Bamboo charcoal as a cost-effective catalyst for an air-cathode of microbial fuel cells

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Abstract

In this study, bamboo charcoals (BCs) obtained by pyrolyzing bamboo branches (*Phyllostachys pubescens* Mazel) in a N₂ atmosphere were used as high-performance, cost-effective catalysts for the oxygen reduction reaction (ORR) in microbial fuel cells (MFCs). The obtained catalyst (BC-HT) showed a maximum power density ($P_{\max}$) of $1056 \pm 38 \text{ mW m}^{-2}$, which was comparable to that of the commercial Pt/C catalyst ($1039 \pm 15 \text{ mW m}^{-2}$). Additional N and P doping by soaking the carbonated BC in a (NH₄)₃PO₄ solution (BC-HT-NP-HT) resulted in a 65 % higher $P_{\max}$ ($1719 \pm 82 \text{ mW m}^{-2}$) compared to that of Pt/C. This improvement can be attributed to not only the high electrical conductivity, the sufficient amount of N- and P-containing groups, and the presence of many effective active sites (i.e., pyridinic-N, graphitic-N, P-N and P-O-CO₃) but also the high tolerance of BC-HT-NP-HT to the poisoning species under the relevant MFC conditions. These results demonstrated that easily available BCs can be cost-efficient and high-performing catalysts for ORR in air-cathode MFCs.

Keywords: microbial fuel cells; oxygen reduction reaction; electrocatalytic activity; N-containing functional groups; P-containing functional groups

1. Introduction

Microbial fuel cells (MFCs) are promising bioelectrochemical devices for renewable bioenergy, wastewater treatment, biosensing and bioremediation [1, 2]. Despite the attractive merits of MFCs, their power output is insufficient for practical applications. Although various types of MFCs have been proposed, air-cathode MFCs are the most applicable due to their simple structure and direct use of freely available oxygen in air as electron acceptors [3, 4]. However, the performance of air-cathode MFCs is limited by the high overpotential of the oxygen reduction reaction (ORR) in the cathode [3, 5]. Traditionally, Pt catalysts with a typical loading of 0.5 mg cm^{-2} are used in the air-cathode to accelerate the ORR process. However, the prohibitively high cost, low availability and poor stability under fuel cell conditions hinder their widespread application [6]. Therefore, many efforts have been devoted to replacing Pt-based catalysts with materials synthesized from earth-abundant elements, such as manganese oxides [7], iron phthalocyanine [8], and lead dioxide [9].

Among these candidates, nanocarbon-based materials (e.g., carbon nanotubes, nanofibers, and graphene) have been considered one of the most promising alternatives to Pt catalysts, due to their reasonable electrocatalytic activity as well as long-term stability and tunable pore sizes. The introduction of heteroatoms [10-13] can further improve the catalytic activity for ORR by creating charged sites for O_2 adsorption and the effective utilization of carbon π electrons. However, because fabricating and modifying nanocarbons usually require toxic chemicals, sophisticated preparation routes and specialized equipment, synthesizing these catalysts can have a negative environmental impact. To meet the economic and environmental requirements of MFC technologies, inexpensive and commercially available activated carbons (AC) have been used as ORR catalysts in recent studies. It has been

