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The influence and mechanism of different acid treatment to activated carbon used as air-breathing cathode catalyst of microbial fuel cell

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ABSTRACT

Commercial activated carbon (AC) was subjected to various kinds of acid treatment, which were employed as air-breathing cathodes for Microbial fuel cells (MFCs). Obviously, both the acid species and the concentration of acidic solution have an effect on the catalytic activity of AC, and the electrochemical performance of AC was increased after acid treatment. Cathodes used 1 M H_3PO_4 treated AC (AC-H_3PO_4-1) showed the maximum power density of 1546 ± 43 mW m^{-2}, which was 115% higher than the pristine AC. The electrochemical studies showed that AC-H_3PO_4-1 exhibited the least resistance and highest kinetic activity. In addition, Nitrogen adsorption-desorption demonstrated that the acid treatment could increase the total surface area and pore volume, especially the exposure of mesopore to the reactants. Raman, X-ray photoelectron spectroscopy and temperature programmed desorption with ammonia revealed that the degree of graphitization, surface oxygenic functional groups and the acid sites of AC were enhanced after acid treatment. However, too much strong acidic functional groups were detrimental to the oxygen reduction reaction. In general, the treatment of activated carbon with 1 M H_3PO_4 will be a promising way to improve the performance of microbial fuel cells.

1. Introduction

As one type of fuel cells, microbial fuel cells (MFCs) are clean technologies to decompose a wide variety of substrates and materials with bacteria to generate bioelectricity, and their potential application have been targeting at the wastewater treatment [1–5]. Microorganisms played a vitally important role in the degradation of wastewater and the transfer of electrons in MFCs [6,7]. The free air was consumed at cathode where oxygen was reduced. However, oxygen reduction reaction (ORR) is a sluggish reaction and a large portion of potential is lost during the reaction, which inhibited the efficiency of the cell operation [8,9]. Activated carbon (AC) has been widely adopted as an ORR catalyst for MFCs, due to its light weight, low cost, easy accessibility, high surface area *etc* [10,11]. Nevertheless, the performance of MFCs catalyzed by bare AC was unsatisfied for practical application, therefore many efforts have been made to improve its catalytic activity. Highly active non-platinum groups materials such as silver [12], N-type Cu_2O [13], nano spinel Co_3O_4 [14] have been used as cathode catalyst for the MFCs. Some researchers also added the heteroatoms (e.g. nitrogen or phosphorus) into AC through acid and alkali treatment to improve the catalytic performance of activated carbon [15–17].

Recently, acid treatment of carbon materials has been regard as a simple and effective method to enhance the MFC performance. Chen et al. reported phosphoric acid treated AC could achieve a power density of 954 mW m^{-2}, which was 34.8% higher than the bare AC [18]. The capacitive performance of AC was increased distinctly after the treatment with 30 wt% HNO_3 solution [19]. Besides, the selection of acid types was also important, because different kinds of acid have different effects on the physical and chemical properties of activated carbon. For example, to enhance the capacitance of the carbon nanotube, four different acids (HNO_3, H_2SO_4, HCl and HF) were used as the treatment solutions, among which the HF treatment achieved the highest performance [20]. After acid treatment, the carbon nanotube surface was introduced with some oxygen functional groups which was identified to be one of the key factors for performance improvement [21].

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However, Wang et al. came to an opposite result that acidic pretreatment (5.6 M HNO_3, 85 °C) of AC decreased the MFC power output from 804 ± 70 to 537 ± 36 mW m^{-2}, and the ohmic resistance of AC increased by 8% [22] Even though many investigations have been done regarding the effect of acid treatment on carbon materials, the systematic studies of acid treated carbon for MFC application were still limited to our best knowledge.

This study focuses on the effect of acid treatment on the properties of activated carbon, rather than the function of other heteroatom. Therefore all the acid treatments were performed at room temperature to avoid the introduction of heteroatom. After different acid treatment, the ACs had been prepared as air-breathing cathodes. To probe the effectiveness of acid treatment, the MFC performance of different air-breathing cathodes were tested by many electrochemical measurements. The pristine AC and acid treated ACs were also assessed and compared in terms of chemical and physical properties, including surface area, pore structure, degree of graphitization and oxygen functional groups.

2. Experimental

2.1. Functionalization of activated carbon

Activated carbon (AC) was purchased from Yi Huang Co. Ltd, Fujian, China and used without further purification. 1 g AC was dispersed into four kinds of 20 mL acid solution: H_3PO_4, HCl, H_2SO_4, and HNO_3, respectively, and the concentration of the acid solution ranged from 0.5 M to 5 M. The mixture was stirred for 24 h at room temperature, then filtered and thoroughly washed with distilled water until pH = 7. The obtained solids were dried in the oven overnight. The final obtained carbon powder was designated as AC-x-y, where x and y represented the type and the concentration of acid solution, respectively.

