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Low-cost biochar derived from corncob as oxygen reduction catalyst in air cathode microbial fuel cells

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ABSTRACT

Low-cost biochar derived from corncob was prepared by a facile pyrolysis method at controlled temperatures (250–750 °C) and the biochar was employed as oxygen reduction reaction (ORR) catalyst in air cathode microbial fuel cells (MFCs). The obtained biochar at 650 °C (CC-650) showed an excellent electrochemical active area up to 655.89 $m^2 g^{-1}$, and various forms of nitrogen were introduced to the carbon molecular skeleton successfully. The electrochemical measurements indicated that the CC-650 with the highest contents of graphitic and pyridinic nitrogen can accelerate the electron transfer to participate in ORR by a four-electron pathway. In MFCs tests, the maximum output voltage and power density with CC-650 cathode was 0.221 V and 458.85 mW m^{-3} respectively, which was significantly higher than those of the other biochar. Our results demonstrated a potential route based on sustainable and economical biochar as promising oxygen reduction catalyst for MFCs.

1. Introduction

In recent years, yielding clean power has become the serious concern all over the world because of the depleting of a large amount of fossil fuel [1,2]. Microbial fuel cells (MFCs) are electrochemical conversion devices that can oxidize the biodegradable matters by electrochemically active bacteria and generate electricity [3], which has been demonstrated to be a potential technique for harvesting renewable electricity from waste [4]. The electron and proton from the anode chamber are transferred to the cathode through the external circuit and proton exchange membrane, respectively. Subsequently, the chemical reaction involves electrons, protons and electron acceptors, and electrical current is produced during this process [5]. Oxygen, which is abundant in the ambient environment, has been widely used as electron acceptor in air cathode MFC [6]. Consequently, the oxygen reduction reaction (ORR) of cathode has become the key for MFC development. The precious metal catalyst Pt/C has been extensively used to improve the ORR performance because of its excellent electrocatalytic activity [7]. However, it should be emphasized that the commercial Pt/C is not an ideal electrocatalyst for industrial application in MFCs due to low abundance, high cost and vulnerability to sulfide [8,9]. In order to replace or reduce the commercial Pt/C use in MFCs, some non-precious materials, such as graphene [10], activated carbon [11,12], and graphitic [13], have been confirmed as effective ORR catalyst due to their much low cost, light weight, high surface area and easy accessibility [14].

Nitrogen-doped carbon nanomaterials have attracted wide attention as effective ORR catalyst because the pyridinic nitrogen in carbon can accelerate the ORR [15,16]. It should be noted that the metal-free nitrogen doped carbons show excellent electrocatalytic performance compared to Pt/C. Feng et al. reported that nitrogen dopes carbon nanotubes exhibited higher electrocatalytic activity than the commercial Pt/C, thanks to the presence of pyridinic

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nitrogen [17]. Except for one lone pair of electrons, the pyridinic nitrogen can transfer electron to the conjugated π bond, further accelerate the ORR by facilitating the reductive oxygen adsorption [18]. However, Luo et al. prepared the nitrogen doped graphene with pyridinic nitrogen and they did not achieve remarkable ORR electrocatalytic activity [19]. Accordingly, the pyridinic nitrogen may not be the significant factor determining the electrochemical activity of materials. Wang et al. suggested that the graphitic nitrogen in the carbon can boost the electron transfer from the carbon electronic band to the anti-bonding orbitals of oxygen, further expanding the ORR electrocatalytic activity of materials [20]. Consequently, it is very important to explore the active sites of catalysts so that the ORR mechanism can be better understood.

Biochar materials derived from biomass have been widely explored as a low-cost catalyst to replace commercial Pt/C for MFC. Many researches have prepared the lost-cost biochar from agricultural byproduct such as coconut shell [21], orange peels [22], amaranthus waste [23], banana peel [24], water hyacinth [25], but very few studies are related to the corncob as ORR electrocatalyst for MFC application. Corncob is a natural and widely available agricultural byproduct with carbon, nitrogen, and oxygen elements, and the yield of corn reached 215 million tons in 2003 and corncob accounts for about 17% of corn quantity [26]. The physical and chemical properties of biochar are largely affected by raw materials and production temperature. To obtain the high surface area and conductivity, the raw materials needed to be exposed to high temperature environment [27]. The high temperature biochar can exhibit excellent conductivity and superior electrochemical performance in fuel cells, lithium-ion batteries and supercapacitors [4]. Moreover, the corncob can introduce much heteroatoms (N, K, P, S, B, Fe), which is beneficial to increase limiting current density and accelerate the ORR activity [28]. Consequently, the biomass can take place of the traditional ammonia to be explored the nitrogen-doped electrocatalyst.

