Short communication

# Cellulose-derived nitrogen and phosphorus dual-doped carbon as high performance oxygen reduction catalyst in microbial fuel cell

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HIGHLIGHTS

- Nitrogen and phosphorus dual-doped carbon was prepared from cellulose.
- Ammonium phosphate was used as doping source.
- The dual-doped carbon show high electrocatalytic activity for ORR in MFCs.
- This study provided a facile and sustainable way to prepare ORR catalyst for MFC.

GRAPHICAL ABSTRACT
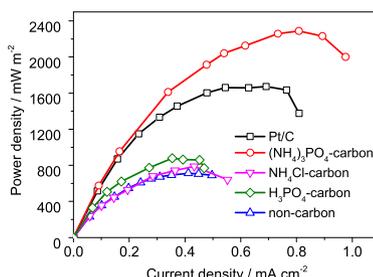
ABSTRACT

Microbial fuel cells (MFCs) couple functions of waste removal and electricity generation. The future success of MFCs inevitably depends on the increase of performance at decrease of material cost. Therefore, the use of renewable and sustainable materials, e.g. cellulose, to prepare high performance materials for MFCs would be an inevitable trend. In this communication, nitrogen and phosphorus dual-doped carbons were prepared by pyrolysis of cellulose using ammonium phosphate as doping source and employed as oxygen reduction reaction (ORR) catalyst in air-cathode of MFCs. A maximum power density of 2293 ± 50 mW m^{-2} was generated by the air-cathode using the dual-doped carbon catalyst, which was higher than the air-cathode using Pt/C catalyst with Pt load of 0.5 mg cm^{-2} (1680 ± 32 mW m^{-2}). This study provided a facile and sustainable way to prepare low-cost and high-efficient ORR catalyst for scaled-up MFC applications.

1. Introduction

In the last decade, many progresses for the development of bioelectrochemcial technologies had been achieved, and the concept of direct conversion of waste chemicals to available electric power by microbial fuel cells (MFCs) was a major application target and driving force. For the MFCs, the cathode was one of the key components which determined the final power generation. Oxygen was believed to be an ideal electron acceptor for the cathode reaction in MFCs because it was abundant in source. However, slow oxygen reduction reaction (ORR) generally required the participation of catalyst. The primary used ORR catalyst in MFCs was Pt, however, the characteristics of high cost and low long-term instability hindered its practical application in MFCs. Later, a series of non-precious metal-based ORR catalysts were developed as alternatives to Pt. Products pyrolyzed from complexes of metals, e.g. phthalocyanines or porphyrins, were firstly examined in MFCs

[1–3]. Thereafter, other metal complexes and metal oxides, such as manganese oxides [4,5], Fe compounds [6–9], were considered. Recently, some low-cost carbon materials had been developed for ORR catalysts in MFCs and showed efficient ORR electrocatalytic activities, such as activated carbon (AC) [10–13], biochar derived from sewage sludge [14]. However, the performances of the AC catalysts were varied with the preparing methods and raw materials. And the biochar catalyst was likely to contain undefined components, such as pathogens and heavy metals, and would bring secondary pollution to the environment.

Since the first report of N-doped carbon nanotubes with a high-efficient electrocatalytic activity towards ORR in alkaline media, the use of heteroatom doped carbons as ORR catalysts in the chemical fuel cells had attracted extensive attentions [15]. However, the carbons used as ORR catalysts in the cathode of MFCs were only limited to the N-doping, such as N-doped carbon nanotubes [16,17] and graphene [18], which had been proved to show high efficient electrocatalytic activity for ORR. Other heteroatom doped carbons (such as P, S and B) were also developed recently [19], however their catalytic activity for ORR in neutral condition was still unknown. Moreover, most hetero-atom doped carbon ORR catalyst were based on the carbon nanomaterials and involved in complex and rigorous preparation processes, thus their use for scale-up MFC would face a tremendous challenge. The exploration of low-cost, high-efficient and environmental-friendly ORR catalysts for the future development of MFCs are extremely important.