1 77 demonstrated that the ORR performance of AC catalysts is closely related to the type
2 78 of carbon source and the modification process of the carbon surface. Watson et al.
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4 79 compared the catalytic activity of AC catalysts derived from different precursors and
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6 80 found that AC catalysts derived from bituminous coal and peat showed better ORR
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8 81 performances than those derived from coconut shell or hardwood [5]. Further
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10 82 pretreatment of the AC by an acidic or alkaline solution before nitrogen doping [14]
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12 83 or by ammonia gas [15] has been found to be an effective method to improve the
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14 84 ORR activity due to the increased N content of the catalysts. Recently, Liu et al.
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16 85 prepared a P-self-doped carbon catalyst for ORR in MFC by direct pyrolysis of
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18 86 cellulose phosphate [16]. In a later work from the same laboratory, a P, N-doped
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20 87 carbon catalyst was fabricated by the direct pyrolysis of cellulose with ammonium
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22 88 phosphate [17]. It was demonstrated that with the use of catalysts, the air-cathode
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24 89 MFC showed a higher performance compared with that of Pt/C. However, the
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26 90 industrial production of cellulose includes chemical pulping, separation, and
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28 91 purification processes [18]. These processes may undermine MFC's ability to avoid
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30 92 contributing to environmental problems. Thus, from a practical application viewpoint,
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32 93 obtaining ORR catalysts that not only have superior performance but also
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34 94 environmental friendliness and cost-effectiveness remains a challenge.
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43 95 Bamboo is a grass-like plant and is widely grown in the Asia-Pacific region. In
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45 96 Asia, bamboo forest covers an area of over 180,000 km², which is approximately
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47 97 1.8 % of China's total land area [19]. While forest cover continues to decrease
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49 98 globally, the bamboo forest area has annually increased by 3 % in China due to its
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51 99 rapid growth and short growth period [20]. Bamboo charcoal (BC), usually produced
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53 100 by pyrolyzing bamboo at temperatures above 800 °C, is characterized by a low price
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55 101 (approximately 20-30 % of the AC price [21]), a porous structure, a high electrical
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conductivity, and a high adsorption capacity. Therefore, BC is widely used to replace AC as the adsorbent for the removal of environmental pollutants from water or air in China. Interestingly, these features also meet the requirements of ORR catalysts for MFC cathodes, implying that BC may be a promising cathode catalyst. Moreover, bamboo is typically composed of 0.4 to 5 wt.% nitrogen and 0.01 to 0.13 wt.% phosphorus [22], which can act as self-dopants for the formation of N- or P-doped ORR carbon catalysts during BC production.

In this study, an inexpensive and environmental-friendly BC catalyst for the air-cathode in MFC was obtained by directly pyrolyzing moso bamboo in a N₂ atmosphere. To enhance the electrocatalytic activity of the BC catalyst, additional N and P doping by (NH₄)₃PO₄ was used. The electrocatalytic activity of the BC catalysts was evaluated using a rotating disk electrode (RDE) and linear sweep voltammetry (LSV) in the growth medium of an operative MFC. Based on the number of electrons transferred, the reaction pathway towards ORR of the catalysts was discussed and compared with the commercial AC and Pt/C catalysts. In addition, BC catalysts were characterized by the physicochemical techniques, and their application in MFCs was justified in an air-cathode MFC.

2. Methods and Materials

2.1 Preparation of catalysts and fabrication of air-cathodes

A schematic illustration of the synthetic procedure for producing BC catalysts is shown in Fig. 1. The bamboo branches (*Phyllostachys pubescens* Mazel) were washed with deionized water and dried at 100 °C overnight. Then, the dried branches were cut into small pieces (approximately 2 mm wide and 10 mm long) and were used as precursors for BC-HT, BC-NP-HT and BC-HT-NP-HT. For BC-HT, the bamboo

pieces were directly carbonated in a tube furnace (JQF1100-30, China) at 900 °C for 2 h under a N₂ atmosphere to produce the pyrolyzed sample. The resulting sample was then ground and sieved with a 2000-mesh sieve to obtain the BC-HT catalyst. To increase the N and P content of the BC catalyst, two different synthetic processes were applied using (NH₄)₃PO₄ as the dopant. For BC-NP-HT, 20 g of dried bamboo pieces was used to absorb N and P by soaking in 100 mL of a 1 M (NH₄)₃PO₄ solution for 24 h before carbonation. For BC-HT-NP-HT, the pyrolyzed sample (20 g) was used to absorb N and P and was pyrolyzed again at 900 °C for 2 h under a N₂ atmosphere. For comparison, 10 wt.% Pt/C (Alfa Aesar Chemical Co., LTD, China) and a commercial AC powder (944 m² g⁻¹, Boyi Chemical Reagent co., LTD, Chongqing, China) were used as the reference catalysts for the air cathode of the same MFC. The commercial AC powder was used because it contained a high N content and its electrical conductivity was rather low.

Air cathodes were fabricated by the rolling-press method, as previously described [23]. The cathodes consisted of a stainless steel mesh (SSM) with a catalyst layer (CL) rolled on the water facing side and a gas diffusion layer (GDL) rolled on the air facing side. The mass ratio of polytetrafluoroethylene (PTFE) and catalyst for the CL was 1:4, and the catalyst loading was 50 mg cm⁻². The GDL was fabricated using commercial carbon black (Vulcan XC72, Cabot Co. Ltd) and a PTFE emulsion (60 wt.%, Hesin, Shanghai, China), with a mass ratio of 6:4. SSM with a mesh opening size of 40 M (type 304, Dingrunsiwang Manufacturing Co. Ltd., Hebei, China) was selected as the current collector. Similar to the air cathodes with carbon catalysts, the Pt-based air cathode was also fabricated using the rolling-press method, with a Pt loading of 0.5 mg cm⁻².

