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Nitrogen-doped activated carbon as metal-free oxygen reduction catalyst for cost-effective rolling-pressed air-cathode in microbial fuel cells

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ABSTRACT

To increase the performance of MFCs, nitrogen-doped activated carbon (AC) for rolling-pressed air-cathode was synthesized using inexpensive melamine as nitrogen source by pyrolysis. The ratio of melamine to activated carbon (N/C) and pyrolysis temperature were optimized to be 10 and 900 °C. To clarify how the structure and active nitrogen content in different preparations influence the ORR performance, series of characterizations were carried out, and a good agreement between the content of pyridinic type N and high ORR activity was observed. As a dominant four electron cathode catalyst, AC-N10-900 exhibited the best performance both in electrochemical and MFCs tests in comparison with AC and Pt/C. The maximum power density was 1042 mW m^{-2}, which was 65.4% and 116.2% higher than that of AC and Pt/C. Therefore, AC-N10-900, one of cost-effective and metal-free MFCs cathode catalysts towards ORR, is expected to alternate precious metal for high performance in MFCs.

1. Introduction

Microbial fuel cells (MFCs), which are capable of treating wastewater and simultaneously generating electrical energy [1], are evergrowingly concerned for the fact that they positively meet the demands of modern society [2]. In MFCs, the electrochemical active bacteria growing on the anode biodegrade organic matters in substrate by catabolic metabolism to release electrons, which transfer to the cathode through an external circuit and then reduce O_2 to H_2O in the cathode [1]. As a promising biotechnology, MFC is widely studied in the application of various wastewater treatment [3]. However, it still faces the difficulties of low catalytic activity for oxygen reduction reaction (ORR) [4], low power density output [5], high cost of cathode catalyst [6] and low treatment efficiency [7] in practical application. As a result of this, an alternative cost-effective cathode is urgently to be discovered to increase the power density output and decrease the cost of MFCs.

ORR, the main reaction in cathode, is one of the major impact factors for MFCs performance. The sluggish ORR kinetics at cathode of MFCs is one of the common problems [8,9]. Apart from this, a four electron process is favorable, in which H_2O severs as the cathode reduction product. To overcome the slowness of cathodic ORR, many efforts have been made to develop various cathode materials [10,11]. Low cost and unique properties make activated carbon a promising cathode material for MFCs [12]. Previous studies have proved that cathode made of AC nearly had the same performance as that of a platinum one. Dong et al. reported AC had the maximum power density of 802 mW m^{-2}, which was even higher than 560 mW m^{-2} of Pt/C [13].

Many measures have been taken to facilitate the activity of AC based ORR catalyst in order to enhance the performance of MFCs [14]. Co-doping of non-noble metal and non-metal is one of the frequent methods to modify carbon materials [15]. Hao et al. used evaporation-induced self-assembly method to prepare N-MoS_2/C. As an ORR catalyst co-doped with Mo and heteroatom (S and N), its maximum power density (815 mW m^{-2}) was 56.7% higher than Pt/C [16]. The excellent performance may be due to the improvement of the catalytic activity of catalysts [17]. However, the above catalysts still face the problem of low stability, especially for fuel cell applications [18,19]. And the declination of stability under fuel cell working conditions is due to the disappearance of catalytic activity sites of metal [20].

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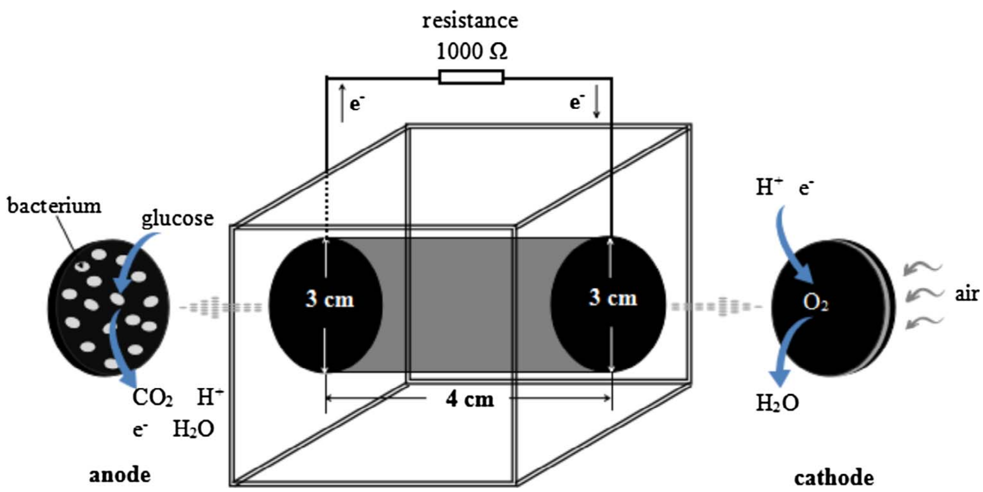

Fig. 1. The schematic diagram of the MFC experimental apparatus.