Cellulose is abundant in the environment and available at a low cost. In this study, we report a facile method for preparation of N and P dual-doped carbon from cellulose. The dual-doped carbon catalysts were prepared by directly pyrolyzing the cellulose in the presence of ammonium phosphate. Air-cathode MFC based on the dual-doped carbon ORR catalyst generated a high power density of 2293 ± 50 mW m^{-2}, which was much higher than that of MFC based on the Pt/C ORR catalyst with about 1680 ± 32 mW m^{-2}.

2. Experimental

2.1. Catalyst preparation and characterization

N-doped, P-doped, and the N and P dual-doped carbons were synthesized via pyrolysis of cellulose in the presence of NH$_4$Cl, H$_3$PO$_4$ and (NH$_4$)$_3$PO$_4$, respectively, and denoted as NH$_4$Cl–carbon, H$_3$PO$_4$–carbon and (NH$_4$)$_3$PO$_4$–carbon, respectively. Undoped carbon was also prepared by pyrolysis of pure cellulose under the same condition and denoted as *free-carbon*. Cellulose (microcrystalline power of 0–50 μm particle size) was purchased from J&K Chemical Company. Typically, 10 g cellulose was immersed in 50 mL 1 M (NH$_4$)$_3$PO$_4$ solution and stirred at room temperature for 24 h; after filtration and drying, the solid cake was loaded onto a porcelain boat and placed in an electric furnace under N$_2$ atmosphere, then heated to the set temperature with a heating rate of 5 °C min^{-1} and annealed for 1 h at the final temperature. After cooling down, the resulted carbon powder was rinsed with distilled water for 3 times and dried in vacuum at 100 °C for 4 h. 3 M NH$_4$Cl was used for the preparation of NH$_4$Cl–carbon and 1 M H$_3$PO$_4$ was used for the preparation of H$_3$PO$_4$–carbon. Without specification, the sample (NH$_4$)$_3$PO$_4$–carbon was prepared in 1 M (NH$_4$)$_3$PO$_4$ and pyrolyzed at 900 °C. Samples prepared from different (NH$_4$)$_3$PO$_4$ solution concentration and pyrolyzing temperature were denoted as *concentration-temperature*, for example, the *1M-900* is prepared from 1 M (NH$_4$)$_3$PO$_4$ and pyrolyzed at 900 °C. X-ray photoelectron spectroscopy (XPS, Thermo escalab 250Xi, USA) was performed to identify the elements on the surface

of the samples. Raman spectra were obtained using a LabRAM HR Raman spectrometer.

2.2. Electrode preparation and electrochemical test

Rotating ring-disk electrode measurements (RRDE, disk area = 0.2475 cm^2, collect efficiency is 40%) were conducted to evaluate the ORR electrocatalytic activity in 50 mM PBS solution. The electrode was first mechanically polished with 1 μm and then 0.05 μm alumina powder using an abrasive paper (to obtain mirror-like surfaces), then washed with both ethanol and deionized water (sonicated for 5 min in each), and finally dried in desiccators (relative humidity RH = 0%). Catalysts (1 mg) were dispersed in a mixture containing 25 μL of Nafion dispersion (supplied as a 5% mass dispersion in aliphatic alcohol/water mixture) and 250 μL of deionized water using sonication. Immediately after dispersion, 15 μL of the catalyst slurry was pipetted onto the RRDE electrode surface. 20 wt% Pt/C catalyst was used as the reference control. The electrodes were dried at room temperature before electrochemical testing.

Air-cathodes were fabricated by a rolling method using stainless steel mesh as current collector as previously described [20]. The detailed description of rolling method was listed in the Supplementary information. The mass ratio of catalyst/PTFE was controlled to be about 4/1, the load of catalyst was controlled to be about 20 mg cm^{-2}. Similar to the air-cathodes with doped carbons, the air-cathode of Pt catalyst in this paper was also processed by the rolling method using stainless steel mesh as current collector and Pt/C (20 wt%, Alfa Aesar) as ORR catalyst. The load of Pt was controlled to be about 0.5 mg cm^{-2}.

