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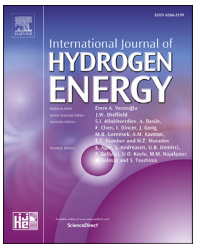

A green, cheap, high-performance carbonaceous catalyst derived from *Chlorella pyrenoidosa* for oxygen reduction reaction in microbial fuel cells

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ABSTRACT

Lack of low-cost, stable, and effective catalysts for the oxygen reduction reaction (ORR) is one of the key factors limiting the practical application of microbial fuel cells (MFCs). In this paper, a non-metal high-performance ORR catalyst, prepared by directly pyrolyzing *Chlorella pyrenoidosa* (CP) in N_2 atmosphere, was proposed. It was found that the ORR activity of the CP catalysts was highly dependent on the carbonization temperatures. The MFC with the catalyst carbonized at 900 °C (CP900) delivered the highest P_{max} (maximum power density) value of 2068 ± 30 mW m^{-2}, which was 13% higher than that with commercial 20 wt% Pt/C (1826 ± 37 mW m^{-2}) at the same catalyst loading. CP900 also showed good structural stability, maintaining 57.4% of the activity after 10,000 s operation at −0.3 V (vs. Ag/AgCl), significantly higher than 48.5% for Pt/C. The Brunauer–Emmet–Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical analyses indicated that the superior performance of CP900 was due to the high graphitization, the appropriate N and P doping, and the improved catalyst utilization due to the presence of abundant mesopores and macropores. These results demonstrated that CP900 could be a cost-efficient, stable and high performance alternative to the commercial Pt/C for MFC applications.

Introduction

Domestic wastewater is now being looked at as more of a valuable nutrition resource than as a waste, a worthless product or pollution [1,2]. Microbial fuel cells (MFCs), utilizing electrochemical active bacteria attached on the anode to convert the chemical energy in wastewater to electricity, represent a novel and green technology to alleviate the energy crisis and environmental problems [3]. However, several

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limiting factors, such as slow anodic and cathodic reaction rate, the high ohmic resistance, the high mass transfer resistance of the reactants to the active sites of the electrode, hindered their widespread application. Among these factors, the high overpotential and sluggish reaction kinetics of the oxygen reduction reaction (ORR) are considered to be major limitations [4,5]. A typical ORR process involves two pathways: one is the production of water through a four-electron pathway; the other is the production of hydrogen peroxide through a two-electron pathway. The direct reduction of oxygen molecules to water is more preferable for the ORR process due to the four-electron route possessing a much lower energy loss and an ability of direct reduction of O_2 without oxidative intermediates [6,7].

At present, platinum nanoparticle supported on high surface area carbon (Pt/C) is the most common catalyst for ORR. However, Pt-based catalysts are not suitable to the real application of MFCs because of its high cost, low activity and durability in MFC relevant conditions of neutral pH and the presence of poison species [8]. Recently, many reports have demonstrated that carbon nanomaterials, such as carbon nanotubes [9], graphene [10], carbon nanofibers [11], and other alternatives [12–14] exhibited a considerable ORR activity. Nevertheless, carbon nanomaterials are quite costly for wastewater treatment due to the complicated, high-cost production process. In addition, to increase the ORR activity, expensive and toxic chemical agents are usually used as the sources of heteroatom dopant [10,11,15,16]. All of these factors are against the practical application of the carbon nanomaterials in MFCs.

Biomass materials are low-cost, eco-friendly, and renewable. Previous studies have reported that N, P-doped carbon materials derived from biomass showed a high activity and a superior stability for ORR [8,15–20]. However, conventional dopants for carbon was either expensive or harmful to environment and human health because most of the nitrogen sources were derived from organic monomers containing nitrogen element and/or ammonia [8,15,21,22]. Therefore, the development of high performance heteroatom doped ORR catalysts from a low-cost and non-toxic source was still of great interest in the commercialization of the MFC technology. *Chlorella pyrenoidosa* (CP) is natural and cheap microalgae ($19 kg^{-1}), and is commonly used as nourishment. CP usually contains 55–60 wt% protein, 6 wt% water, phosphorus (1.8 wt %), unsaturated fatty acid, carbohydrate, fibre, minerals and vitamins. During carbonization, nitrogen and phosphorus contained in protein and phospholipid can be directly used as the dopant to generate the affordable and green N, P doped carbon catalysts for ORR.

