measured at 5 min intervals using a data acquisition system (CT-3008-5V50 mA-S4, Xinwei, China). Current (I) was calculated by $I = E/R_e$, where R_e represents the external resistance; power (P) was calculated as $P = IE$ as previously described [21]. External resistances were changed from 1000 to 50 Ω in decreasing order, with every 30 min for each external resistance, in order that the polarization and power density curves of the larger MFCs can be obtained. For the smaller MFC, each resistor was used for a full fed-batch cycle. The CE was calculated as CE (%) $= C_p/C_t \times 100\%$, where C_p is produced coulombs that calculated by integrating the current over time, and C_t is the theoretical amount of coulombs based on COD removal [21]. Overall energy recovery was calculated as NER $= E_p/V_a$ (or COD), where E_p (kWh), is the produced total energy calculated by integrating the power over time, V_a is the anode liquid volume and COD is the removed COD within a batch operation.

Electrochemical property and impedance behavior of the cathodes were studied by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (CHI 604E, ChenHua Instruments Co., Ltd., Shanghai, China). LSV test was conducted in the absence of bacteria and substrate. A three-electrode system was used for measurements, consisting of a working electrode (cathode with 12.56 cm^2 projected surface area), a counter electrode (Pt wire) and an Ag/AgCl reference electrode (218, Shanghai REX Instrument Factory). Potential was scanned from 0.3 to −0.3 V (vs. Ag/AgCl electrode) with scan rate of −1 mV s^{-1}.

EIS tests were performed at the end of a batch operation and conducted at polarized conditions of 0 V, −0.1 V, and −0.2 V (vs. Ag/AgCl), which were similar to the operating potentials of the cathodes in MFCs, over a frequency range of 100 kHz to 10 mHz with a sinusoidal perturbation of 10 mV amplitude [10]. EIS is a useful electrochemical technology that can be employed to measure the internal resistance (R_{int}) of the cathode [22,23]. Total cathode resistance, including charge transfer resistance (R_{ct}), diffusion resistance (R_d) and solution resistance (R_s), were determined by fitting and simulating the measured impedance data to an equivalent electrical circuit using Zview 2.0 software.

Oxygen permeability of a cathode was calculated in terms of oxygen transfer coefficient (k) as previous report [9]. Oxygen concentrations were continuously measured at 30 min intervals for 5 h using a dissolved oxygen probe (OHAUS STARTER 300D, USA), which was fixed in the center of the anode chamber filled with oxygen-free deionized water.