Using ammonium bicarbonate as pore former in activated carbon catalyst layer to enhance performance of air cathode microbial fuel cell

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HIGHLIGHTS

- Porosity increased by addition of NH_4HCO_3 as pore former.
- The maximum power density was enhanced by 33% with pore former ratio of 0.2.
- Charge transfer resistance decreased by 44%.
- Exchange current density improved by 2.4 times.
- Catalyst layer with smaller pores increased oxygen reaction sites.

ARTICLE INFO

ABSTRACT

The rolling catalyst layers in air cathode microbial fuel cells (MFCs) are prepared by introducing NH_4HCO_3 as pore former (PF) with four PF/activated carbon mass ratios of 0.1, 0.2, 0.3 and 1.0. The maximum power density of 892 ± 8 mW m^{-2} is obtained by cathodes with the mass ratio of 0.2, which is 33% higher than that of the control reactor (without PF, 671 ± 22 mW m^{-2}). Pore analysis indicates the porosity increases by 38% and the major pore range concentrates between 0.5 μm–0.8 μm which likely facilitates to enrich the active reaction sites compared to 0.8 μm–3.0 μm in the control and other PF-cathodes. In addition, pore structure endows the cathode improved exchange current density by 2.4 times and decreased charge transfer resistance by 44%, which are the essential reasons to enhance the oxygen reduction. These results show that addition of NH_4HCO_3 proves an effective way to change the porosity and pore distribution of catalyst layers and then enhance the MFC performance.

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1. Introduction

Microbial fuel cells (MFCs) can generate electricity by decomposing organic or inorganic matters in wastewater [1–3]. Exoelectrogenic microorganisms are enriched on anode surface and metabolizes to release electrons [4,5] which transfer to the cathode through an external circuit. Chemicals, such as ferricyanide [6], permanganate [7] and oxygen [8] can be used as electron acceptors at the cathode chamber, together react with the protons transported from anode chamber to maintain the whole circuit.

Air cathode using the most cost-effective oxygen as exhaustless electron acceptor is an important cathode type. It is proved that factors such as the catalyst types, the binder materials as well as the cathode structures can affect the performance of the air cathode [9–11]. Traditional catalyst Pt has a higher oxygen reduction reaction (ORR) rate, however, in addition to the expensive cost, Pt catalyst is easily poisoned by some common anions like sulfide in wastewater [12,13] and electrode reactions are seriously interfered in this case.

In recent years, MFCs with non-metal catalysts, such as carbon nanotubes [14], carbon foam [15], and nitrogen-doped carbon powders [16] attract a lot of attentions and obtain power density comparable to that of Pt catalyst. Activated carbon catalyst with Ni mesh matrix output the maximum power density of 1220 ± 46 mW m^{-2} compared to 1060 mW m^{-2} obtained by Pt due

to higher specific surface areas [17]. VITO graphite cathode with metallic mesh current collector increased maximum power density by 28 times to the Pt (loading rate of 0.15 mg cm^{-2}) in MFC [18]. Previous reports also indicated the comparable catalytic activity of activated carbon (1310 ± 70 mW m^{-2}) to Pt (1295 ± 13 mW m^{-2}) [19], and activated carbon mixed with carbon black (1560 ± 40 mW m^{-2}) to Pt (1640 ± 10 mW m^{-2}) [20]. More recently, the rolling air-cathode [21] with advantages of much lower cost and larger scale displayed an excellent performance because of abundant pores in catalyst layers [22,23] which was comprised by activated carbon and hydrophobic polytetrafluorethylene (PTFE). Previous studies demonstrate electrode performances are improved after adding pore former (PF) due to reduced mass transfer resistance [24,25], increased the electrochemical active area [26] and considerable triple phase boundary for catalytic reaction [27]. Porous structure of membrane electrode assembly can be modulated by introducing PF in the catalyst layer, in most cases, ammonium salt has been generally used as PF due to lower thermolysis temperature and higher solubility to enhance the performance of proton exchange membrane fuel cells and direct methanol fuel cells [24—26] but barely reports in MFCs.

In this paper, we applied NH_4HCO_3 as PF to improve the electrochemical activities of carbon catalyst layer. Various pore size distributions in catalyst layers were fabricated by mixing activated carbon with four different content of NH_4HCO_3. The surface morphology and internal pore distribution of the catalyst layers were measured by scanning electron microscope and mercury intrusion porosimetry. The exchange current density and internal resistance of cathodes were also investigated to determine the effect of PF on cathode electrochemical activities and MFC performance.

