Porous nitrogen-doped carbon nanosheet on graphene as metal-free catalyst for oxygen reduction reaction in air-cathode microbial fuel cells

Qing Wen *, Shaoyun Wang, Jun Yan, Lijie Cong, Ye Chen, Hongyuan Xi

College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

A R T I C L E   I N F O

Article history:
Received 28 May 2013
Received in revised form 11 October 2013
Accepted 16 October 2013
Available online 25 October 2013

Keywords:
Microbial fuel cell
Nitrogen-doped carbon
Oxygen reduction reaction

A B S T R A C T

Porous nitrogen-doped carbon nanosheet on graphene (PNCN) was used as an alternative cathode catalyst for oxygen reduction reaction (ORR) in air-cathode microbial fuel cells (MFCs). Here we report a novel, low-cost, scalable, synthetic method for preparation of PNCN via the carbonization of graphite oxide–polyaniline hybrid (GO–PANI), subsequently followed by KOH activation treatment. Due to its high concentration of nitrogen and high specific surface area, PNCN exhibited an excellent catalytic activity for ORR. As a result, the maximum power density of 1159.34 mW m⁻² obtained with PNCN catalyst was higher than that of Pt/C catalyst (858.49 mW m⁻²) in a MFC. Therefore, porous nitrogen-doped carbon nanosheet could be a good alternative to Pt catalyst in MFCs.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Microbial fuel cell (MFC) is one of the most promising methods to generate electrical energy from organic and inorganic matter [1]. Oxygen has been considered as the most favorable cathodic electron acceptor among various oxidants due to its easy availability in the environment with the capacity to give a high power output [2]. However, without catalysts the kinetic reaction rate of the oxygen reduction is very low and the performance of an air-cathode MFC is quite poor [3]. As a commonly used catalyst for oxygen reduction reaction (ORR) in MFCs, platinum has been shown as a very efficient and low-cost method to obtain various types of nitrogen-rich carbon materials retaining the morphology of the precursors [22–25]. Among them, polyaniline (PANI) has been used as an attractive precursor for synthesis of nitrogen-doped carbon material. For instance, G. Wu et al. reported the nitrogen-doped graphene sheets as a new catalyst for ORR, which was prepared by the carbonization of polyaniline and Co precursors using MWNTs as a template [26].

Recently, nitrogen-doped carbon materials have attracted considerable attention in practical and fundamental research of ORR in alkaline medium due to their high catalytic activity, excellent reliability and environmental friendliness [12–18]. Maldonado and Stevenson reported that nitrogen-induced defects on carbon structure can increase the edge plane exposure which supports additionally the catalytic activity [19]. The synthesis of N-doped carbon materials often uses chemical vapor deposition (CVD) process under the exposure of reactive gases (NH₃) [20,21], however, it usually produces reaction cost due to its complicated procedure. Newly, the carbonization of N-containing polymers such as poly pyrrole, poly (p-phenylene), pshonallypyrrolidone, polycry-lonitrile, polyaniline (PANI) and melamine, is an easy way to obtain various types of nitrogen-rich carbon materials retaining the...
mostly used in metal-air batteries or fundamental research of ORR. However, in this study we also focused on the application of PNCN in MFCs. Due to its high surface area and high nitrogen content, the prepared porous nitrogen-doped carbon material in this study exhibited a high catalytic activity with the maximum power density of 1159.34 mW m$^{-2}$ compared to Pt/C (858.49 mW m$^{-2}$) in MFCs.

In the present study, the catalyst characterization was investigated through Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), BET and X-ray photoelectron spectroscopy (XPS). The evaluation on the ORR activity of NCN and PNCN were investigated through linear sweep voltammetry (LSV). Further performance examination was evaluated in MFCs with NCN and PNCN catalyst air cathodes.

2. Experimental

2.1. Catalyst preparation

Graphite oxide (GO) was synthesized from natural graphite (300 μm, Qingdao Graphite Company) by a modified Hummer’s method [30]. Exfoliation of GO (20 mg) in 40 mL of H$_2$O were achieved by ultrasonication in an ultrasonic bath (KQ-600KDE, 600 W). After that, 86 mL of 0.25 M aniline monomers (solvent: 1 M HCl) were added into the above suspension and sonicated for 1 h. Afterwards, 86 mL of 0.25 M ammonium persulfate (APS, solvent: 1 M HCl) were rapidly added into the above mixture and stirred for 8 h at 0–2°C, the yellow-brown suspension gradually changed to deep green color. Finally, the prepared GO–PANI nanocomposite was washed repeatedly and dried in a vacuum oven at 80°C for 24 h.