In this article, the biochar derived from corncob was synthesized by a facile, low-cost, and readily scalable pyrolysis approach. The nitrogen-doped biochar was prepared by thermal treatment of biomass under different temperature ranging from 250 °C to 750 °C, and the biochar was used as the ORR electrocatalyst to study the effect of the nitrogen doping states and the total nitrogen concentration in the pyridinic or graphitic nitrogen on ORR activity. Herein, the physical and electrochemical properties of nitrogen doped biochar were evaluated. The aim of this study was to explore the nitrogen doped biochar as the ORR catalyst for MFC application, to better elucidate the relationship between the nitrogen species and electrocatalytic activity.

2. Materials and methods

2.1. Preparation of biochar using corncob as precursor

Corncob was obtained from a local farmland in Guangzhou, Guangdong province of China. The procedure for the preparation of biochar from corncob was summarized in Scheme 1. The fresh corncob was sun dried for five days, and then the dried corncob was grinded into powder. Finally, the powder was heated under N_2 atmosphere between 250 °C and 750 °C for 2 h by a programmable furnace to obtain the biochar. For simplicity, these samples were denoted according to heating temperature as CC-250, CC-350, CC-450, CC-550, CC-650 and CC-750, respectively.

2.2. Characterization of biochar

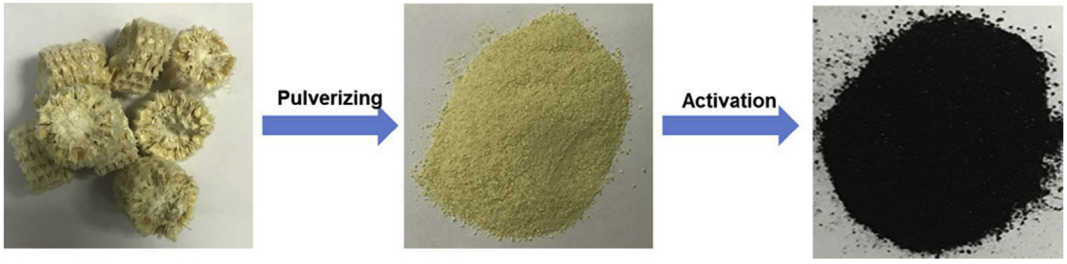
The surface morphologies of these samples were obtained using a field emission scanning electron microscopy (SEM, Carl Zeiss EVO LS10, UK). The structure and composition were analyzed by X-ray diffraction (XRD, Bruker D8, Germany) with a Cu Kα radiation (λ = 0.1541 nm). The Raman spectrum scanning was performed by a Renishaw (Renishaw inVia-Reflex microscope) at a range of 100–3500 cm^{-1} with a 514.5 nm laser. X-ray photoelectron spectroscopy (XPS) measurements were operated with a Thermo Scientific K-Alpha XPS system with a monochromatic Al Kα X-ray source.

2.3. Cathode preparation and operation

Seven single chamber MFCs were constructed with Plexiglas, with an effective volume of 350 ml. Carbon felt with an effective area of 16 cm^2 was used as anode electrode. Carbon cloth (CC) with a project area of 36 cm^2 was used as cathode electrode containing a catalyst layer (0.5 mg CC cm^{-2}), a carbon base layer, and a diffusive layer. The detail preparation process of cathode electrode was consistent with the previous report [29]. The distance between anode electrode and cathode electrode was 3 cm, and two electrodes were separated by the proton exchange membrane (PEM). Carbon felts, carbon cloths and PEMs were purchased from Shanghai Hesen Electric Co., Ltd. A titanium wire with an external resistance of 1000 Ω was used to connect the anode electrode and air cathode. All MFCs were run in batch mode with a magnetic stirring at 30 °C. The inoculum bacteria in all anode chambers were originated from a stable operating MFC over one year in our lab [30]. The anode chamber was filled with sodium acetate (0.5 g L^{-1}), phosphate buffer solution (0.13 g L^{-1} KCl, 0.31 g L^{-1} NH_4Cl, 4.97 g L^{-1} $NaH_2PO_4 \cdot 2H_2O$, 2.75 g L^{-1} $Na_2HPO_4 \cdot 12H_2O$), vitamins (5 ml L^{-1}) and trace minerals (5 ml L^{-1}) [31]. Besides, the anode medium was replaced when the voltage decreased below 50 mV during voltage output.

2.4. Electrochemical characterization for ORR

The output voltage of MFCs was recorded by a digital multimeter (M2700, Keithley, USA). The current and power were calculated according to the ohmic law. The power density and polarization curves were measured by varying external resistance



Scheme 1. Schematic procedure for the preparation of biochar from corncob.