2.2 Electrochemical analyses

The electrochemical measurements were performed using an electrochemical workstation (ParSTAT MC, Princeton, USA). The electrochemical properties were studied using a three-electrode system in which a Pt foil served as the counter electrode and a Ag/AgCl (saturated with KCl) electrode served as the reference electrode. The working electrode was a 3-mm diameter glassy carbon electrode (GC, BAS.inc., Japan) coated with catalyst ink. To obtain the same catalyst loading on the GC electrode, the catalyst ink was prepared by dispersing 40 mg of the catalyst samples (BC-HT, BC-NP-HT, BC-HT-NP-HT, AC and Pt/C) in a mixture containing 1.9 mL of isopropyl alcohol and 0.1 mL of Nafion solution (5 wt.%), followed by ultrasonic treatment for 30 min. The working electrode was prepared by dropping the catalyst ink (5 μ L) onto the top of the GC electrode and drying at room temperature. The catalyst loading on the GC electrode was 1.4 mg cm⁻². Prior to being coated, the GC electrode was polished with 0.05 μ m Al₂O₃ powders, followed by rinsing with deionized water.

To simulate the relevant MFC conditions, all of the electrochemical measurements were performed in the growth medium discharged from a working air-cathode MFC operated at 50 Ω in continuous flow mode at 0.5 mL min⁻¹. Before the experiments, the growth medium was filtered using a microfiltration membrane (0.8 μ m, polyether sulfone membrane, Haiyan Xindongfang Plasticizing Technology Co., LTD, China) to remove the suspended bacterial cells. Then, the pH of the growth medium was adjusted to 7 using 0.1 M NaOH, and N₂ was sparged into the growth medium until the electrochemical experiments were performed. The electrochemical measurements were also performed in 50 mM phosphate buffer solution (PBS, 11.82 g L⁻¹ Na₂HPO₄, 2.32 g L⁻¹ KH₂PO₄; pH 7) for comparison. The RDE tests were conducted using a

RRDE-3A Rotating Ring Disk Electrode (ALS Co., Ltd, Japan). The RDE experiments were first performed in N₂-sparged growth medium to obtain the baseline current, and then, the tests were switched to the air-sparged solution. To remove possible contaminants or excess oxygen trapped in the pores of the carbon, the working electrode was polarized from 0.2 to −0.8 V vs. Ag/AgCl at 100 mV s^{−1} until the current response of each cycle was the same. For the LSV tests, the potential of the working electrode was scanned from 0.3 to −0.8 V vs. Ag/AgCl at 10 mV s^{−1} and at different rotation rates, from 400 to 2500 rpm. To ensure that the current in the current-potential plot only contains faradic currents related to ORR, the current obtained under nitrogen sparging was subtracted from that obtained under air sparging [24]. The potentials reported in this study were the values vs. the Ag/AgCl electrode, unless otherwise noted.

The average electron transfer number (*n*) and the kinetic current (*j_K*) for ORR were calculated using Koutecky–Levich (K-L) plots [25], as shown below:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_K} + \left(\frac{1}{0.62nFS D^{2/3} \omega^{-1/6} C} \right) \omega^{-1/2} \quad (1)$$

where *j* is the current (A), *F* is Faraday's constant (96485 C mol^{−1}), *n* is the average number of electrons transferred in the reaction, *S* is the projected surface area of the disk electrode (cm²), *D* is the diffusion coefficient of oxygen (cm² s^{−1}), *C* is the oxygen concentration in the solution (mol cm^{−3}), *v* is the kinetic viscosity (cm² s^{−1}), and *ω* is the rotation rate of electrode (rad s^{−1}).

Electrochemical impedance spectroscopy (EIS) of the air-cathodes was recorded over a frequency range of 10 mHz to 100 kHz at open circuit potential (OCP) with a sinusoidal perturbation signal amplitude of 10 mV. The EIS tests were conducted using the anode as the counter electrode, a Ag/AgCl (saturated with KCl) electrode as

the reference electrode, and air cathodes with different catalysts as the working electrodes. Nyquist plots were used to interpret the spectra. A least-squares fitting program (Zview 2) was employed to simulate the Nyquist plots according to equivalent circuits.

