



Short communication

Phosphorus-doped carbon derived from cellulose phosphate as efficient catalyst for air-cathode in microbial fuel cells

Qin Liu^a, Shuiliang Chen^{a,b,*}, Yan Zhou^{a,b}, Suqi Zheng^a, Haoqing Hou^{a,*}, Feng Zhao^b^a Department of Chemistry and Chemical Engineering, Jiangxi Normal University, 330022 Nanchang, China^b Institute of Urban Environment, Chinese Academy of Sciences, 1799 Jimei Road, 361021 Xiamen, China

HIGHLIGHTS

- P-doped carbon catalyst was prepared via direct pyrolysis of cellulose phosphate.
- The P-doped carbon catalyst showed high catalytic activity for ORR in MFCs.
- The high catalytic activity was ascribed to the P-dopings in the carbon catalyst.
- This study provided a low-cost and promising cathodic catalyst for scale-up MFCs.

ARTICLE INFO

Article history:

Received 21 January 2014

Received in revised form

11 March 2014

Accepted 16 March 2014

Available online 27 March 2014

Keywords:

Microbial fuel cells

Phosphorus

Oxygen reduction reaction

Air-cathode

Cellulose phosphate

ABSTRACT

Phosphorus-doped (P-doped) carbon was prepared via direct pyrolysis of cellulose phosphate for efficient oxygen reduction catalyst in air-cathode of microbial fuel cells (MFCs). Air-cathodes with P-doped carbon catalysts were assembled by rolling method and their performances in MFCs were studied. A maximum power density of $1312 \pm 82 \text{ mW m}^{-2}$ was produced by air-cathode with P-doped carbon catalyst prepared at 1000°C . This result was higher than the air-cathode with Pt/C catalyst and three times as that with P-free carbon catalyst derived from pure cellulose. This study demonstrated that the P-doped carbon derived from cellulose phosphate was a cost-efficient and promising cathodic catalyst for scale-up MFCs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

As one of “green” energy resources, microbial fuel cells (MFCs) have attracted much attention for a combination of electricity generation and wastewater treatment in recent years [1,2]. Air-cathode MFC is considered as one of the best scale-up configuration, since it does not require aeration and the oxygen is the most sustainable and environmental-friendly electron acceptor [3]. However, the slow oxygen reduction reaction (ORR) at the cathode generally requires the participation of catalyst. Pt is believed to be the most effective ORR catalyst for chemical fuel cells, as well as in

MFCs. However, the disadvantages of high cost and poor durability hinder its large-scale use in MFCs [4]. Consequently, numerous efforts were made to explore cost-efficient alternatives to Pt for ORR in the cathode of MFCs. Pyrolyzing products of phthalocyanines and porphyrins were firstly developed as high efficient ORR catalysts for MFCs [5–7]. Thereafter, other metal complexes and metal oxides, such as manganese oxides [8,9], lead dioxide [10] and Fe compounds [11–14], were also considered. However, the long-term instability and the toxicity blocked their use in practical applications of MFCs.

Recently, carbon-based materials were widely used as the ORR catalyst in MFCs due to the good characteristics of high electrocatalytic activity, environmental-friendly and relatively low-cost. Nitrogen-doped carbon-based catalysts [15–19] were demonstrated to exhibit excellent ORR electrocatalytic activity in air-cathode of MFCs. It was reported that the doping heteroatom

* Corresponding authors. Department of Chemistry and Chemical Engineering, Jiangxi Normal University, 330022 Nanchang, China.

E-mail addresses: slichenjxnu@jxnu.edu.cn, shuiliangchen@163.com (S. Chen), haoqing@jxnu.edu.cn (H. Hou).

played an important role for the improved ORR electrocatalytic activity. In fact, many other heteroatom-doped carbon materials (such as P, S, B and I) were also reported to exhibit high electrocatalytic activity for ORR, but most of them were performed in alkaline or acid medium [20–24]. The use of these catalysts in neutral condition was rare. Moreover, these doped carbon catalysts were based on the carbon nanomaterials, such as carbon nanotubes and graphene, and involved in a complex preparation process. They faced the challenge of large-scale production and their use in scale-up MFCs applications, e.g. wastewater treatment was hindered.