Porous nitrogen-doped carbon nanosheet (PNCN) was prepared as follows: the as-prepared precursor was heated to 850°C and pyrolyzed for 2 h under nitrogen flow. Then the carbonized sample (NCN) and KOH were mixed with a weight ratio of 1:4, and were heated up to 850°C for 1 h. Subsequently, the activated sample was washed with 0.5 M HCl solution and distilled water for several times until the pH value remained constant, followed by drying at 100°C for 12 h.

2.2. Electrode preparation

The air-cathode was manufactured by pressing wet-proof gas diffusion layers (50 wt.% Na$_2$SO$_4$ and 50 wt.% polytetrafluoroethylene (PTFE)), catalyst layer (86 wt.% activated carbon, 12 wt.% NaFion (5%, HESEN, China), and 2 wt.% acetylene black powder, containing 5 mg cm$^{-2}$ PNCN catalyst) and stainless steel net. As controls, the Pt/C (20%, HESEN, China), NCN and active carbon air cathodes were fabricated using the same procedure. The Pt/C and NCN catalyst were also loaded onto the air cathode at 5 mg cm$^{-2}$. In order to investigate the ORR performance, the linear sweep voltammetry (LSV) was performed in a three-electrode configuration. The working electrodes were prepared as follows: 10 mg of catalyst and 4.3 mg of acetylene black was added into 20 mL of alcohol and then subjected to ultrasonic vibration for 1 h. Subsequently, 60 μL of NaFion was added into the resulting suspension, and then heated by electric furnace until it became a paste. Finally, each catalyst paste was pasted onto carbon paper (2 cm$^2$) by brush and then dried at a room temperature for 48 h.

2.3. MFC construction and operation

MFC was constructed as previously described [31]. The air-cathode single chamber MFC was built with a cylindrical plastic tube, which had an inner diameter of 6 cm and total height of 8 cm. The air-cathode (5 × 2 cm$^2$) was placed on one side of the outer surface of the MFC, where as the anode was cylindrical carbon brush with a diameter of 4 cm. Two electrodes were separated by 1 cm. For comparing the performance of MFCs with different cathode catalysts, four air-cathode single chamber MFC reactors with PNCN, NCN, Pt/C and non-catalyst air cathodes, were set up for the experiments. MFC reactors were inoculated using anaerobic sludge collected from another MFC which had been operated continuously in our lab. MFC reactors were operated using nutrient buffer solution (NBS) containing the following: acetate, 1 g/L; KCl, 130 mg L$^{-1}$; NaH$_2$PO$_4$·2H$_2$O, 4.97 g L$^{-1}$; Na$_2$HPO$_4$·12H$_2$O, 2.75 g L$^{-1}$; and other trace elements required for microorganism growth as reported by Liu and Logan [32]. The nutrient buffer solution (200 mL) was refreshed when the voltage decreased to below 50 mV, forming a fed-batch. All experiments were conducted at a room temperature (24 ± 1°C).

2.4. Analysis and calculation

The output voltage was measured across an external resistor (1500Ω resistor except where indicated otherwise) using a data acquisition system connected to a computer. Polarization curve of MFCs and the performance of the electrode potential were measured as previously described [33]. Power density was according to P (mW m$^{-2}$) = 1000U × J, where J is the current density (A m$^{-2}$), which is calculated as J = U/(R×A) based on external resistance R (Ω), current density I (A) and area A (m$^2$). Power density was calculated by: W = Ω×E×(1000×J) (W m$^{-2}$). Power density was calculated by: W = Ω×E×(1000×J) (W m$^{-2}$).

In this experiment, polyaniline (PANI) nanosheets grown on the surface of GO are fabricated through the chemical polymerization process under the aid of ammonium persulfate (Fig. 1A, B). After the carbonization of PANI-GO hybrid material, carbon nanosheets from the pyrolysis of PANI still maintain their sheet morphology with the width/length less than 15 nm homogeneously covered on graphene sheet (Fig. 1C). Subsequent activation with KOH results in the formation of PNCN with large surface area (Fig. 1D). N$_2$ adsorption–desorption isotherms of PNCN exhibits type IV isotherms with a distinct hysteresis loop at a relative pressure p/p$_0$ ranging from 0.4 to 1, as well as higher Brunauer–Emmett–Teller surface area of 1398 m$^2$ g$^{-1}$ compared with the carbonized sample NCN (183 m$^2$ g$^{-1}$) (Fig. 2). The increased BET surface area can be attributed to the chemical activation treatment, which is a very efficient method to obtain carbons with high surface area and micro-pore distribution [28]. The first step in the chemical activation with KOH is a redox reaction between NCN and KOH. In this step, the produced metallic potassium can be inserted/intercalated in NCN. Thus K intercalation compounds are formed during the activation reaction. As it is well known that these derivatives are unstable in air, especially due to moisture [29]. When the K intercalation compounds are exposed to air, metallic potassium produced during the redox reaction will lead to the separation and degradation of the graphitic layers which gives rise to a high portion of micro-pore.