In order to overcome the bottleneck of stability of metal existed catalysts and further lower the cost of MFCs, metal-free catalysts for ORR in MFCs have been a research hotspot. As a non-metal atom, nitrogen is widely used as dopant, for the doping of N atoms leads to the defects of two adjacent C, which is of great significance for the formation of ORR active site [21]. As a result of this, ORR activity is enhanced [22,23]. Zhang et al. synthesized nitrogen-doped AC via a pretreatment method, and it resulted in a higher maximum power density (650 mW m^{-2}) than direct nitrogen-doped AC (410 mW m^{-2}) and commercial Pt/C (450 mW m^{-2}) [24]. The study demonstrated proper pretreatment of AC before N doped exhibited distinct improvement for ORR catalytic activity, however its performance still needs to be improved. Faced with this, an ORR cathode catalyst for MFCs with the advantages of simple and convenient preparation, low-cost raw materials as well as high performance is urgently needed.

Air-cathode, a commonly used MFC cathode, is able to achieve higher power density than aqueous cathode, where water is bubbled with air for sufficient oxygen to electrode. And the improvement is attributed to the decrease of internal resistance [25,26]. Besides, it also wins out others for the fact that it can both reduce the cost as well as the negative energy budget caused by aeration [27]. Rolling-press process, as a labor-saving and low-cost method, which is more accurate and stable than brushed ones, is more popular in MFCs for the optimization of the three-phase interfaces [13,28].

In this study, a cost-effective and metal-free cathode material (N-doped AC) was prepared by simple pyrolysis treatment, and further fabricated on air-cathode by rolling-press method. Melamine (a solid, low-cost and easily obtained nitrogen source) was pyrolyzed with AC to enable that N was doped on AC. The purposes of this study were: (1) to optimize preparation conditions (the best ratio of melamine to AC and the optimal pyrolysis temperature), (2) to explain the high ORR performance of the optimized catalyst by series of characterizations, (3) to identify the outstanding performance of prepared catalyst by comparing with AC and Pt/C in electrochemical test and MFCs. This N-doped cathode catalyst is expected more promise to replace AC and Pt/C in practical application.

2. Experimental

2.1. Method of AC modification

The preparation of nitrogen doped AC was based on a simple pyrolysis treatment with AC (Xinsen, Fujian, China) and melamine (Aladdin, Shanghai, China) as starting materials. First, one hour grinding was conducted in an agate ball mill with different mass ratios of melamine to AC to get homogeneous mixture. After that, pyrolysis of the above mixture was performed in a tube furnace (Kejin, Hefei, China) at the desirable temperature for 1 h in argon atmosphere with the flow rate of 80 mL min^{-1} and the heating rate of 10 °C min^{-1}, then the catalysts were prepared.

2.2. Fabrication of air-cathode

Pt/C air-cathodes were prepared by brushing, while AC and N-doped AC air-cathodes were made by rolling-press method [13]. The gas diffusion layers of AC based air-cathodes were prepared by rolling carbon black (CB) (Hesen, Shanghai, China) together with polytetrafluoroethylene (PTFE) (60 wt%, Hesen, Shanghai, China) at a mass ratio of 3:7 on one side of a stainless steel mesh, which was then heated at 340 °C for 20 min in a muffle furnace (Zhonghuan, Tianjin, China). The catalyst layers were made from samples of untreated AC and nitrogen doped AC (AC-N) as the same method onto the opposite side of the stainless steel mesh (the mass ratio of PTFE to AC or AC-N was 1:6). After rolling procedure, the completed cathodes were put in the air at room temperature for at least 24 h to drive away alcohol.

2.3. Construction and operation of MFCs

Single-chamber MFC was employed with a 3 cm-diameter inner cylindrical plastic chamber and the space between electrodes was 4 cm. The inner liquid volume was 28 mL. Anode was made of carbon cloth (Shenzhou, Jilin, China) and an external resistance of 1000 Ω was used to connect electrodes. The schematic diagram of MFC experimental apparatus adopted was shown in Fig. 1. All MFCs were inoculated by sewage from treatment plant. At the beginning of cell culture, sewage (500 mL L^{-1}) together with nutrient solution (500 mL L^{-1}) containing 50 mM phosphate buffer solution (PBS, pH = 7) (Table S1) [14], glucose (1 g L^{-1}), trace mineral (12.5 mL L^{-1}) and vitamin (5 mL L^{-1}) were added to MFCs each cycle. After the formation of anodic biofilm, only nutrient solution was added. All reactors were incubated at room temperature (about 25 °C). The cell voltage across the external circuit was measured every 30 min with a data acquisition system (PISO-813, ICP DAS Co., Ltd.). Before measuring power density and polarization curves, MFCs were first stabilized for 2 h at open circuit voltage. The external resistance was reduced from 9000 to 70 Ω. Each resistance was tested for a fixed time to ensure a steady voltage. A reference electrode (KCl saturated calomel electrode, SCE) was used to measure the electrode potential.

2.4. Characterizations of materials

Nitrogen adsorption-desorption isotherms were collected at 77 K