Acidic and alkaline pretreatments of activated carbon and their effects on the performance of air-cathodes in microbial fuel cells

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HIGHLIGHTS

- The power density was increased by 16% when activated carbon was pretreated by KOH.
- KOH pretreatment increased micropore area and decreased charge transfer resistance.
- Ohmic resistance was decreased by 7% after KOH pretreatment.
- Adsorbed OH^- was found on the surface of KOH treated activated carbon.
- HNO_3 pretreatment incurred a corrosion of SSM and decreased power by 33%.

ARTICLE INFO

ABSTRACT

Activated carbon (AC) is a high performing and cost effective catalyst for oxygen reduction reactions (ORRs) of air-cathodes in microbial fuel cells (MFCs). Acidic (HNO_3) and alkaline (KOH) pretreatments on AC at low temperature (85 °C) are conducted to enhance the performance of MFCs. The alkaline pretreatment increased the power density by 16% from 804 ± 70 to 957 ± 31 mW m^{-2}, possibly due to the decrease of ohmic resistance (from 20.58 to 19.20 Ω) and the increase of ORR activities provided by the adsorbed hydroxide ion and extra micropore area/volume after alkaline pretreatment. However, acidic pretreatment decreased the power output to 537 ± 36 mW m^{-2}, which can be mainly attributed to the corrosion by adsorbed proton at the interface of AC powder and stainless steel mesh and the decreased pore area.

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1. Introduction

Microbial fuel cells (MFCs) are capable to convert chemical energy in pollutants into electrical energy directly with simultaneous wastewater treatment. The single-chambered design using air cathode attracts more and more attentions since it is simple to construct with little cost of operation. For example, it does not require any external energy to supply oxygen and only needs cost-free oxygen as the electron acceptor from the air. It is recently reviewed that the power density of an MFC is approximately in proportion with the specific surface area of the cathode, indicating that the performance of MFCs is mainly limited by the cathode (Logan, 2012). With an optimized reactor design and Pt as the catalyst, the maximum power density up to 4.3 W m^{-2} was reported based on the area of the air cathode (Fan et al., 2012).

However, the cost of the air-cathode is too high to be enlarged and utilized in wastewater treatment plant because precious metal (such as Pt) is needed as the oxygen reduction reaction (ORR) catalyst to decrease the overpotential. Zhang et al. (2009) found that the activated carbon (AC) exhibited a comparable or even higher performance than Pt when it was pressed on a nickel mesh with polytetrafluoroethylene (PTFE) as the binder. It was further demonstrated that the AC air-cathode made by rolling-press method had the advantage of extremely high reproducibility. The maximum power density reached 802 mW m^{-2} with an optimal AC/PTFE mass ratio of 6:1 in the catalyst layer (CL) (Dong et al., 2012b). This value was increased by 35% to 1086 mW m^{-2} when the heating of CL was avoided (Dong et al., 2013). The dominant pore size formed by PTFE and carbon particles of both CL and gas diffusion layer (GDL) was 6 μm, and these pores are considered as main channels for gaseous transport. Catalytic kinetic analysis

preliminarily showed that the area of micropores is in proportion with the electron transfer number of ORR, indicating that micropores with a diameter <2 nm could be the site where 4-electron ORR happens (Dong et al., 2012a).

It had been reported that the ORR performance of carbon catalysts can be increased after pretreatments. The ORR current was increased when non-porous graphite granules were activated by nitric acid (Erable et al., 2009). Using both HNO_3 and HCl as reagents of pretreatment, Shi et al. (2012) found that the maximum power density of nitrogen doped carbon black (non-porous) increased by 105% from 310.8 ± 15 mW m^{-2} (the untreated control) to 638.6 ± 12 mW m^{-2}. All these enhancements were attributed to the addition of nitrogen associated functional groups on the surface of carbon.

However, so far as we know, the effects of chemical pretreatments of AC on its ORR performance have not been investigated in MFCs. ORR in electrolyte occurs following two possible pathways, including a complete four electrons reduction to H_2O and a two electrons reduction to H_2O_2. Four electrons oxygen reduction was believed to take place at the three phase interfaces (TPIs) where AC particles, oxygen and electrolyte simultaneously exist (Dong et al., 2012b). Therefore the characteristics of carbon surface, such as carbon surface pH (Yan et al., 2004), are crucial to the cathodic performance. In this study, acidic and alkaline pretreatments had been performed on AC and the effects on MFC performance were investigated.

2. Methods

2.1. Pretreatments of AC

HNO_3 and KOH were individually utilized for acidic and alkaline pretreatments of AC (1500 m^2 g^{-1}, Xinsen Carbon Co. Ltd., Fujian, China). Acid treated AC (AC-A) or base treated AC (AC-B) were prepared by submerging AC powders into HNO_3 (5.6 M) or KOH (3 M) solutions and heating at 85 °C for 6 h (mixed with a magnetic stirrer). After the solutions cooled down to room temperature, each powder was soaked in acidic or alkaline solution for 24 h and rinsed in deioned water for three times using suction filter to remove residual acid or base. Finally, different AC powders were dried in vacuum drier for 12 h.