The future success in the cathode of MFCs inevitably requires low-cost and high-efficient ORR catalysts. In recent years, many low-cost carbon materials were developed for ORR catalysts in MFCs and showed efficient ORR electrocatalytic activities, such as activated carbon (AC) [25–28], biochar derived from sewage sludge [29]. However, the performance of the AC catalysts varied with the preparing methods and raw materials, while the biochar catalyst would bring the secondary pollution to environment due to the existence of pathogens and heavy metals.

Herein, a low-cost P-doped carbon material was developed for high-efficient ORR catalyst in air-cathode of MFCs. It was reported that P-doped carbon materials were mainly synthesized by chemical vapor deposition (CVD) process or nanocasting method and the triphenylphosphine was usually employed as the P resource. The resulted P-doped carbon materials were reported to show good catalytic activity towards ORR in alkaline medium [20,21]. The P-doped carbon materials in this paper were prepared by direct pyrolysis of cellulose phosphate which is derivative of cellulose and has advantages of low cost and sustainability. The performances of the P-doped carbon catalysts in the cathode of MFCs were evaluated systematically and compared with the Pt/C catalyst.

2. Experimental

2.1. Preparation of catalyst and assembly of air-cathode

Cellulose phosphate particles (50–150 μm in diameter) were loaded onto porcelain boat and placed into an electric furnace equipped with a quartz tube. The samples were heated to 800, 900, 1000 and 1100 $^{\circ}\text{C}$ with a heating rate of 5 $^{\circ}\text{C min}^{-1}$ under N_2 atmosphere, respectively, and annealed for 1 h at the final temperature. The as-prepared carbon catalysts were denoted as CP-800, CP-900, CP-1000, CP-1100, respectively. P-free carbon was also prepared by pyrolysis of chromatographically pure microcrystal cellulose (MC) (Sigma–Aldrich) at 1000 $^{\circ}\text{C}$ for comparison and denoted as MC-1000. The elemental analyses were conducted by energy dispersive spectroscopy (EDS, Oxford X-MAX) and X-ray photoelectron spectroscopy (Thermo ESCALAB 250). Air-cathodes were fabricated by rolling method as previously described [26]. The mass ratio of catalyst/PTFE was controlled to be 4/1. Similar to the P-doped carbon catalyst air-cathodes, the Pt-based air-cathode in this paper was also processed by rolling method for the first time by using stainless steel mesh as current collector and the load of Pt was controlled to be about 0.5 mg cm^{-2} .

2.2. Electrochemical test

Linear sweep voltammetry (LSV) method was used to evaluate the catalytic activity of the ORR catalysts in a three-electrode system equipped with a graphite plate counter electrode and an Ag/AgCl reference electrode. The LSV measurements were controlled by a potentiostat (CHI660D) over a voltage range of +0.3 to -0.3 V at a scan rate of 1 mV s^{-1} . All LSV tests were conducted in 50 mM PBS solution (pH = 7.0 and conductivity = 6.533 mS cm^{-1}) at 35 $^{\circ}\text{C}$.

2.3. MFCs construction and operation

Cubic single-chamber air-cathode MFCs configuration (4 cm in length, 3 cm in diameter) was used to measure the performance of MFCs as previously described [30]. Graphite fiber brushes (2.5 cm in length and 2.5 cm in outer diameter) heat-treated at 450 $^{\circ}\text{C}$ for 30 min were served as anodes. All MFCs were inoculated with solution 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 $^{\circ}\text{C}$ 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 is 7.0 and contains 10.9233 g L^{-1} $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 3.042 g L^{-1} $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.31 g L^{-1} NH_4Cl , 0.13 g L^{-1} KCl). The conductivity of the medium was about 6.533 mS cm^{-1} . The medium was refreshed when the voltage dropped below 100 mV, similar to reference [1].