2.3 Physical and chemical characterization

X-ray diffraction (XRD) measurements were performed on an Empyrean XRD system using Cu K α radiation (40 kV, 40 mA and $\lambda=0.154$ nm) over a range of 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. The XPS spectra were acquired using a Thermo Fisher ESCALAB 250Xi spectrometer with a 150 W monochromatic Al K source. To provide information about the chemical environment, a narrow scan was performed for certain elemental core levels with a pass energy of 30 eV to obtain high-resolution spectra. The obtained data were analyzed with the Avantage program provided by Thermo Fisher Scientific Corporation. The bulk content of P and N in the carbon-based catalysts was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Vista MPX) and an elemental analyzer (Vario EL III), respectively. The conductivity of the carbon catalysts was measured using the conventional four-point method (RTS-8, Four Probes Technology Co. Ltd., China) [26]. Typically, 0.5 g carbon sample was put into a mold, pressed at 30 MPa for 15 min at room temperature. Then the mold was unloaded and the sample released was used for electrical conductivity measurement. During the measurement, four probes arranged in a straight line were contact with the surface of the sample. Then, a constant DC current (A) was passed through the two outer probes, and the voltage (V) across the inner two probes was measured. The electrical conductivity σ (S cm⁻¹) was calculated according to the following equation:

$$\sigma = \frac{\frac{1}{X_1} + \frac{1}{X_3} - \frac{1}{X_1 + X_2} - \frac{1}{X_2 + X_3}}{2\pi \frac{U}{I}} \quad (2)$$

Where X_1 , X_2 and X_3 are the probe spacing (cm).

2.4 MFC Experiments

Five single-chamber cube-shaped MFCs (4 cm long and 3 cm in diameter) were constructed as previously described [27]. The carbon fiber brush anode (25 mm diameter, 25 mm length) was placed horizontally in the cylindrical chamber. The cathode was assembled on the side of the reactor and was faced to air. The MFCs were inoculated with the effluent from an acetate-fed MFC that was successfully operated for over two years, and then, they were filled with pre-sterilized and deoxidized growth medium. The medium was a solution composed of 2.04 g L⁻¹ sodium acetate, 11.82 g L⁻¹ Na₂HPO₄, 2.32 g L⁻¹ KH₂PO₄, 0.1 g L⁻¹ NH₄Cl, 0.5 g L⁻¹ NaCl, 0.1 g L⁻¹ MgSO₄·7H₂O, 15 mg L⁻¹ CaCl₂·2H₂O and 1.0 mL L⁻¹ trace elements, which was reported in the previous study [28]. All of the MFCs were operated in fed-batch mode at 1000 Ω in a room with a constant temperature (30 ± 1 °C). The growth medium in the MFCs was replaced when the voltage dropped to < 50 mV.

The voltages of the MFCs were recorded at 30 s intervals using a data acquisition system (Agilent 34970A, Agilent Technologies, Inc., USA). To enable a reliable comparison to previous studies, polarization and power density curves were measured by a forward scan (varying the external resistance from 6000 to 15 Ω with a time interval of 20 ~ 40 mins) until a stable voltage output at each step (< 1 mV 5 min⁻¹) was reached. The tests were conducted in a temperature-controlled room at 30 ± 1 °C and repeated three times to obtain error bars. The current density and power density were normalized to the projected area of the air cathodes (7 cm²).

3 Results and discussion

3.1 Physical characterization of the catalysts

Fig. 2a shows the XRD patterns of the AC and BC catalysts. The peak parameters are also listed in Table 1. Note that AC exhibited a C(002) peak near 25.5° and a (100) peak near 45° , corresponding to parallel graphene layers and the 2D in-plane symmetry along the graphene layers, respectively. Compared with the C(002) peak of AC, there was a dramatic negative shift of the C(002) peak in the BC samples, which implies that N and P doping increased the interlayer spacing of the C(002) crystal plane in the BC samples. From Table 1, it is also noted that AC exhibited a higher full width at half maximum (FWHM) value of the C(002) peak compared with the BC catalysts. This result indicates a lower graphitization degree of the sample. Among the BC catalysts, BC-NP-HT exhibited a slightly higher FWHM value, revealing that the addition of $(\text{NH}_4)_3\text{PO}_4$ before carbonation induced a more disordered graphitic structure. The comparable FWHM values of BC-HT-NP-HT and BC-HT (Table 1) suggest that the addition of N and P after carbonating the bamboo precursors had little effect on the graphitization degree of the BC catalysts. From the XRD results, it is clear that the average graphitization degree of the carbon catalysts increased in the following order: $\text{AC} < \text{BC-NP-HT} < \text{BC-HT} \approx \text{BC-HT-NP-HT}$.