The ORR electrocatalytic activities of the catalysts were conducted on the RRDE electrodes and the air-cathodes by using linear sweep voltammetry (LSV) respectively. A three-electrode system equipped with a Pt foil counter electrode and an Ag/AgCl reference electrode was used for test. The LSV measurements were controlled by a potentiostat (CHI660D) over a voltage range of +0.3 to −0.3 V. The scan rate for the RRDE electrodes is 5 mV s^{-1}, for the air-cathode is 1 mV s^{-1}. All LSV tests were conducted in O$_2$ saturated 50 mM PBS solution (pH 7.0) at 35 °C.

The electron transfer numbers (n) were calculated based on the RRDE tests according to the equation [21]:

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

where I_d is the disk current, I_r is the ring current. N refers to the collection efficiency of Pt ring, and here the value 0.4 is adopted.

2.3. MFCs construction and operation

Single-chamber cubic air-cathode MFC configuration (4 cm in length, 3 cm in diameter) was used for the measurements as previously described [22]. Graphite fiber brushes (2.5 cm long and 2.5 cm in outer diameter, Jilin Chemical Fiber Group Co., Ltd., China) heat-treated at 450 °C for 30 min were served as anodes. All MFCs were inoculated from another MFC which was inoculated with wastewater from wastewater treatment plant (Qingshan, Nanchang) and had been run for more than 5 months. Each MFC was operated at 35 °C and fed with a medium containing acetate (1 g L^{-1}), vitamin solution (12.5 mL L^{-1}), trace element solution (12.5 mL L^{-1}) in 50 mM phosphate buffer solution (PBS: pH 7.0, 10.9233 g L^{-1} Na$_2$HPO$_4$·12H$_2$O, 3.042 g L^{-1} NaH$_2$PO$_4$·2H$_2$O, 0.31 g L^{-1} NH$_4$Cl, 0.13 g L^{-1} KCl). The medium was refreshed when the voltage dropped below 100 mV.

A 1000 Ω resistor was loaded between the anode and air-cathode. The curves of voltage versus time (V–t) were measured

using a date acquisition system (HIOKI LR8431-30) at 1 min interval. Polarization and power density curves were measured by varying the external resistance from 100 MΩ to 30 Ω, with each resistor used for a complete cycle. Both the current and power density results were reported normalized to the projected area of the air-cathode (7 cm^2). All the electrode potentials were measured versus the Ag/AgCl (+0.197 V vs. SHE, saturated KCl, 25 °C) reference electrode.

3. Results and discussion

3.1. Elemental analysis

The preparation of N and P dual-doped $(NH_4)_3PO_4$–carbon was realized by soaking the cellulose in 1 M $(NH_4)_3PO_4$ solution and then pyrolyzing at 900 °C. The salt $(NH_4)_3PO_4$ served as N and P doping source. The XPS results shown in Fig. 1A and Table S1 revealed that, except for the main elements of C and O, the $(NH_4)_3PO_4$–carbon contained N and P atoms with content of about 2.17% and 2.22%, respectively, representing the formation of N and P dual-doping in the $(NH_4)_3PO_4$–carbon. Fine P2p and N1s spectra in the dual-doped $(NH_4)_3PO_4$–carbon were observed and shown in Fig. 1B. Two peaks of 132.7 and 134.1 eV (Fig. 1Ba and Bc) were displayed in the high-resolution spectra of P$_{2p}$ and assigned to P–C and P–O groups, respectively, which contributed to the electro-catalytic activity for ORR [23]. Three peaks of 398.5, 401.3 and 402.0 eV were separated from the N1s signal (Fig. 1Bb and Bd), which were assigned to the pyridinic, quarternary and pyridinic N$^+$–O$^-$ types, respectively. Moreover, the ORR electrocatalytic active pyridinic (398.5 eV) and quarternary (401.3 eV) type N atoms [15,19] were the dominant N type in the $(NH_4)_3PO_4$–carbon.