A 1000 Ω resistor was loaded between the anode and air-cathode. Voltage across the resistor was measured using a data acquisition system (HIOKI LR8431-30) at 1 min interval. Polarization and power density curves were measured by varying the external resistance from 100 $\text{M}\Omega$ to 30 Ω , with each resistor used for a complete cycle. Both the current density 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 reference electrode (filled with saturated KCl, has a potential of +0.198 V versus SHE). At least three measurements had been conducted for each reported result.

3. Results and discussion

3.1. Materials preparation

The cellulose phosphate is a kind of P-containing derivative of cellulose and show characteristics of low cost and renewability. It is well-known that cellulose materials can be used to make carbon materials through a direct high-temperature pyrolysis process. In this paper, the cellulose phosphate is chosen as both the phosphorus and carbon sources to synthesize P-doped catalyst through a direct high-temperature pyrolysis process. The elemental analysis and content of the as-prepared carbon materials prepared at different temperatures are shown in Figs. S1 and S3. As shown in the XPS (Fig. S3), P-doping signal could be found in the cellulose phosphate-derived carbons, but not in the pure cellulose-derived carbon. It demonstrated that the P-doped carbon could be

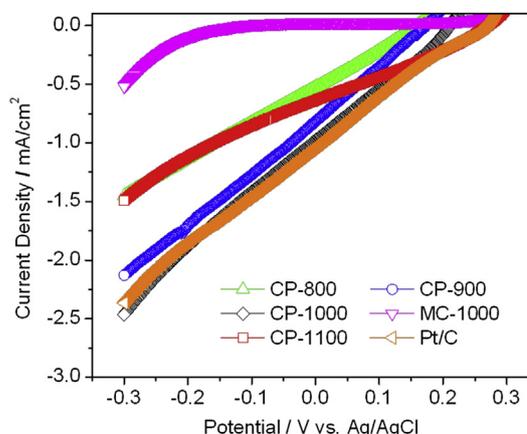


Fig. 1. LSV curves of air-cathodes with different ORR catalysts. Scan rate is 1 mV s^{-1} .

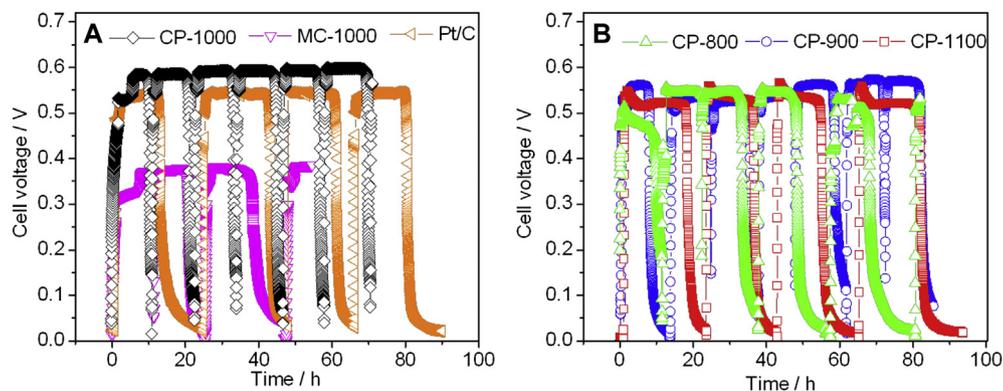


Fig. 2. Voltage–time curves of air-cathode MFCs based on different ORR catalysts. (A) CP-1000, MC-1000 and Pt/C; (B) CP-800, CP-900 and CP-1100. A external resistor of 1000 Ω is loaded between the anode and cathode.

prepared by pyrolysis of cellulose phosphate. The P content in the P-doped carbon decreased with increase of pyrolyzing temperature according to the EDS spectra in Fig. S1.