This study aimed to prepare the ORR catalysts by direct pyrolyzing CP in N_2 atmosphere at different temperatures. The effect of carbonization temperature on the textural, crystallinity and surface properties of catalysts was studied by Nitrogen adsorption–desorption, X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis, respectively. The factors that affect the electrocatalytic performance of the CP catalysts inn both phosphate buffer solution (PBS) and the growth medium discharged from an operating MFC were analyzed.

Materials and methods

Material syntheses

CP powder (XI′ An Tianbin Biotechnology Co. Ltd.) dried at 50 °C was used as the precursor. Then, it was pyrolyzed at high temperatures in N_2 atmosphere. Temperature was initially raised from room temperature to 300 °C at 5 °C min^{-1}, then to the temperatures of 600, 700, 800, 900 and 1000 °C (obtained samples were denoted as CP600, CP700, CP800, CP900, and CP1000, respectively) at 8 °C min^{-1} and held for 2 h in N_2 atmosphere. After cooling down to room temperature in the same atmosphere, the carbonized products were ground by ball milling for 8 h, and then soaked in 2 M HCl for 24 h to remove metallic impurities. The obtained sample was rinsed using deionized water until a pH 7 was reached. The catalyst was obtained after filtration and desiccation at 60 °C overnight. The synthesis process of the catalysts was shown in Fig. S1.

Physical and chemical characterizations

XRD measurements were carried out by an Empyrean XRD system using Cu Ka radiation (40 kV, 40 mA and k = 0.154 nm) over a range from 5° to 90° at a scan rate of 2° min^{-1}. Raman spectroscopy of the samples was performed on a Renishaw inVia unit using an Ar ion laser with an excitation wavelength of 514.5 nm. Nitrogen adsorption-desorption isotherms of the catalysts were recorded at 78 K with a Micromeritics ASAP 2460 Brunauer Emmett Teller (BET) analyzer. The specific surface area of the catalysts was calculated by using the multiple-point BET method. The pore-size distribution (PSD) curves of the catalysts were obtained by using the Barret–Joyner–Halenda (BJH) method. The surface analysis for the catalyst was performed by XPS using a Thermo Fisher ESCALAB 250Xi spectrometer with a 150 W monochromatic Al K source.

Electrochemical characterizations

The ORR activity of the catalysts was evaluated by an electrochemical workstation (ParSTAT MC-1000, Princeton, USA) at 30 °C using a conventional three-compartment electrochemical cell. The counter and reference electrodes were a platinum wire and a Ag/AgCl (saturated KCl solution, +0.197 V vs. SHE) electrode, respectively. To prepare the working electrode, catalyst ink was made by mixing 16.0 mg catalyst, 0.1 mL Nafion solution (5 wt%, DuPont), 1.25 mL anhydrous ethanol and 0.65 mL ultra-pure water. The catalyst concentration in the suspension was 8.0 mg mL^{-1}. The catalyst ink was then ultrasonicated and stirred for at least 15 min. This process was repeated for three times to achieve a uniform suspension. Then 10 μL suspension were drop onto the surface of a 4 mm diameter glassy carbon (GC) electrode disk (BAS. Inc., Japan) and dried at room temperature. The catalyst loading on the RRDE was 0.64 mg cm^{-2}. As a benchmark, a commercial Pt/C catalyst (20 wt%, JM) was also loaded onto another GC electrode in the same way with a Pt loading of 80 μg cm^{-2}, corresponding to a catalyst loading of 0.40 mg cm^{-2}.

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