The carbon structure of the samples was further evaluated by Raman spectroscopy. As shown in Fig. 2b, all of the samples exhibited two obvious peaks at approximately 1335 cm^{-1} (D-band) and 1585 cm^{-1} (G-band). The D and G bands reflect the vibration of sp^3 and sp^2 hybridized carbon atoms, indicating the disordered graphite and the ordered state on the catalyst surfaces, respectively. Therefore, the graphitization degree of the catalysts can be quantified by the integrated intensity ratio

(I_D/I_G) of the D and G bands [29]. As shown in Fig. 2b and Table 1, AC had the highest I_D/I_G values (2.97), followed by BC-NP-HT (2.83), BC-HT-NP-HT (2.75) and BC-HT (2.70). These results are in good agreement with the XRD results. The highest I_D/I_G value of the AC catalyst suggests that the average graphitization degree of the sample, which reflects the electrical conductivity, was the lowest among the carbon catalysts. Compared with BC-HT and BC-HT-NP-HT, the higher I_D/I_G value of BC-NP-HT further confirmed that the average graphitization degree of the former was better than that of the latter. Additionally, the FWHM value of the D band for the catalysts, corresponding to the amount of disordered carbon, showed a similar trend of $AC > BC-NP-HT > BC-HT-NP-HT \approx BC-HT$. Therefore, the XRD and Raman data synergistically support the finding that the addition of $(NH_4)_3PO_4$ before carbonation induced a more disordered graphitic structure, while doping N and P after carbonating the bamboo precursors had a negligible effect on the average graphitization degree of the catalysts.

Table 1 also lists the electrical conductivity of the carbon-based catalysts. It is clear that the electrical conductivity of the carbon-based catalysts increased in the order of $AC < BC-NP-HT < BC-HT < BC-HT-NP-HT$. This trend is in agreement with the data from the XRD and Raman results. As has been demonstrated, the electrochemical performance of the carbon catalyst is directly related to their electrical conductivity.

In preliminary experiments, the BC samples were ultrasonically dispersed in 1.0 M HCl and was washed several times to remove the inherent metallic impurities. However, acid treatment didn't cause noticeable changes in the ORR activity of the BC catalysts. These results imply that the N and P containing functional groups on the surface of the catalysts were responsible for the ORR activity. Therefore, the surface

composition (with an analysis depth of several nanometers) and the chemical state of N and P bonded onto the surface of the catalysts were detected by XPS (Fig. 3). The full XPS scan of the BC catalysts shown in Fig. 3a reveals the presence of signals for C1s, O1s, N1s and P2p, confirming the existence of N and P in the samples. The bulk contents of N and P in the catalysts were also evaluated by an elemental analyzer and ICP-AES, respectively (Table 2). The surface contents of N and P in the catalysts were considerably higher than those in the bulk, indicating that N and P atoms were preferentially distributed on the surface of the catalysts. Table 2 also shows that AC had the highest surface N content of 5.4 % and the lowest surface P content of 0.58 %. Noticeable amounts of N and P found in BC-HT indicate that N and P inherently contained in bamboo precursors were successfully incorporated into the carbon structure [30, 31, 32]. Compared with BC-NP-HT, BC-HT-NP-HT had higher N and P contents. These results imply that soaking in $(\text{NH}_4)_3\text{PO}_4$ after carbonation induced more effective N and P doping. In general, doped carbon materials with high N and P contents would lead to more active reaction sites, thus resulting in good ORR activity.