3.2. Electrochemical performance

LSV was conducted to evaluate the electrochemical performance of the P-doped carbon catalyst in the air-cathodes under neutral condition (50 mM PBS, pH = 7.0). As shown in Fig. 1, compared to the P-free carbon MC-1000 from the microcrystal cellulose at 1000 $^{\circ}\text{C}$, the P-doped carbons displayed higher current response towards ORR, indicating that the P doping in the carbon played a key role for the improved performance. With increase of pyrolysis temperature, the ORR current response of the air-cathodes with P-doped carbon catalysts increased. The degree of the ordered carbon structure and P content were

believed to have the comprehensive influences in the electro-catalytic activity of the P-doped carbon. The Raman spectra in Fig. S2 revealed that the degree of ordered carbon structure in the P-doped carbon catalysts increased as the temperature increased. Among these doped carbon catalysts, the CP-800 had a higher P content (Fig. S1), but it showed lower degree of ordered carbon structure according to the Raman spectra in Fig. S2. The air-cathode with CP-1000 catalyst prepared at 1000 $^{\circ}\text{C}$ showed the best performance among the cathodes with P-doped carbon catalyst prepared at different temperature, which was comparable to the cathode with Pt/C catalyst (load 0.5 mg cm^{-2} Pt). Further increasing the pyrolyzing temperature to 1100 $^{\circ}\text{C}$, the cathodic performance decreased greatly due to the decrease of P content. The state of P dopings in the CP-1000 was characterized by XPS (Fig. S3). Two peaks of 133.4 and 135.4 eV (inset of Fig. S3A) were observed in the high-resolution spectra of P_{2p} and

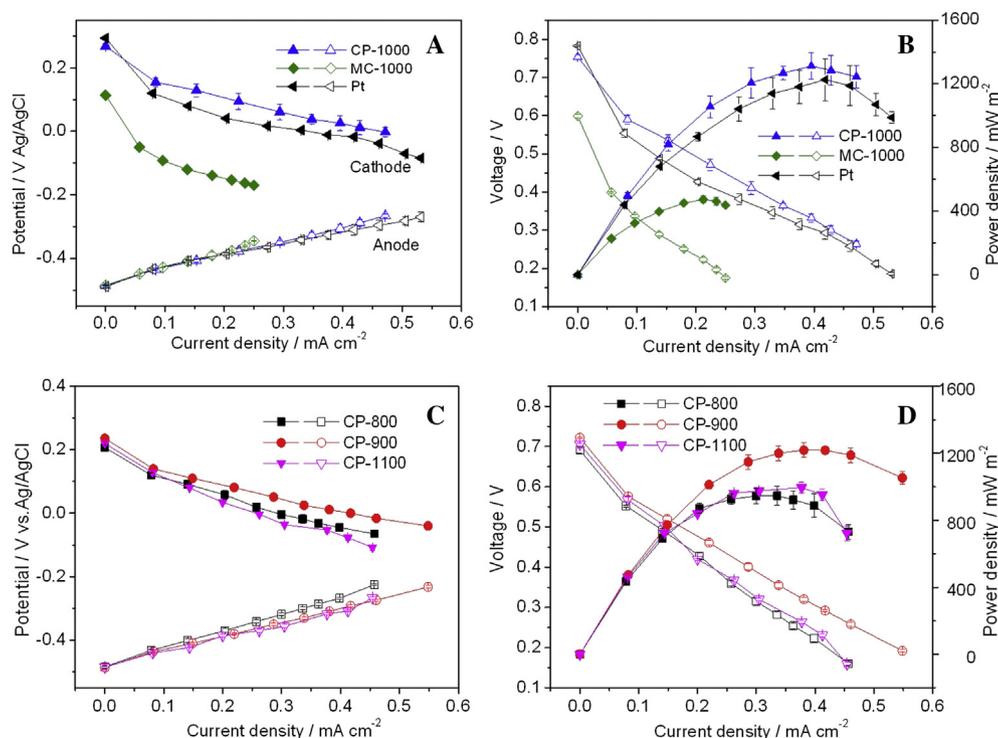


Fig. 3. (A and C) Anode and cathode potentials of MFCs with different air-cathodes at different current densities; (B and D) polarization and power density curves of MFCs with different air-cathodes.

assigned to P–C and P–O groups, respectively, which was reported to contribute to the highly electrocatalytic activity for ORR [21].

