Bioresource Technology 214 (2016) 348–354

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Low-cost adsorbent derived and in situ nitrogen/iron co-doped carbon as efficient oxygen reduction catalyst in microbial fuel cells

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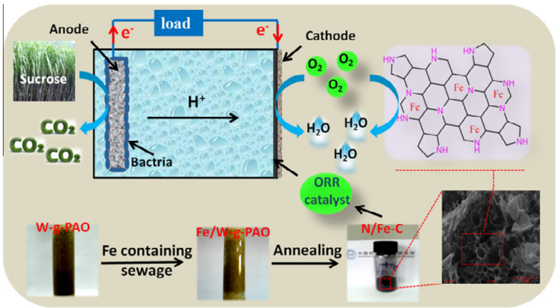
HIGHLIGHTS

- In situ N/Fe co-doped carbon (N/Fe–C) is prepared from low-cost adsorbent.
- Electricity production is enhanced in MFCs with N/Fe–C compared to Pt/C.
- N/Fe–C is low-cost, environmental-friendly and makes waste profitable.

GRAPHICAL ABSTRACT

Low-cost adsorbent derived N and Fe co-doped porous carbon was employed as efficient ORR catalyst in MFCs.



ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form 19 April 2016
Accepted 22 April 2016
Available online 26 April 2016

Keywords:
Microbial fuel cells
N/Fe co-doped carbon
Oxygen reduction catalyst
Low-cost adsorbent

ABSTRACT

A novel low-cost adsorbent derived and in situ nitrogen/iron co-doped carbon (N/Fe–C) with three-dimensional porous structure is employed as efficient oxygen reduction catalyst in microbial fuel cells (MFCs). The electrochemical active area is significantly improved to 617.19 $m^2\,g^{-1}$ in N/Fe–C by Fe-doping. And N/Fe–C (4.21 at.% N, 0.11 at.% Fe) exhibits excellent electrocatalytic activity with the oxygen reduction potential of −0.07 V (vs. Ag/AgCl) which is comparable to commercial Pt/C. In MFCs tests, the maximum power density and output voltage with N/Fe–C are enhanced to 745 mW m^{-2} and 562 mV (external resistance 1 kΩ), which are 11% and 0.72% higher than Pt/C (0.5 mg Pt cm^{-2}), respectively. Besides, the long-term stability of N/Fe–C retains better for more than one week. Moreover, the charge transfer resistance (Rct) values are recorded by the impedance measurements, and the low Rct of N/Fe–C is also result in better catalytic activity.

1. Introduction

Efficient and low-cost electrocatalytic materials toward oxygen reduction reaction (ORR) are crucial for a variety of renewable energy applications (Wang et al., 2012), such as metal-air batteries (Suntivich et al., 2011) and air-cathode MFCs (Li et al., 2012) in response to the ever increasing energy crisis as well as ecocrisis (Bashyam and Zelenay, 2006). As we know that the noble metal platinum (Pt) has an excellent catalytic activity for ORR due to its low over-potential, and is widely used in many fields (Cheng et al., 2006; Lefebvre et al., 2009). However, the scarcity, high cost, and poor durability of Pt have hindered its widespread applications, especially in MFCs (Lefebvre et al., 2009). Moreover, noble

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http://dx.doi.org/10.1016/j.biortech.2016.04.111
0960-8524/

Pt is readily poisoned by the contaminants within waste water in MFCs (Li et al., 2012). Therefore, it is urgent to develop alternative ORR catalysts for Pt/C in MFCs.

Recently, a continuously increasing attention have been paid on efficient, Pt-free and low-cost ORR catalysts for MFCs, including (a) products carbonized from complexes of metals, e.g. phthalocyanines (Zhao et al., 2005) or porphyrins (Trojanek et al., 2012), (b) metal complexes and metal oxides, such as manganese oxides (Liu et al., 2010) and iron compounds (Li et al., 2015b), (c) low-cost heteroatom-doped carbon, such as activated carbon (AC) (Zhang et al., 2014), biochar derived from sewage sludge (Yuan et al., 2013) and carbon derived from cellulose (Liu et al., 2015a).

Heteroatom-doped carbon materials have demonstrated promising catalytic performance in ORR (Choi et al., 2011; Huggins et al., 2015). Since the report of N-doped carbon nanotubes with efficient ORR activity in the alkaline media (Zhang et al., 2015), the heteroatom-doped carbon materials were widely used as ORR catalysts in chemical fuel cells (Sa et al., 2014), and had attracted extensive attentions (Feng et al., 2011; Yang et al., 2013). Nevertheless, the carbon materials used as ORR catalysts in the air-cathode MFCs were nearly limited to the nonmetallic-doping, such as N-doped graphene and nanotubes, which had shown an outstanding electrocatalytic activity for ORR. Besides, some other heteroatom co-doped carbon materials (such as S, P, B and Fe) were also developed recently and investigated in alkaline or acid media, however, their ORR activity in neutral condition, especially in MFCs, was still unknown (Chen et al., 2014; Hu et al., 2015; Liu et al., 2014). Moreover, almost all of heteroatom-doped carbon ORR catalysts were based on nanomaterials which inevitably involved in complex and rigorous preparation processes, and difficult for mass production. For scale-up MFCs, they would inevitably suffer a challenge that the large demand of catalysts. Therefore, it is vital to develop low-cost, high-efficient and environmental-friendly ORR catalysts for the commercialization of MFCs.