To study the nature of N and P bonding on the surface, high resolution XPS spectra of N1s and P2p for all of the samples were recorded (Fig. 3b-c and Fig. S1). The deconvolution of the N1s spectrum in Fig. 3b shows that the ORR-active N-containing species, including graphitic-N (~ 401.1 eV), pyrrolic-N (~ 399.9 eV) and pyridinic-N (~ 398.1 eV), were found for all of the carbon catalysts [33, 34]. According to the results listed in Table 2, pyrrolic-N was the dominant N species in AC, while the relative ratio of pyrrolic-N in all of the BC catalysts showed a much lower value, ranging from 32.1 to 34.6 %. Table 2 also shows that the relative ratio of graphitic-N in BC-HT (42.6 %) and BC-NP-HT (46.0 %) was higher than that of pyridinic-N (~ 22 %), whereas BC-HT-NP-HT exhibited a higher pyridinic-N content

(37.7%) compared to the graphitic-N content of 27.8 %. Previous studies have proposed that the ORR activity of carbon-based materials is dependent on the relative content of pyridinic-N and graphitic-N [10, 33, 34]. Lai et al. suggested that graphitic-N improved the limiting current density, while pyridinic-N was beneficial for more positive onset potentials [10]. Recently, Yasuda et al. demonstrated that pyridinic-N favored the efficient four-electron ORR pathway (the direct reduction of O_2 to H_2O) compared to graphitic-N, which induced the indirect two-electron pathway involving H_2O_2 formation [33]. Considering the highest total N content and the highest relative ratio of pyridinic-N in BC-HT-NP-HT among the BC catalysts, a good ORR catalytic performance of the catalyst can be expected.

Fig. 3c shows that the deconvolution of P2p for BC-HT and BC-NP-HT exhibited three prominent peaks, which can be assigned as P-C (~132.8 eV), P-N (~133.5 eV) and C-O-PO₃ (~134.4 eV) [35]. However, for BC-HT-NP-HT, only P-N (~133.4 eV) and C-O-PO₃ (~134.6 eV) are observed in the P2p spectrum. The absence of P-C bonding in BC-HT-NP-HT indicates that most of the P in the sample was mainly incorporated onto the carbon surface by bonding to nitrogen or the bridging oxygen atoms. Correspondingly, higher contents of P-N (53.1 %) and C-O-PO₃ (46.9 %) were found in BC-HT-NP-HT compared to the BC-HT and BC-NP-HT catalysts. The high contents of P-N and C-O-PO₃ in BC-HT-NP-HT are conducive to improving the ORR activity because previous studies have demonstrated that P-N and C-O-PO₃ were highly reactive and stable active centers for ORR [12, 36].

3.2 Electrochemical characterization of the catalysts

The RDE curves of AC, BC, BC-NP-HT, BC-HT-NP-HT and Pt/C in PBS solution are presented in Fig. 4a. It is clear that AC had the lowest onset potential of

-150 mV and the lowest limiting current density of 0.59 mA cm^{-2} , indicating a poor electrocatalytic activity for ORR. The onset potentials of BC-HT and BC-NP-HT for ORR were comparable (ca. -70 mV) and were more positive compared with those of AC. However, a noticeable positive shift of the onset potential and an increase in the limiting current density were observed for BC-HT-NP-HT. These improvements can be attributed to the highest total N and P content and the highest relative ratio of pyridinic-N, P-N and P-O-CO₃ in BC-HT-NP-HT among the BC catalysts [16]. Among the catalysts used in this study, Pt/C exhibited the best electrocatalytic activity in PBS solution, i.e., the most positive ORR onset potential of +250 mV and the highest limiting current density of 1.45 mA cm^{-2} .

In a practical air-cathode MFC without a proton exchange membrane (PEM), ORR catalysts are usually operated in a complex electrolyte containing not only a substrate but also species such as metabolites, Cl^- , SO_4^{2-} , S^{2-} and HPO_4^{2-} at a level of several to hundreds of mM. It is known that even trace amounts of these species (i.e., 0.1 mM) in an electrolyte induce a serious blockage of active sites for ORR and enhance H_2O_2 formation, thus leading to a drastic change in both the ORR activity and reaction pathway of ORR catalysts [37]. Therefore, to reveal the true ORR activity of the BC catalysts in MFCs, RDE tests of AC, BC-HT, BC-NP-HT, BC-HT-NP-HT and Pt/C (Fig. 3b) were also conducted in the growth medium discharged from an operational air-cathode MFC (pH 7). Note that although AC showed a similar onset potential for ORR in the growth medium, the limiting current density significantly decreased from 0.58 to 0.18 mA cm^{-2} , implying that the active sites of the AC catalysts were blocked under the relevant MFC conditions. It is also interesting to note from Fig. 4b that for Pt/C, two current plateaus (from -70 to -180 mV and from -420 to -600 mV) were observed, suggesting that Pt/C underwent an