3.3. MFCs performance

Single chamber air-cathode MFCs were built by using graphite brush anodes and air-cathodes with different ORR catalysts. The cell voltages were recorded versus time for about six cycles. As shown in Fig. 2, the air-cathode with CP-1000 catalyst generated a stable and high voltage of about 0.61 V, which was higher than the air-cathodes with P-doped carbon prepared at other temperature and Pt/C catalysts (0.54 V). While the air-cathode with P-free carbon catalyst from pure cellulose only displayed a voltage of about 0.38 V. Moreover, according to the $V-t$ curves, after running for more than six cycles (over 80 h), no voltage decay was observed for the cathode with CP-1000 catalyst, indicating a very good stability.

The polarization and power density curves of MFCs equipped with different air-cathodes were measured and shown in Fig. 3. In order to exclude the effect of anode on the performance MFCs, the potentials of anodes and cathodes were measured respectively and shown in Fig. 3A and C. The anode potentials for all the MFCs were almost the same while the cathodic potentials varied with different catalysts, representing that the performance of MFCs was only determined by the air-cathode. The power density generated by the air-cathodes with different catalysts were shown in Fig. 3B and D and their maximum power density sequence was: MC-1000 ($474 \pm 21 \text{ mW m}^{-2}$) < CP-800 ($946 \pm 56 \text{ mW m}^{-2}$) < CP-1100 ($995 \pm 32 \text{ mW m}^{-2}$) < CP-900 \approx Pt/C ($1220 \pm 44 \text{ mW m}^{-2}$) < CP-1000 ($1312 \pm 82 \text{ mW m}^{-2}$). The air-cathode with CP-1000 catalyst showed the best MFC performance. It generated a maximum power density of $1312 \pm 82 \text{ mW m}^{-2}$, which was nearly three times as that with the P-free MC-1000 catalyst ($474 \pm 21 \text{ mW m}^{-2}$) and slightly higher than that with Pt/C catalyst. The air-cathode with Pt/C catalyst in this paper was prepared by rolling method and generated a power density of about $1220 \pm 44 \text{ mW m}^{-2}$ in MFC, which was similar to the air-cathode prepared by brushing Pt/C catalyst onto carbon mesh and run under the similar conditions [26]. This result further confirmed that the CP-1000 catalyst showed high efficient electrocatalytic activity in MFCs. Moreover, the high efficient electrocatalytic activity of the P-doped carbon catalysts could be ascribed to the P doping in the carbon catalyst.

4. Conclusions

The P-doped catalyst was successfully prepared by pyrolyzing cellulose phosphate and showed outstanding catalytic activity for ORR in the air-cathode of MFCs. The maximum power density generated by the air-cathode with P-doped carbon catalyst was $1312 \pm 82 \text{ mW m}^{-2}$, which was higher than the air-cathode with Pt/C catalyst. The high catalytic performance could be ascribed to the P doping in the carbon catalyst. The cellulose phosphate was one kind derivative of cellulose and show characteristics of low-cost, renewability and easy mass production. Thus, the P-doped carbon

would be a low-cost and high-performance ORR cathode catalyst for scale-up MFCs.

Acknowledgement

This research was supported by the National Natural Science Foundation of China (51202096, 21322703), the Science and Technology Project of Jiangxi Province (20121BBE50024) and China Postdoctoral Science Foundation (2012M520407).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.060>.

