Journal of Power Sources 272 (2014) 895–899

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Bifunctional quaternary ammonium compounds to inhibit biofilm growth and enhance performance for activated carbon air-cathode in microbial fuel cells

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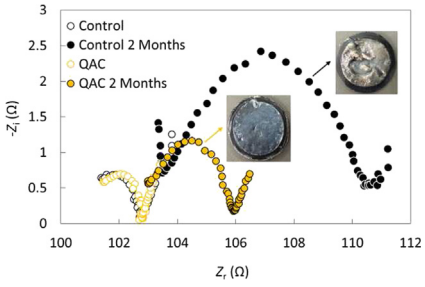
HIGHLIGHTS

- Bifunctional QAC was modified to activated carbon by forced evaporation.
- The maximum power density increased by 17% after QAC modification.
- The growth of cathodic biofilm was significantly inhibited after QAC modification.
- The decay of power density decreased from 31 to 21% by the antibacterial QAC.
- QAC epoxy clogged pores in catalyst layer and decreased the cathodic performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form
28 August 2014
Accepted 2 September 2014
Available online 16 September 2014

Keywords:
Microbial fuel cells
Quaternary ammonium compounds
Biofilm inhibition
Anion transfer

ABSTRACT

The slow diffusion of hydroxyl out of the catalyst layer as well as the biofouling on the surface of cathode are two problems affecting power for membrane-less air-cathode microbial fuel cells (MFCs). In order to solve both of them simultaneously, here we simply modify activated carbon air-cathode using a bifunctional quaternary ammonium compound (QAC) by forced evaporation. The maximum power density reaches 1041 ± 12 mW m^{-2} in an unbuffered medium (0.5 g L^{-1} NaCl), which is 17% higher than the control, probably due to the accelerated anion transport in the catalyst layer. After 2 months, the protein content reduced by a factor of 26 and the power density increases by 33%, indicating that the QAC modification can effectively inhibit the growth of cathodic biofilm and improve the stability of performance. The addition of NaOH and QAC epoxy have a negative effect on power production due to the clogging of pores in catalyst layer.

1. Introduction

As a green and promising technology, microbial fuel cell (MFC) is able to convert waste biomass into electricity directly. However, the power density of MFC is limited by the oxygen reduction reaction (ORR) performance of the cathode [1,2]. Compared with cathodes

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http://dx.doi.org/10.1016/j.jpowsour.2014.09.008
0378-7753/

submerged in water, the air-cathode is an advanced design that can substantially decrease the operational cost by supplying oxygen through the passive diffusion of air. However, precious metals such as Pt are usually needed to decrease the overpotential of ORR and achieve a high power output [3,4], which restrict the future application of MFCs in wastewater treatment. To solve this problem, recently, activated carbon (AC) is demonstrated as the substitute of Pt with a comparable power output [5].

The performance of AC air-cathode is mainly limited by the activation compared to Pt cathode [6] and OH^- concentration overpotentials, which can be alleviated by both increasing the ORR activity of AC powder and accelerating anion transport in the catalyst layer [7]. It was found that ORR electron transfer numbers of different commercially available ACs made from coal, peat, coconut shell, hardwood and phenolic resin were varied from 2.1 (hardwood-based) to 3.6 (peat-based) with a corresponding power density varied from 630 to 1620 mW m^{-2} [6]. After a simple pretreatment on AC powder by KOH solution to increase active sites for ORR, the maximum power density can be increased by 16% [8]. Different from above works, the problem of OH^- transport in the catalyst layer was recently confirmed, which attracts increasing attentions [9]. According to the calculation based on potential loss of the Pt/C air-cathode, Popat et al. found that the concentration of H^+ in the catalyst layer was zero when the solution pH is neutral, so that the ORR for MFC cathode is $2H_2O + 4e^- + O_2 = 4OH^-$ [9]. Both the addition of anion exchange resin and in-situ anchoring of quaternary ammonium compound (QAC) had been demonstrated to be effective to increase the power density by decreasing the local pH in catalyst layers, with a maximum power density up to 2781 ± 36 mW m^{-2} [10].

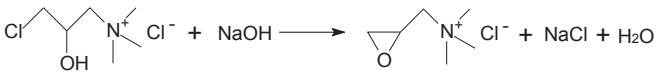
The removal of membrane from MFCs increased the maximum power density by 47% [11]. However, these membrane-less system usually suffers from the increase of internal resistance due to the forming of biofilm on the surface of air-cathode. Based on the analysis using microelectrodes, Yuan et al. found that the pH increased from 9.4 ± 0.3 to 10.0 ± 0.3 when the surface of catalyst layer was covered by biofilm in buffered system, indicating that the OH^- transport was seriously inhibited [12]. Silver nanoparticles, reported as a bifunctional precious metal material, had been applied to the catalyst layer in order to inhibit the growth of biofilm on the cathode and decrease the activation overpotential of ORR [13].