2. Materials and methods

2.1. Cathode preparation

The cathodes were prepared by rolling gas diffusion layer and catalyst layer on both side of stainless steel mesh (60-mesh) as described by Dong et al. [21,23]. Carbon black (Hesen Electrical Co., Ltd, Shanghai, China) and PTFE (60 wt %, Hesen, Electrical Co., Ltd, Shanghai, China) with a mass ratio of 3:7 used as gas diffusion layer were firstly agitated to form a paste. After rolling the paste into a film with 0.35 mm thickness, the gas diffusion film was rolled on one side of stainless steel mesh and then sintered at 340 °C for 25 min. Activated carbon powder (Carbosino Material Co., Ltd, Shanghai, China) was weighed corresponding to 0.06 g for every 1 cm^2 of catalyst layer, NH_4HCO_3 was then added into carbon powder with four mass ratios of NH_4HCO_3: activated carbon = 0 (denoted as control), 0.1 (N/C 0.1), 0.2 (N/C 0.2), 0.3 (N/C 0.3) and 1.0 (N/C 1.0). The mixture was stirred with PTFE binder thoroughly by ultrasonic agitation to form catalyst paste which was further rolled to be a film. After rolling the catalyst layer onto another side of stainless steel mesh, the prepared cathodes were heated at 160 °C in a muffle furnace to remove PF and finally cut into circles with 4 cm diameter for use.

2.2. MFCs setup and operation

The cube-shaped, single chamber MFCs were constructed by placing anode and cathode on opposite sides in a plastic (Plexiglas) cylindrical chamber with 4 cm in length by 3 cm in diameter (liquid volume of 28 mL, projected surface area of the cathode of 7 cm^2) as previously reported [28]. All anodes were carbon fiber brush pretreated by heating 30 min at 450 °C [29]. The prepared electrodes

with different PF content were used as MFC cathodes while PF-free cathode was used as the control.

All MFCs were inoculated with 20% domestic wastewater collected from a municipal pipe network (Harbin, China) and 80% medium which contained glucose (1 g L^{-1}), 50 mM phosphate buffer solution, vitamins (5 mL L^{-1}) and minerals (12.5 mL L^{-1}) prepared as described [30]. The medium was replaced when the voltage decreased below 50 mV. All reactors were operated in duplicate in fed-batch mode at 30 °C with external resistance of 1000 Ω.

2.3. Morphology and pore structure analysis

The surface morphology of the cathode was examined by scanning electron microscope (SEM, S-4700, Hitachi Ltd.) equipped with energy dispersive X-ray spectrum (EDX). The internal porous structure in catalyst layers was obtained with mercury-intrusion porosimetry. Porosity and pore distribution were calculated using a pore-size analyzer (Autopore IV 9500, Micromeritics Instrument, USA) based on the amount of mercury penetration under applied pressure which included pores from 3 nm to 400 μm.

2.4. Electrochemical analysis

All electrochemical activities of cathodes were conducted by Auto Lab PGSTAT128N (Metrohm, Swiss) in an abiotic electrochemical cell with 50 mM phosphate buffer solution. Air cathode (projected surface area of 7 cm^2) and Pt sheet (1 cm^2) were used as the working electrode and the counter electrode while an Ag/AgCl (saturated KCl, +197 mV versus standard hydrogen electrode; SHE) reference electrode was selected.

Tafel plot was recorded by sweeping the overpotential ($|\eta|$) from 0 to 100 mV at 1 mV s^{-1}, where $\eta = 0$ is the open circuit potential of the cathode versus Ag/AgCl reference electrode [31]. Electrochemical impedance spectroscopy (EIS) was carried out at cathode potential of −0.1 V over a frequency range of 100 kHz to 10 mHz with the amplitude of 10 mV. The experimental data are fitted into an equivalent circuit (Fig. S1) (Zsimpwin software 3.10) with the assumption that the cathode reaction is affected by reaction kinetics and mass diffusion, the component R_s represents for solution resistance, R_{ct} for charge transfer resistance, Q for constant-phase element which describes the imperfect capacitor of double layer, and Z_w for diffusion resistance [32].

2.5. Calculations

The voltages across external resistor were recorded every 30 min using a data acquisition board (PISO-813, ICP DAS CO., Ltd.) connected to a personal computer. Power density and polarization curves were obtained by varying the external resistor over a range from 1000 to 50 Ω. Current density was calculated from $I = U/RA$, and power density obtained with $P = U^2/RA$, where U (V) is the voltage, R (Ω) is the external resistance, and A (m^2) is the projected surface area of the cathode. Anode and cathode potentials were measured using Ag/AgCl as reference electrode. The coulombic efficiencies (CEs) were calculated based on COD removal [33].

Oxygen permeability of cathode was characterized by mass transfer coefficient as previously described [34,35] and calculated based on formula (1)

$$k = -\frac{v}{At} \cdot \ln\left[\frac{Cs - C}{Cs}\right] \quad (1)$$

where v is the volume of the MFC reactor, A the cross-sectional area of cathode, C the oxygen concentration in the solution at time t