inefficient two-electron pathway and proceeded via a hydroperoxide anion (HO_2^-) intermediate. Additionally, the onset potential of Pt/C in the growth medium was significantly shifted to a more negative potential of +120 mV, and the limiting current density dramatically decreased to 0.61 mA cm^{-2} . The low limiting current density and poor ORR kinetics of Pt/C may arise from the detrimental effects of the poison species in the growth medium [37, 38]. For BC catalysts (BC, BC-NP-HT and BC-HT-NP-HT), the presence of poisoning species in the growth medium had little effect on the onset potential and only led to a slight decrease in the limiting current density of the BC catalysts. These results suggested the high tolerance of the BC catalysts to the poisoning species under the relevant MFC conditions. Among all of the BC catalysts, BC-HT-NP-HT had the most positive onset potential, ~30 mV, and the highest limiting current density, 1.23 mA cm^{-2} , demonstrating that BC-HT-NP-HT is a promising ORR catalyst with a low cost and high catalytic performance under the MFC relevant conditions.

To further investigate the ORR mechanism, the RDE curves for the Pt/C, AC, and BC catalysts (Fig. S2a-j) were tested at various rotating rates from 400 to 2500 rpm in both a PBS solution and the growth medium. The transferred electron number (n) per oxygen molecules of the Pt/C, AC, and BC catalysts at -0.5 V was calculated from the slope of K-L curves (Fig. S3a-e, Fig. 4c). For the ORR in PBS solution, the n values for AC, BC, BC-NP-HT and BC-HT-NP-HT, and Pt/C are 1.2, 3.2, 3.4, 3.4 and 4.0, respectively. These values changed to 0.2, 2.6, 3.0, 3.2 and 1.7, respectively, in the case of ORR in the growth medium. The similar n value for the BC catalysts in PBS solution and growth medium indicates that poisoning species in the growth medium had little effect on the ORR mechanism of the BC catalysts.

3.3 Air cathode performance

To ensure the steady state condition of the ORR reaction, the LSV of the air cathodes was recorded at a very low scan rate of 0.1 mV s^{-1} in an operating MFC (Fig. 5a) [39]. According to the LSV results, it is clear that the air cathode based on BC-HT-NP-HT showed the highest current response of 0.89 mA cm^{-2} at -0.15 V vs. Ag/AgCl, while BC-HT, BC-NP-HT and Pt/C exhibited a comparable performance of 0.39 , 0.36 and 0.39 mA cm^{-2} , respectively. EIS was conducted for the air cathodes in the same electrolyte to determine the cathode resistance at the open circuit potential. To interpret the EIS results, equivalent circuits were utilized to identify the components of the cathode internal resistances, as previously described (Fig. S4a for the Pt/C cathode and Fig. S4b for the BC cathode) [23, 25, 29]. As seen in Fig. 5b, S4 and Table S1, the air cathode based on AC showed the highest ohmic resistance (R_0) and interface ohmic resistance (R_{in}) due to the poor electrical conductivity resulting from the low average graphitization degree. It is also clear that the air cathode based on Pt/C showed a higher charge transfer resistance (R_{ct}) of 22.24Ω compared with BC catalysts. This result can be attributed to the poisoning effect of the impurities contained in the growth medium. Among the catalysts used in this study, BC-HT-NP-HT showed the lowest R_{ct} value (0.43Ω), which could be explained by the high electrical conductivity, the sufficient amount of N- and P-containing groups, the highest relative ratio of active pyridinic-N, P-N and P-O-CO₃ groups and the high tolerance to the poisoning species under the relevant MFC conditions.

3.4 MFC performance

To evaluate the power generation of carbon-based catalysts in MFC applications, five air-cathode MFCs were prepared using air cathodes with different catalysts. As

shown in Fig. 6a and 6b, the maximum power density ($P_{\max}$) obtained by the MFC using AC as the ORR catalyst was only $420 \pm 13 \text{ mW m}^{-2}$. The MFC with BC-HT exhibited a $P_{\max}$ value of $1056 \pm 38 \text{ mW m}^{-2}$, which was close to that of Pt/C ($1039 \pm 15 \text{ mW m}^{-2}$). These results suggest that directly pyrolyzed moso bamboo could be a good alternative ORR catalyst for Pt/C. The comparable $P_{\max}$ value between BC-HT and BC-NP-HT ($993 \pm 96 \text{ mW m}^{-2}$) implies that doping N and P before carbonation has no significant effect on the MFC performance. A 65 % $P_{\max}$ increase for BC-NP-HT-NP ($1719 \pm 82 \text{ mW m}^{-2}$) compared to Pt/C indicated that incorporating N and P after carbonation was an effective method for preparing a high-performance and cost-effective ORR catalyst from BC.