In order to simultaneous inhibit the growth of cathodic biofilm and accelerate OH^- transport in the catalyst layer, we simply added QAC to the catalyst layer by forced evaporation. Electrochemical performance as well as biomass growth were investigated after 2 months of operation.

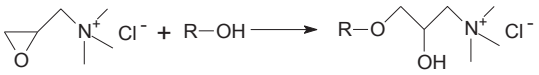
2. Materials and methods

2.1. Preparation of air-cathodes

Rolling pressed AC air-cathodes were prepared according to the procedure reported by our group [14]. The catalyst layer was made of activated carbon (Xinsen Carbon Co. Ltd., Fujian, China) and Polytetrafluoroethylene (PTFE) emulsion (60 wt%, Hesen, Shanghai, China) with an optimized mass ratio of 6:1 [15]. The gas diffusion layer was made of carbon black and PTFE, with stainless steel meshes (Type 304N, 60 meshes, Detiannuo Commercial Trade Co. Ltd., Tianjin, China) as the current collector. For the QAC modified cathode (marked as QAC), 153 μL of QAC solution ($C_6H_{15}Cl_2NO$, 69%, Dongying J&M Chemical Co., Ltd, Shandong, China) per gram AC was added in ethanol during the stirring of AC and PTFE at 80 °C water bath, so that all the QAC accessed into AC by forced evaporation. In order to enhance the anchoring of quaternary ammonium to AC, additional 33 mg NaOH per gram AC was also added to ethanol to ensure the reactions listed in Eq. (1) and (2) (QAC-NaOH). For QACE and QACE-NaOH, QAC was substituted by the epoxy intermediate in Eq. (2) ($C_6H_{14}ClNO$, 95%, Dongying J&M Chemical Co., Ltd, Shandong, China) with a dose of 167 μg per gram AC based on the same molarity of quaternary ammonium as QAC. Each cathode was prepared in triplicate. The unmodified AC cathode was used as the control. Before each measurement, cathodes were soaked in 0.5 g L^{-1} of NaCl solution for at least 12 h.



(1)



(2)

2.2. MFC configuration and operation

Single chambered membrane-less cubic MFCs were constructed with a total volume of 28 mL as described previously [11]. Carbon fiber brush cleaned by acetone was employed as anodes [16]. All MFCs were inoculated by the effluent from an MFC operated over 2 years. They were pre-acclimated for 2 months using unmodified AC air-cathodes before switching to each sample. In order to make results closer to real application, the unbuffered medium with a comparable conductivity as real wastewater [17] contained (per liter) 0.5 g NaCl, 1 g NaAc, 12.5 mL trace minerals and 5 mL vitamins (conductivity of 1.65 ± 0.02 mS cm^{-1}, pH = 7.2 ± 0.1) [10]. MFCs were operated at 1 kΩ in a constant temperature room (30 °C).

2.3. Electrochemical, material and biological measurements

In an abiotic reactor, 10 cycles of cyclic voltammetry was performed over a potential window from 0.3 to −0.2 V at a scanning rate of 1 mV s^{-1} to obtain a highly repeatable current. All potentials mentioned in this work was versus Ag/AgCl (3 M KCl, 0.195 V versus standard hydrogen electrode). The currents of negative scanning in the last cycle were recorded and compared. Electrochemical impedance spectroscopy (EIS) was measured at open circuit potential over a frequency range of 100 kHz to 0.1 Hz with a sinusoidal perturbation signal amplitude of 10 mV (Autolab PGSTAT 302N, Metrohm, Switzerland). Nyquist plots were fitted by the equivalent circuit reported previously (Fig. S1) [18]. Polarization curves and power density curves were measured at the beginning and at the end of 2 months by varying the external resistance from 1 kΩ to 50 Ω, with a time interval of 30 min to stabilize the voltage. A mercury porosimeter (Autopore IV, Micromeritics) was utilized to analyze the porous characteristics of each catalyst layer before and after treatment. The content of protein in the cathodic biofilm was measured according to the bicinchoninic acid method using a BCA protein assay kit (Solarbio, Beijing) [19]. Biofilm was carefully removed from the surface of the catalyst layer and then transferred to 50 mL of 0.2 M NaOH solution. After dispersed using ultrasonic machine for 30 min, the solution was filtrated and analyzed for protein according to the introduction of manufacturer.

3. Results

3.1. Power generation

All cells with unmodified cathode reached 0.51 ± 0.01 V in 0.5 g L^{-1} NaCl solution (1 kΩ) after 2 months of acclimation, showing that the anodic biofilm was well formed. Voltages varied