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Activated carbon derived from chitosan as air cathode catalyst for high performance in microbial fuel cells

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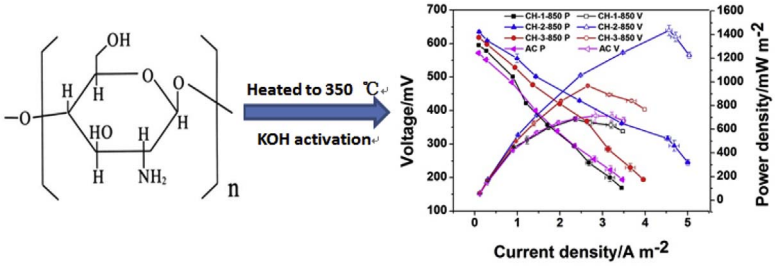
HIGHLIGHTS

- Carbons derived from chitosan and activated with KOH were used in air cathode.
- CH-2-850 showed the maximum power density of 1435 mW m^{-2}, 101% higher than the AC.
- KOH activation at high temperature enlarges the surface area of CH.
- MFC performance of CH increased after activation because the resistance reduced.
- Higher nitrogen doping (pyridinic-N) leaded to improve the performance of CH.

GRAPHICAL ABSTRACT



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ABSTRACT

Chitosan with rich of nitrogen is used as carbon precursor to synthesis activated carbon through directly heating method in this study. The obtained carbon is activated by different amount of KOH at different temperatures, and then prepared as air cathodes for microbial fuel cells. Carbon sample treated with double amount of KOH at 850 °C exhibits maximum power density (1435 ± 46 mW m^{-2}), 1.01 times improved, which ascribes to the highest total surface area, moderate micropore and mesoporous structure and the introduction of nitrogen. The electrochemical impedance spectroscopy and powder resistivity state that carbon treated with double amount of KOH at 850 °C possesses lower resistance. The other electrochemical measurements demonstrate that the best kinetic activity make the above treated sample to show the best oxygen reduction reaction activity. Besides, the degree of graphitization of samples increases with the activated temperature increasing, which is tested by Raman. According to elemental analysis and X-ray photoelectron spectroscopy, all chitosan samples are nitrogen-doped carbon, and high content nitrogen (pyridinic-N) improves the electrochemical activity of carbon treated with KOH at 850 °C. Thus, carbon materials derived from chitosan would be an optimized catalyst for oxygen reduction reaction in microbial fuel cell.

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1. Introduction

Microbial fuel cells (MFCs) are an advanced system that converts energy from the oxidation of organic material to generate electric power and have great potential application in wide fields such as wastewater treatment [1,2]. Noteworthily, oxygen reduction reaction (ORR) of cathode is still a relatively limited factor in MFC performance [3]. At present, activated carbon (AC) is used as air cathode, which persistently attracts considerable attention because of its low cost, high surface area and good catalytic character. AC with modification of N or P was promising to enhance the electrochemical performance as demonstrated in the available literature [4,5].

AC can be prepared from different carbon precursors, including coal, wood, peat, coconut and polymers and so on, by physical and chemical activation methods [6–9]. For example, the prepared carbonaceous materials from petroleum were featured with a high surface area and naturally doped with oxygen containing groups [10]. Chitosan (2-amino-2-deoxy-D-glucose), the second most abundant biopolymer after cellulose, is a biopolysaccharide derive from the chitin in crustacean cells, insect exoskeletons and fungus cell walls [11]. Because the chitosan polymer is naturally rich of nitrogen and possesses specific acid–base properties [12], some works had been reported in preparation of carbon materials using chitosan as carbon precursor. Kucinska et al. described a method of converting chitosan into activated carbon using Na_2CO_3 solution as activating agent, which got a porous carbon with a low surface area (400 m^2/g) [12]. Chitosan was dissolved into diluted acetic acid and then hydrothermally carbonized at a mild temperature, which was a common method to obtain activated carbon [13]. Meanwhile, a few researchers studied the synthesis of chitosan-based ACs by a chemical activation process using KOH as an activation agent, which mixed the obtained carbon aerogels and KOH solution together [14].

Over the years, carbon materials compounded by chitosan were used to study the electrochemical properties. C-T-1:1 sample (porous carbon synthesized via solution-phase method using chitosan as carbon resource) was endowed with high-performance supercapacitors [15]. Chitosan with rich N content has been successfully utilized to obtain high performance N-doped graphic carbon electrocatalyst [16]. Generally, N-doped treatment greatly improved the catalytic activity and durability for ORR of carbon powders [17,18]. Nitrogen-doped carbon nanofibers presented in the work of Chen et al. might be a promising candidate for the electrode material of high performance supercapacitor [19]. Also, the prepared carbon materials with high nitrogen content lead to more active sites for facilitation of oxygen reduction, resulting in higher electrocatalytic activity towards ORR [20].