2.2. Air-breathing cathode preparation

All the air-breathing cathodes were prepared by a rolling-press method as detailed elsewhere [23]. Typically, a gas diffusion layer (GDL) was laminated on one side of a stainless steel mesh (SSM) and faced the air, the other side was covered with a catalyst layer (CL). GDL was made by rolling carbon black (Jinqiushi Chemical Co. Ltd, Tianjin, China) and PTFE (60 wt%, Hesen, Shanghai, China) at a mass ratio of 3:7, following by annealing at 340 °C for 20 min. CL was consisted of acid treated AC and PTFE with a mass ratio of 6:1, and the same rolling process was applied to the CL. Finally, the prepared air-breathing cathodes was dried at 40 °C for 12 h.

2.3. MFC construction and operation

Details of configuration of single-chamber MFC was fully described in previous literature [24]. The cylindrical single chamber with a diameter of 3 cm and a volume of 28 mL, the spacing distance between cathode and anode was 4 cm. The anode was a piece of carbon felt (Jilin Carbon Co. Ltd, Jilin, China). Titanium wire with highly anti-corrosion and good conductivity was employed to connect the electrodes with an external resistance of 1000 Ω. In the first 3 ~ 4 cycles (one cycle 2 days), the MFCs were inoculated by half domestic wastewater and half phosphate buffered saline (PBS, pH = 7) with 2 g L^{-1} of acetate solution [25]. All devices were conducted at 30 °C in a thermostatically controlled chamber.

2.4. Electrochemical characterization

The polarization curves were obtained by varying the external resistance from 9000 to 70 Ω after stabilizing for 6 h at an open circuit potential (OCP). The cell potential was recorded for 10 min at each resistance to ensure a stable voltage. Individual polarization behaviors of cathode and anode were recorded simultaneously. The intrinsic activities of various cathodes were studied using a three-electrode system, in which a saturated Ag/AgCl, a platinum sheet (1 cm^2) and the prepared air-breathing cathodes were used as reference, counter and working electrode, respectively. Linear sweep voltammetry (LSV) was conducted on a potentiostat (Versa

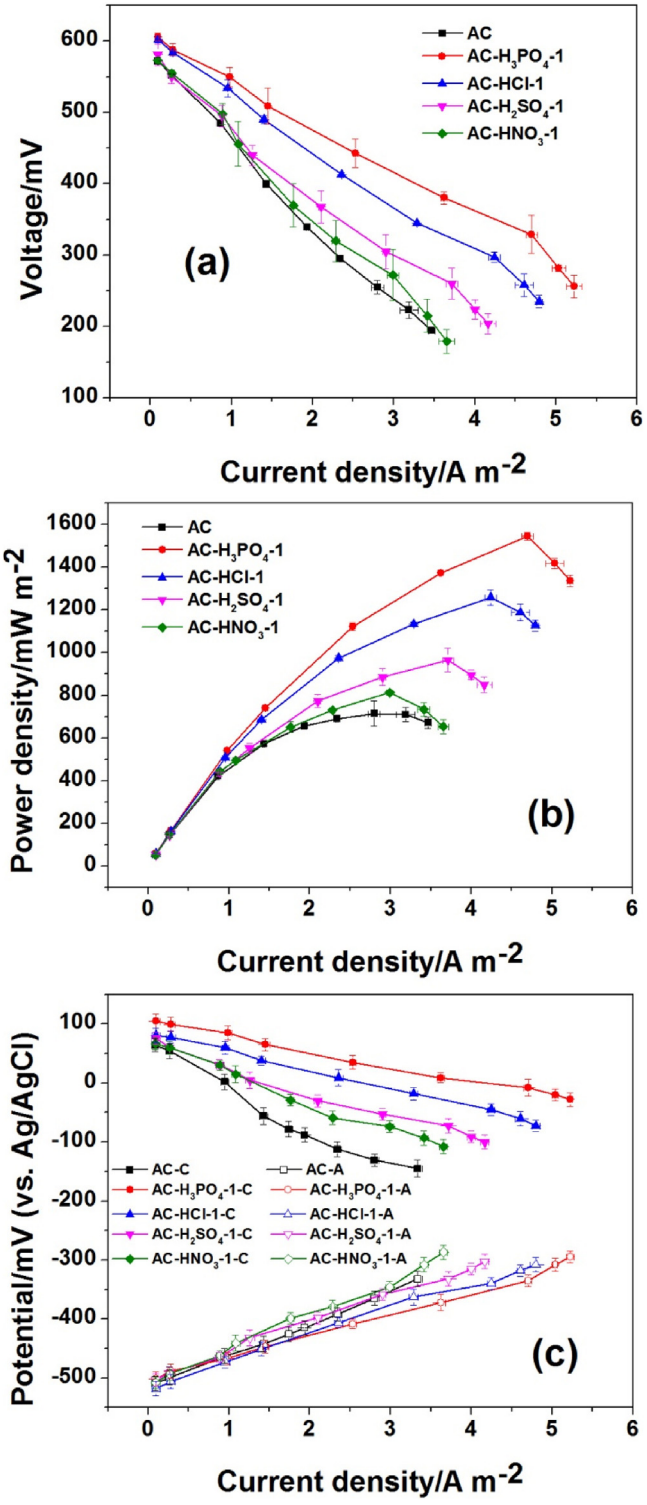

Fig. 1. (a) The overall polarization curves, (b) power density and (c) polarization curves of AC–x-1.