Waste wool, a low-cost, renewable material and abundant in nature, which is made up of keratin and contains plenty of N element, had been used as adsorbent for waste water treatment by grafting modified in our previous work (Cao et al., 2014). In detail, wool graft polyacrylamidoxime (W-*g*-PAO) was synthesized as adsorbent to load heavy metal ions as well as Fe^{3+} (Fe/W-*g*-PAO) and F^{-}. We proposed that it had ORR activity by carbonizing Fe/W-*g*-PAO, due to the fact that it contains some necessary doped elements, such as N and Fe. And the strong chemical coordination between Fe and amino on Fe/W-*g*-PAO, which was different from traditional physical blending for the preparation of heteroatom-doped carbon materials, can be beneficial to the Fe-doping in resultant carbon materials. Moreover, it should be noted that the helix structure of keratin inside the Fe/W-*g*-PAO may form porous structure after annealing.

Herein, in situ nitrogen and iron co-doped carbon derived from low-cost adsorbent was prepared, which not only served as an efficient ORR catalyst but also took full use of waste source. The wool graft polyacrylonitrile (W-*g*-PAO), one adsorbent for heavy metal ions and Fe^{3+}, was first used to treat iron-containing solution in adsorbing column (Fe/W-*g*-PAO), followed by annealing with atmosphere protection to form nitrogen and iron co-doped carbon (N/Fe–C). The electrocatalytic activity of N/Fe–C was studied by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) on rotating disk electrode (RDE) electrochemical system. To further check ORR activity, N/Fe–C was employed as electrocatalyst in single-chamber air-cathode MFCs. The results showed that N/Fe–C possessed outstanding ORR activity with the high output voltage and power density. Therefore, taking into consideration of the low-cost of N/Fe–C, it was a promising ORR catalyst for the practical applications of MFCs.

2. Experimental

2.1. Materials

The precursor (W-*g*-PAO) was prepared by two-step method in our previous work (Cao et al., 2014). Briefly, wool graft polyacrylonitrile was prepared by free radical polymerization, and then the nitrile groups were converted to amidoxime groups in hydroxylamine hydrochloride solution.

Carbon cloth (HCP331N) and Pt/C catalyst (JM 20 wt%) were purchased from Shanghai Heshen company; Polyvinyl fluoride (PTFE, 60%) and whole fluorine sulfonic acid polyvinyl fluoride (Nafion, 5%) were purchased from Shandong Dong Yue company. Carbon black (F24X016) was purchased from Alfa Aesar. All other chemicals were purchased from Beijing chemical works and used directly without further purification.

2.2. Preparation for catalysts

The preparation procedure for nitrogen and iron co-doped carbon is shown in Fig. S1 (Supplementary Materials, and all figures that named with letter S are showed in Supplementary Materials, hereinafter). Typically, 5.0 g W-*g*-PAO was cut into pieces and packed into column to treat the iron-containing solution. The simulated ferric chloride solution ($0.5\ g\ L^{-1}$) acted as iron-containing sewage, and the current velocity of sewage was kept at $2\ mL\ min^{-1}$ using constant-flow pump. Lots of literatures have reported that more Fe-doping active sites represented better ORR activity in Fe-doped carbon materials (Qiao et al., 2015; Yan and Xu, 2014). Thus, to achieve more Fe-doping active sites in N/Fe–C, not stop the Fe-loading process until W-*g*-PAO reached saturated adsorption capacity after 24 h, that yielding sewage with same concentration of Fe^{3+} as feed-sewage. After Fe-loading, Fe/W-*g*-PAO was collected and dried at 35 °C over night. Subsequently, Fe/W-*g*-PAO was annealed at 1000 °C at a ramp rate of $5\ °C\ min^{-1}$ for 2 h with the nitrogen atmosphere protection. And then the sample was cooled down to room temperature and acid-leached in 1 M HCl at 60 °C for 3 h to remove unstable matters. Finally, the as-prepared N/Fe–C was collected by centrifugation, washed using deionized water and dried at 35 °C overnight. And prior to electrochemical and MFCs tests, N/Fe–C was treated by grinding method by mortar.

For comparison, raw wool and W-*g*-PAO were prepared as well following the similar way as described above for N/Fe–C without the iron-loading process, and the as-prepared products were abbreviated as N_1–C and N_2–C for raw wool and W-*g*-PAO, respectively.

2.3. Performance evaluation and analysis

Scanning electron microscopy (SEM) images were performed on a JSM-6510LV (JEOL, Tokyo Japan). High-resolution transmission electron microscopy (TEM) was performed on a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectrum (XPS) was collected on a PHI 5000 Versaprobe II system from ULVAC-PHI, Inc. X-ray diffraction (XRD) were investigated by X-ray powder diffractometer with Cu Kα radiation as the X-ray source for excitation operating at 40.0 kV and 40.0 mA within the 2θ ranged from 5° to 90°.

Electrochemical measurements were carried out in three-electrode cell with CHI 660E Electrochemical Workstation (CH Instruments, China). Ag/AgCl electrode (saturated KCl) and Pt electrode were used as the reference and counter electrodes, respectively. The working electrode was rotating (glassy carbon) disk electrode (RDE, disk diameter 3 mm). For preparation of ink,