XPS analyses showed that the NH_4Cl–carbon contain 3.64% N atom and the H_3PO_4–carbon had a P content of 2.07%, demonstrating the successful incorporation of N and P into the NH_4Cl–carbon and H_3PO_4–carbon, respectively. The fine XPS spectra in Fig. 1B revealed that the doping states of the N1s and P2p in the $(NH_4)_3PO_4$–carbon were similar to that of the N1s in the NH_4Cl–carbon and P2p in the H_3PO_4–carbon, respectively.

3.2. Electrochemical performance

As shown in Fig. 2A, the RRDE curves of $(NH_4)_3PO_4$–carbon showed an initial ORR potential of about +0.2 V, which was more positive than that of the NH_4Cl–carbon, H_3PO_4–carbon and *free-carbon*, indicating better ORR electrocatalytic activity for the $(NH_4)_3PO_4$–carbon. Fig. 2A and B showed that the $(NH_4)_3PO_4$–carbon generated a lower disc current response and a higher ring current response than the 20 wt% Pt/C catalyst, indicating a lower ORR electrocatalytic activity. The electron transfer numbers (n) of different catalysts at different potential were calculated from the RRDE measurements and shown in Fig. 2C. The average n of the $(NH_4)_3PO_4$–carbon is about 3.5, which was slightly lower than that of Pt/C catalyst. It indicated a nearly four-electron pathway of ORR on the $(NH_4)_3PO_4$–carbon catalyst. It should be noted that the RRDE measurements was only for indication of ORR catalytic activity, but did not represent actual electrocatalytic performance of catalysts in the MFCs.

To evaluate the practical ORR catalytic activities of different catalysts in MFCs, air-cathodes were built by a rolling method. Compared to the traditional brushing method, the rolling method was demonstrated to show advantages of (a) more uniform and stable electrode performance, (b) enhanced power output, (c) decreased labor cost and increased production efficiency [20]. The LSVs of the air-cathodes were recorded using a very low scan rate of 1 mV s^{-1} which was popularly used in numbers of works [10,20,24]. As shown in Fig. 3A, compared to the *free-carbon* catalyst without doping, the air-cathodes with doped carbon catalysts displayed an obvious current response in the voltage range of −0.3–0.3 V (vs. Ag/AgCl). The ORR current response for the air-cathode using the $(NH_4)_3PO_4$–carbon catalyst was higher than that using the NH_4Cl–carbon and H_3PO_4–carbon catalyst, demonstrating a higher electrocatalytic activity towards ORR. The $(NH_4)_3PO_4$–carbon air-cathode also showed a higher ORR current response than the Pt/C-based air-cathode prepared by the same rolling method with a Pt load of 0.5 mg cm^{-2}.
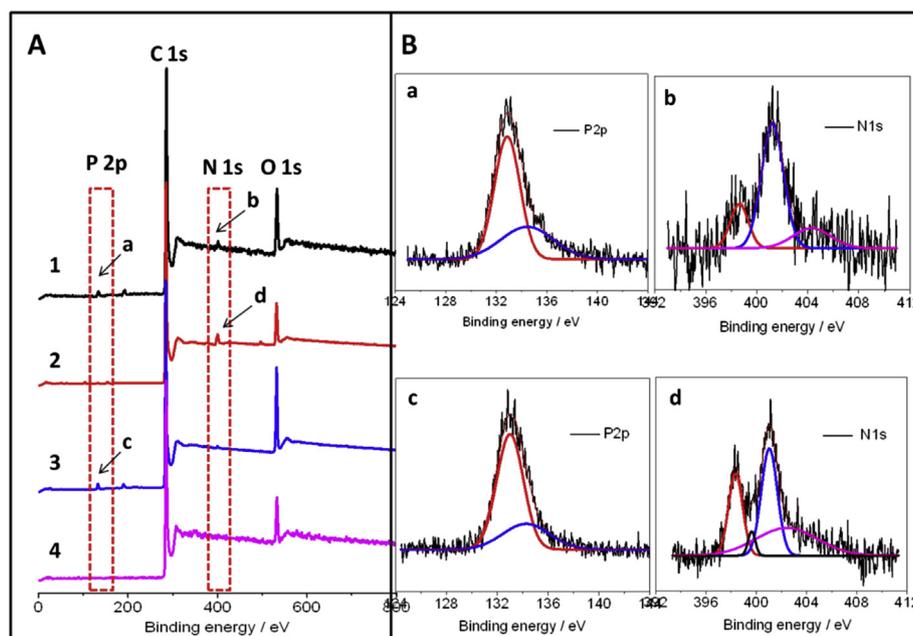