References

- [1] B.E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, *Environ. Sci. Technol.* 40 (2006) 5181–5192.
- [2] B.E. Logan, K. Rabaey, *Science* 337 (2012) 686–690.
- [3] H. Liu, B.E. Logan, *Environ. Sci. Technol.* 38 (2004) 4040–4046.
- [4] F. Zhao, F. Harnisch, U. Schröder, F. Scholz, P. Bogdanoff, I. Herrmann, *Environ. Sci. Technol.* 40 (2006) 5193–5199.
- [5] F. Zhao, F. Harnisch, U. Schröder, F. Scholz, P. Bogdanoff, I. Herrmann, *Electrochem. Commun.* 7 (2005) 1405–1410.
- [6] H.L. Shao Cheng, Bruce E. Logan, *Environ. Sci. Technol.* 40 (2006) 364–369.
- [7] L. Deng, M. Zhou, C. Liu, L. Liu, C. Liu, S. Dong, *Talanta* 81 (2010) 444–448.
- [8] I. Roche, K. Katuri, K. Scott, *J. Appl. Electrochem.* 40 (2010) 13–21.
- [9] X.-W. Liu, X.-F. Sun, Y.-X. Huang, G.-P. Sheng, K. Zhou, R.J. Zeng, F. Dong, S.-G. Wang, A.-W. Xu, Z.-H. Tong, H.-Q. Yu, *Water Res.* 44 (2010) 5298–5305.
- [10] J. Morris, S. Jin, J. Wang, C. Zhu, M. Urynowicz, *Electrochem. Commun.* 9 (2007) 1730–1734.
- [11] E. Martin, B. Tartakovsky, O. Savadogo, *Electrochim. Acta* 58 (2011) 58–66.
- [12] L. Fu, S.J. You, G.Q. Zhang, F.L. Yang, X.H. Fang, Z. Gong, *Biosens. Bioelectron.* 26 (2011) 1975–1979.
- [13] L. Wang, P. Liang, J. Zhang, X. Huang, *Bioresour. Technol.* 102 (2011) 5093–5097.
- [14] P. Wang, B. Lai, H. Li, Z. Du, *Bioresour. Technol.* 134 (2013) 30–35.
- [15] L. Feng, Y. Yan, Y. Chen, L. Wang, *Energy Environ. Sci.* 4 (2011) 1892–1899.
- [16] X. Shi, Y. Feng, X. Wang, H. Lee, J. Liu, Y. Qu, W. He, S.M.S. Kumar, N. Ren, *Bioresour. Technol.* 108 (2012) 89–93.
- [17] S. Chen, Y. Chen, G. He, S. He, U. Schröder, H. Hou, *Biosens. Bioelectron.* 34 (2012) 282–285.
- [18] L. Feng, L. Yang, Z. Huang, J. Luo, M. Li, D. Wang, Y. Chen, *Sci. Rep.* 3 (2013), <http://dx.doi.org/10.1038/srep03306>.
- [19] S. Li, Y. Hu, Q. Xu, J. Sun, B. Hou, Y. Zhang, *J. Power Sources* 213 (2012) 265–269.
- [20] Z.-W. Liu, F. Peng, H.-J. Wang, H. Yu, W.-X. Zheng, J. Yang, *Angew. Chem. Int. Ed.* 50 (2011) 3257–3261.
- [21] D.-S. Yang, D. Bhattacharjya, S. Inamdar, J. Park, J.-S. Yu, *J. Am. Chem. Soc.* 134 (2012) 16127–16130.
- [22] Z. Yang, Z. Yao, G.F. Li, G.Y. Fang, H.G. Nie, Z. Liu, X.M. Zhou, X. Chen, S.M. Huang, *ACS Nano* 6 (2012) 205–211.
- [23] L. Yang, S. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Wang, Q. Wu, J. Ma, Y. Ma, Z. Hu, *Angew. Chem. Int. Ed.* 50 (2011) 7132–7135.
- [24] Z. Yao, H. Nie, Z. Yang, X. Zhou, Z. Liu, S. Huang, *Chem. Commun.* 48 (2012) 1027–1029.
- [25] F. Zhang, S. Cheng, D. Pant, G.V. Bogaert, B.E. Logan, *Electrochem. Commun.* 11 (2009) 2177–2179.
- [26] H. Dong, H. Yu, X. Wang, *Environ. Sci. Technol.* 46 (2012) 13009–13015.
- [27] V.J. Watson, C. Nieto Delgado, B.E. Logan, *Environ. Sci. Technol.* 47 (2013) 6704–6710.
- [28] V.J. Watson, C. Nieto Delgado, B.E. Logan, *J. Power Sources* 242 (2013) 756–761.
- [29] Y. Yuan, T. Yuan, D. Wang, J. Tang, S. Zhou, *Bioresour. Technol.* 144 (2013) 115–120.
- [30] B. Logan, S. Cheng, V. Watson, G. Estadt, *Environ. Sci. Technol.* 41 (2007) 3341–3346.