4. Conclusions

In this study, moso bamboo was used as the precursor for carbon-based ORR catalysts. It was shown that BC-HT obtained by direct pyrolysis of bamboo in a N_2 atmosphere demonstrated a comparable $P_{\max}$ value ($1056 \pm 38 \text{ mW m}^{-2}$) to that of Pt/C ($1039 \pm 15 \text{ mW m}^{-2}$). This result can be attributed to the detrimental effect of poisoning species on the electrocatalytic activity of Pt/C in the growth medium. Additional N and P doping by soaking in a $(\text{NH}_4)_3\text{PO}_4$ solution after carbonation (BC-HT-NP-HT) resulted in a 65 % increase in $P_{\max}$ ($1719 \pm 82 \text{ mW m}^{-2}$) compared to that of Pt/C. The Raman spectroscopy, XRD, electrical conductivity and XPS results showed that the highest performance of BC-HT-NP-HT was attributed to the high electrical conductivity, the sufficient amount of N, P-containing groups, the presence of many effective active sites, such as pyridinic-N, graphitic-N, P-N and P-O-CO₃, and the high tolerance of the catalyst to the poisoning species under the relevant MFC conditions. These results indicated that BC was a good alternative to

the expensive Pt catalyst for practical applications of MFCs.

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Figure Captions

Fig. 1. Schematic of the synthetic procedure of the BC catalysts.

Fig. 2. XRD patterns (a) and Raman spectra (b) of the AC and BC catalysts.

Fig. 3. XPS spectra (a) and deconvolution of the N1s (b) and P2p (c) spectra of BC-HT, BC-NP-HT and BC-HT-NP-HT.

Fig. 4. RDE curves of the catalysts with a scanning rate of 10 mV s^{-1} and an electrode rotation rate of 2500 rpm in an O_2 -saturated PBS solution (a) and autoclaved growth medium (b); (c) comparison of the electron transfer number of the catalysts in the PBS solution and growth medium at -0.5 V vs. Ag/AgCl based on the RDE data.

Fig. 5. (a) LSV of the air-cathodes with different catalysts at 0.1 mV s^{-1} in an operating air-cathode MFC; (b) Nyquist plots of EIS spectra of the air-cathodes (symbols represent experimental data, and lines represent data fit with the equivalent circuit).

Fig. 6. (a) U-I, (b) P-I curves of the MFCs based on the air cathodes with different catalysts.

Tables

Table 1 XRD and Raman peak parameters and electrical conductivity of the BC and AC catalysts

Sample	XRD			Raman spectroscopy			Electrical conductivity (s cm ⁻¹)
	2θ	Interlayer	FWHM	I _D /I _G	FWHM _D	FWHM _G	
	(°)	spacing	(rad)		(cm ⁻¹)	(cm ⁻¹)	
		(nm)					
AC	25.5	0.349	8.81	2.97	241.2	83.2	0.004
BC-HT	23.9	0.374	8.33	2.70	186.9	80.2	0.014
BC-NP-HT	24.2	0.363	8.52	2.83	204.5	82.6	0.010
BC-HT-NP-HT	24.0	0.370	8.35	2.75	190.4	77.9	0.018

Table 2 Atomic concentration of N and P obtained from XPS and an element analyzer/ICP-AES and the relative ratio of the N and P contents in the different samples

Sample	N(wt. %)		N1s (at. %)			P (wt. %)		P2p (at. %)		
	surface	bulk	N _{pyridic}	N _{pyrrolic}	N _{graphitic}	surface	bulk	P-C	P-N	C-O-PO ₃
AC	5.36	4.31	12.3	63.8	23.9	0.58	0.21	13.7	10.6	75.7
BC-HT	0.72	0.12	23.5	33.8	42.6	1.23	0.63	32.4	40.5	27.2
BC-NP-HT	0.77	0.19	21.8	32.1	46.0	1.75	0.74	25.9	41.4	32.7
BC-HT-NP-HT	0.89	0.45	37.7	34.6	27.8	2.23	0.91	N.D. ^a	53.1	46.9

^aN.D.: not detected

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6