Fig. 1. (A) Survey XPS spectra of cellulose doped carbon (1) $(NH_4)_3PO_4$–carbon, (2) NH_4Cl–carbon, (3) H_3PO_4–carbon and (4) *free-carbon*. (B) Detailed XPS spectra of the selected peaks in (A), (a) P2p and (b) N1s fine spectra of $(NH_4)_3PO_4$–carbon, (c) P2p fine spectra of H_3PO_4–carbon and (d) N1s fine spectra of NH_4Cl–carbon.
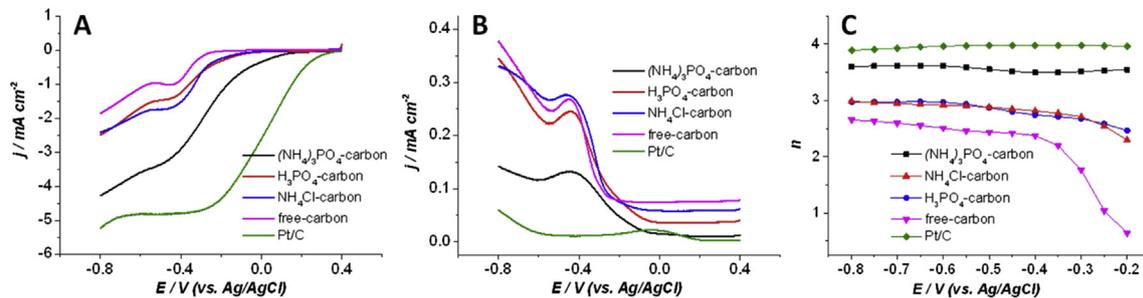
Fig. 2. (A) Disk and (B) ring current response of different catalysts based on the RRDE measurements at rotating speed of 1600 rpm, scan rate is 5 mV s^{-1}. (C) Electron transfer number (n) of different catalysts at different potential.

3.3. Effect of solution concentration and the pyrolyzing temperature

The effects of $(NH_4)_3PO_4$ solution concentration and the pyrolyzing temperature on the electrocatalytic activity of the $(NH_4)_3PO_4$–carbon catalysts were studied. As shown in Fig. S1A, at the same pyrolyzing temperature of 900 °C, the ORR current response increased with increase of $(NH_4)_3PO_4$ concentration from 0.5 to 1 M, representing the enhancement of the electrocatalytic activity in the resulted $(NH_4)_3PO_4$–carbon. Further increase the $(NH_4)_3PO_4$ concentration to 2 M, the ORR current response of the $(NH_4)_3PO_4$–carbon catalyst did not increase anymore. The $V-t$ curves of the MFCs with air-cathodes using $(NH_4)_3PO_4$–carbon catalysts prepared from different concentration of $(NH_4)_3PO_4$ solution were also recorded and shown in Fig. S1B. They displayed the same tendency as the LSV results. A stable cell voltage of over 0.62 V was recorded at the air-cathodes with catalysts of *1M-900* and *2M-900*. The pyrolyzing temperature for the $(NH_4)_3PO_4$–carbon catalysts was also optimized. Based on the LSV and $V-t$ measurement results, the *1M-900* showed better ORR electrocatalytic performance than the catalysts of *1M-800* and *1M-1000*. The effect of pyrolyzing temperature on the ORR electrocatalytic activity could be attributed to the comprehensive functions resulted by the N and P contents and the degree of graphitization of the resulted carbon. It was well-known that higher temperature would increase the degree of graphitization and brought positive contribution to the ORR electrocatalytic activity, but on the other hand decreased the content of the doping atoms and showed negative contribution to the ORR catalytic activity.