However, there is no report on the study of employing chitosan as carbon resource to synthesize carbon powder used as air cathode in MFC. At the same time, the influence of physical and chemical character on electrochemical performance of carbon materials from chitosan has not been studied deeply. In this work, we obtained the porous and high electrochemical performance carbon material by heating chitosan directly. The obtained pre-carbonized carbon was activated by KOH through physical mixture. The structure and surface characters of samples with different activation conditions were investigated in detail. Herein, some electrochemical measures were used to test the electrochemical performance. Nitrogen adsorption-desorption and Raman spectroscopy was used to explore the structure of samples, while the elemental analysis and X-ray photoelectron spectroscopy (XPS) was employed to analysis the element contents of carbon samples.

2. Experimental

2.1. Preparation of AC cathode

Chitosan (Lanjin Technology development Co. Ltd., Shanghai, China) was used as carbon precursor. Before activation, chitosan was directly heated to 350 °C in the presence of nitrogen at a heating rate of 5 °C min^{-1} and kept for 3 h at this temperature. Then, the pre-carbonized char was physically mixed with KOH at the weight ratios ranging from 1 to 3 (KOH: char) and activated in a horizontal furnace. These mixtures were heated to 850 °C for 2 h with a heating rate of 5 °C min^{-1} under a nitrogen atmosphere. The activation product was cooled to room temperature. Then resultant carbon powders were washed with 1 M HCl solution and distilled water until the pH approached 7 and dried in an oven at 110 °C for 1 day. To investigate the effect of the activated temperature on carbon structural changes, the composites with KOH ratio of 1:2 were heated to the temperature of 600–950 °C. The resulting carbon samples were denoted as CH-X-Y, where X is the ratio of KOH/char and Y is the activation temperature, respectively. The product was used in the construction of air cathode.

2.2. Anode and cathode preparation for MFC

The air cathodes were prepared by a rolling-press method as previous studies [21]. Typically, a gas diffusion layer (GDL) was made on one side of a stainless steel mesh and faced to the air, and the other side was covered by a catalyst layer (CL). GDL was made by rolling carbon black (Jinqiushi Chemical Co. Ltd, Tianjin, China) and PTFE (60 wt%, Hesen, Shanghai, China) with a mass ratio of 3:7, following by annealing at 340 °C for 20 min. CL was consisted of activation CH and PTFE at a mass ratio of 6:1 with same rolling process. After the rolling procedure, the prepared air cathodes were dried for at 40 °C for 12 h. Anodes were made of carbon felt, as previous studies [22,23]. The carbon felt was immersed in acetone for 12 h to remove impurities and organic matter, following washed with distilled water before installation in the MFC [24].

2.3. MFC construction and operation

Details of construction of MFC single-chamber was the same as reported previously [25]. The cylindrical single chamber was contained in a diameter of 3 cm and a volume of 28 mL, with 4 cm spacing between cathode and anode. Titanium wire with good conductivity properties and high anti-corrosion was used to connect the cathode and anode. The external resistance was 1000 Ω. In the first 3–4 cycles (one cycle 1–2 days) of cell culture, the MFCs were inoculated by half domestic wastewater and half nutrient solution (the nutrient solution consists of phosphate buffered saline, acetate, peptone, yeast powder, trace mineral and vitamin). Then, the second day, took out 2/3 of the mixture, following added the same amount of wastewater and nutrient solution. The above operation was repeated every day until the voltage was stable (it usually takes one week). And then, just sucked out half of the mixture and added the same volume of the nutrient solution. Usually, we added the nutrient solution every 48 h. The contents of phosphate buffered saline (PBS) solution was described in the supplemental material [26]. All reactors were conducted in a thermostatically controlled chamber at 30 °C.

2.4. Electrochemical characterization

All MFCs were initially stablized 6 h after adding the nutrient solution at open circuit potential (OCP) before measuring power density and polarization curves. The external resistance varied from 9000 to 70 Ω. Each resister ran for 10 min to ensure a stable voltage profile. Linear sweep voltammetry (LSV) was used to evaluate the ORR performance of prepared air-cathodes, which was conducted on a potentiostat (Versa STAT 3, Princeton Applied Research, USA) with three-electrode system. The reference and counter electrode were Ag/AgCl electrode (0.195 V versus a standard hydrogen electrode, Aidahengsheng Electrode Co. Ltd., Tianjin, China) and platinum sheet (1 cm^2), respectively. The prepared cathode described in above served as the working electrode. LSV curves were measured from OCP