2.2. Air-cathode fabrication

All the air-cathodes were made by rolling-press method according to procedures described by us previously (Dong et al., 2012a, 2013). Air-cathodes were consisted of a stainless steel mesh (SSM) with a CL rolled on the water facing side and a GDL rolled on the air facing side. The GDL was made of carbon black (Jinqiushi Chemical Co. Ltd., Tianjin, China) and PTFE emulsion (60%, Hesen, Shanghai, China) with a mass ratio of 3:7, followed by heating at 340 °C for 20 min. CLs were made of AC-A, AC-B and untreated AC with the same mass ratio of 6:1 to PTFE emulsion. Before installed in MFCs, CLs were dried in air at room temperature for at least 24 h.

2.3. MFC tests

Air cathode MFCs were constructed with a cylindrical chamber (28 mL) and an electrode spacing of 4 cm as previously described (Dong et al., 2012b). Both the anode and the cathode have the same projected area of 7 cm^2. Anodes were produced by rolling a mixture of AC, carbon black and PTFE with a mass ratio of 16:2:1 onto a SSM to ensure an enough capacitance of anode and therefore alleviate the effect of power overshoot on the accuracy of power assessment although the performance of the anode could be reduced (Peng et al., 2013). The carbon black utilized here was to enhance the conductivity of the anode. MFCs equipped with different air cathodes (duplicate reactors) were simultaneously inoculated using a pre-acclimated bacterial suspension from an MFC operated for over 1 year. Reactors were fed with 50 mM phosphate buffer solution (PBS, Na_2HPO_4 4.09 g L^{-1}, $NaH_2PO_4·H_2O$ 2.93 g L^{-1}), trace minerals 12.5 mL L^{-1} and vitamins 5 mL L^{-1} with 1 g L^{-1} sodium acetate as the substrate (Wang et al., 2009). The external resistance was fixed at 1000 Ω except as indicated.

2.4. Electrochemical and material analysis

Polarization curves and power density curves were obtained by varying the external resistance from 1000 to 50 Ω with a time interval of 30 min to ensure a stable voltage. Pretreated or untreated AC air-cathodes were soaked in 50 mM PBS in abiotic reactors for at least 24 h before electrochemical tests. A Pt electrode (1 cm^2) was utilized at the counter electrode. Linear sweep voltammetry (LSV) was measured in order to evaluate the ORR performance of each cathode at a scan rate of 0.1 mV s^{-1} from 0.3 to -0.2 V using an Ag/AgCl as the reference electrode (3 M KCl, 0.195 V versus standard hydrogen electrode).

Electrochemical impedance spectroscopy (EIS) of cathodes was carried out over a frequency range of 100 kHz–10 mHz at open circuit potential with a sinusoidal perturbation signal amplitude of 10 mV using a potentiostat (Autolab PGSTAT 302N, Metrohm, Switzerland). Nyquist plots were analyzed according to an equivalent circuit (Fig. S1) by NOVA 1.7. In order to avoid the effect of solution, reference electrode as well as the spacing between them, all the EIS tests were performed in the same reactor using a firmly fixed reference electrode and refilled with the same electrolyte.

Brunauer–Emmett–Teller (BET) measurements were conducted using TriStar II 3020 (Micromeritics, ASAP2010, US) through nitrogen adsorption at 77 K. Pore size distribution was calculated according to Barett–Joyner–Halenda (BJH) model based on the Kelvin equation and corrected for multilayer adsorption, while *t*-plot method was employed to extract the microporous surface area and volume (Dong et al., 2012a). Carbon surface pH was determined by soaking 0.45 g of each dried AC powder in 20 mL of deioned water and stirring by a shaker for 16 h. The pH (SevenEasy Plus, S20P, Mettler Toledo, Switzerland) of filtrate was referred as the pH of AC (Yan et al., 2004). Fourier transform infrared spectroscopy (FTIR) was conducted using BRUKER TENSOR 27 equipped with DigiTectTM detector. Before measurements, each powder was mixed with KBr powder as sample-KBr pellets. The wave number was ranged from 400 to 4000 cm^{-1} as previously described (Yan et al., 2004). X-ray photoelectron spectroscopy (XPS) was performed with a monochromated Al Kα X-ray source (Axis Ultra DLD, Kratos Analytical Ltd., US). Spectra were obtained by scanning the binding energy (BE) from 1200 to 0 eV.

3. Results

3.1. Performance of different air-cathodes

Repeatable and stable voltages were obtained in all MFCs six cycles after inoculation using different air-cathodes. Repeatable and stable voltages of 520 ± 5 mV were obtained in all MFCs 6 cycles (12 days) after inoculation. In order to obtain a mature anodic biofilm, polarization curves were obtained at the 16th cycle (32 days). It was showed that alkaline pretreated AC, here marked as AC-B had the maximum power density of 957 ± 31 mW m^{-2}, with a value 16% and 78% higher than those of untreated AC (804 ± 70 mW m^{-2}) and acidic pretreated AC (AC-A,