3.4. MFCs performance

As shown in Fig. 3B, the air-cathode with the $(NH_4)_3PO_4$–carbon catalyst could generate a stable voltage of 0.636 V, while the air-cathodes with NH_4Cl–carbon, H_3PO_4–carbon or *free-carbon* catalysts only generated voltages of 0.416, 0.484 and 0.355 V,

respectively, which were much lower than that using the $(NH_4)_3PO_4$–carbon catalyst. Under the comparable condition, the Pt/C based air-cathode generated a voltage of 0.615 V. These results revealed that the electrocatalytic activity of the $(NH_4)_3PO_4$–carbon catalyst was better than the NH_4Cl–carbon and H_3PO_4–carbon, and was comparable to the Pt/C catalyst with load of 0.5 mg Pt cm^{-2}.

The polarization curves of the N and P dual-doped $(NH_4)_3PO_4$–carbon catalyst prepared at the optimum condition were measured and compared with the N-doped NH_4Cl–carbon, P-doped H_3PO_4–carbon, *free-carbon*, as well as the Pt/C catalysts. As shown in Fig. 4A, the potential of the anodes in different MFCs were controlled almost the same. Fig. 4B showed that an open circuit voltage of 0.743 V was generated in the MFC with air-cathode using $(NH_4)_3PO_4$–carbon catalyst, which was comparable to that of MFC using Pt/C catalyst (0.5 mg Pt mg cm^{-2}) (0.766 V). The power density curves in Fig. 4C showed that the MFC with $(NH_4)_3PO_4$–carbon catalyst delivered a high maximum power density of 2293 ± 50 mW m^{-2}. It was much higher than that using the NH_4Cl–carbon, H_3PO_4–carbon or *free-carbon* catalysts which delivered power density of 801 ± 13, 872 ± 15 and 715 ± 18 mW m^{-2}, respectively. The higher ORR electrocatalytic activity for the dual-doped $(NH_4)_3PO_4$–carbon catalyst than the mono-doped carbons could be ascribed to the synergic action of the N and P dopings, as illustrated in Refs. [19,25].

The control reference in this study, Pt/C-based air-cathode, was fabricated by rolling method and delivered a maximum power density of 1680 ± 32 mW m^{-2}. This result was comparable to the result from the Pt/C-air-cathode assembled by traditional brushing method reported in Refs. [17,18] under the similar MFC condition. It demonstrated that the Pt/C air-cathode prepared by the rolling method in present study exerted its maximum catalytic potential and could be used for reference control. Comparing to the Pt/C⁻ based air-cathode, the better performance of the air-cathode with the dual-doped $(NH_4)_3PO_4$–carbon catalyst was attributed to (a) the high electrocatalytic activity for ORR with electron transfer number
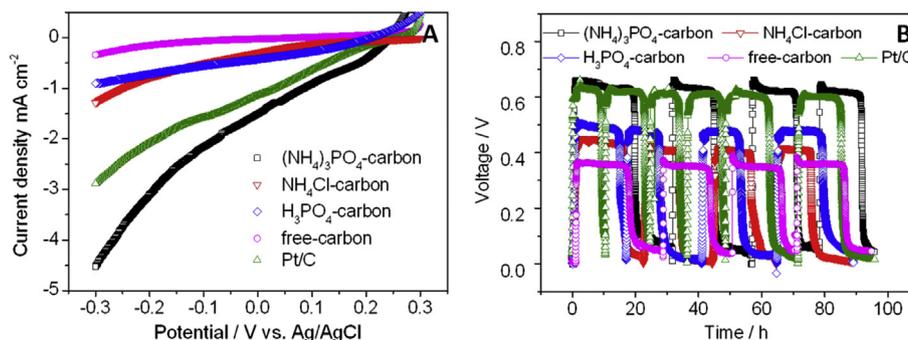

Fig. 3. (A) LSV and (B) $V-t$ curves of air-cathodes with different ORR catalysts under 50 mM PBS, pH = 7.0. Scan rate of LSV is 1 mV s^{-1}.
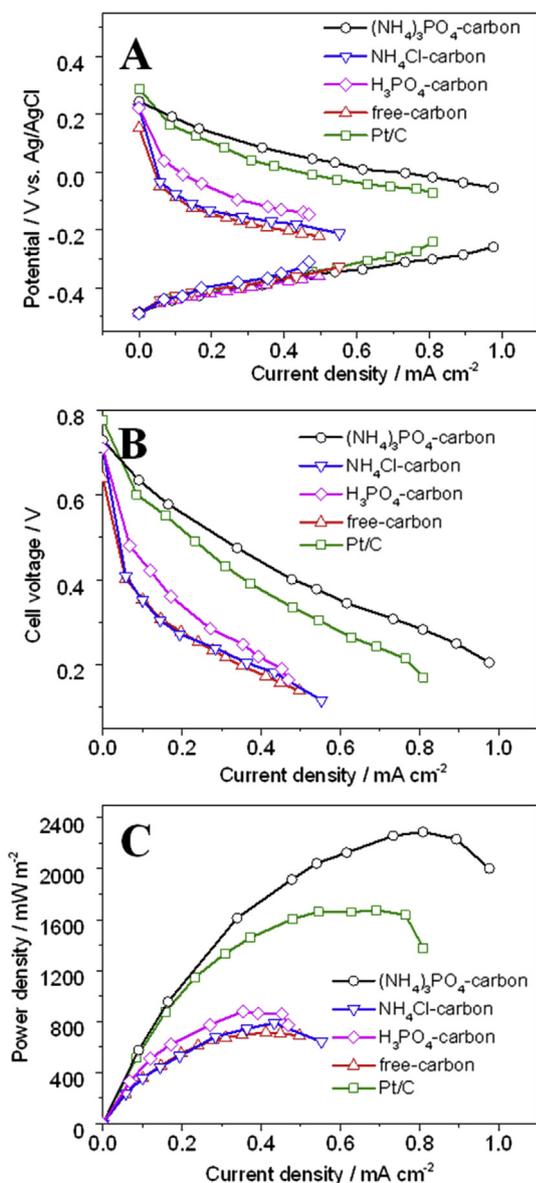
Fig. 4. (A) Anodic and cathodic potential of the MFCs, (B) polarization and (C) power generation curves of MFCs based on the air-cathodes with different catalysts.

recently reported high-performance carbon-based ORR catalysts in MFCs, such as N-doped carbon nanotubes [17], graphene [26], and NH_3-treated activated carbon [13].

4. Conclusion

N and P dual-doped carbon was successfully prepared by direct pyrolysis of cellulose in the presence of ammonium phosphate. The MFCs using the dual-doped $(NH_4)_3PO_4$—carbon catalyst generated a high maximum power density of 2293 ± 50 mW m^{-2}, which was higher than that using Pt/C catalyst. The cellulose is renewable and sustainable and can be available at low cost, and the ammonium phosphate is environmental-friendly. Moreover, the preparation method is simple and easy to be scaled-up. This study provides a renewable and sustainable way for preparation of high-efficient ORR catalyst for MFCs.

Acknowledgment

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.09.102.

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of 3.5 as discussed above and (b) the higher catalyst load. The load of the $(NH_4)_3PO_4$—carbon catalyst on the air-cathode was about 20 mg cm^{-2}, which was 8 times higher than the load of Pt/C (20 wt% Pt/C, 0.5 mg Pt cm^{-2}). But, it had to be noted that the cost of $(NH_4)_3PO_4$—carbon in present study was evaluated to be about 0.5—2 RMB/g according to the cost of raw materials and energy consumption, which was 500 times lower than the Pt/C catalyst of about 450 RMB/gPt/C (20 wt% Pt/C, Alfa Aesar). Hence, the higher load of the $(NH_4)_3PO_4$—carbon catalyst on air-cathode would not raise the cost of the MFC too much. The future success of MFCs inevitably depends on the increase of performance at decrease of material cost, the $(NH_4)_3PO_4$—carbon catalyst in present study would fit the requirement for the future MFC development. As summarized in Table S2, the performance of the cellulose-derived N and P dual-doped $(NH_4)_3PO_4$—carbon was comparable to some