The XPS spectrum has a predominant narrow graphitic C 1s peak at 284.6 eV, along with an obvious N 1s peak at 400.1 eV and an obvious O 1s peak at 536.8 eV (Fig. 3). The N 1s spectra of PNCN consist of pyridinic-N (398.7 eV), pyrrolic-N (401.0 eV), and graphic-N (401.7 eV). Pyridinic-N is a nitrogen atom that bonds to two carbon atoms on the edge of a carbon plane and a carbon vacancy. Many electrocatalytic reactions show increased kinetics on carbon edge planes.
compared with basal planes. This increase in activity is attributed to the ability of edge planes to more readily chemisorb oxygen \[34\]. Meanwhile, pyridinic-N contributes one p-electron to the aromatic π-system and has a lone electron pair in the plane of the carbon matrix. This will increase the electron-donating ability of the catalyst, thus promoting the electrocatalysis of the oxygen–reduction reaction \[35\]. The survey scans confirm that PNCN consists only of carbon (85.13%), nitrogen group (5.74%), and oxygen (9.13%). Generally, the reported concentration of nitrogen in the N-doped carbon nanomaterials was around 1–4% \[36–38\]. Therefore, the as-prepared PNCN with high nitrogen content and porous structure leads to more active sites for facilitation of oxygen reduction, resulting in higher electrocatalytic activity towards ORR.

### 3.2. Electrochemical performance

Fig. 4 shows the results of the LSV for the electrodes with different catalysts in 50 mM L\(^{-1}\) N\(_2\)-saturated or O\(_2\)-saturated PBS (pH = 7.0). As shown in Fig. 4, the electrodes with PNCN, Pt/C and NCN exhibited a clear ORR peak in O\(_2\)-saturated neutral PBS. When the electrodes were scanned in N\(_2\)-saturated neutral PBS, however, no obvious ORR peak was acquired. Under the condition of O\(_2\)-saturated neutral PBS,
the current density of ORR at the electrode with NCN catalyst is 
−5.03 A m⁻² at the potential of −0.35 V, which is much higher than 
that of the electrode with active carbon (−0.18 A m⁻²), indicating 
that NCN has an obviously catalytic activity for ORR. Peak current 
densities of electrodes with Pt/C and NCN were −6.71 A m⁻² and 
−5.03 A m⁻², respectively, indicating that the catalytic activity for 
ORR of NCN performs worse than Pt/C. However, after the activation 
treatment, PNCN performs a bigger oxygen reduction peak current 
(−9.73 A m⁻²) than that of Pt/C catalyst. 

![Fig. 4. Curves of linear sweep voltammetry (scanning rate, 5 mV s⁻¹) of the electrodes with PNCN, NCN, Pt/C and active carbon catalysts in 50 mM L⁻¹N₂-saturated (dotted line) or O₂-saturated PBS (pH = 7.0).](image)

![Fig. 5. Performance of MFCs with different cathode catalysts: (A) power density (Pd/mW m⁻²) and voltage output (U/V), (B) anode and cathode polarization curves (cathode: filled symbols; anode: open symbols); E/V (vs. Ag/AgCl) is the potential of anode and cathode.](image)

In order to investigate the performance of power production in 
the four types of MFCs, polarization curves, electrode potentials, 
and power density curves were obtained at each external resistance when 
a steady voltage reached. Fig. 5A shows the maximum power density 
of the MFCs with PNCN, Pt/C, NCN and active carbon air cathodes are 
1159.34, 858.49, 655.74 and 64.53 mW m⁻², respectively. 

![Fig. 5A](image)

![Fig. 5B](image)

much higher than those of NCN (0.095 V) and Pt/C (0.121 V) cathodes, 
evidently indicating that the performance of PNCN cathode is enhanced 
due to the use of PNCN as catalyst for ORR.

In this study, the internal resistances of MFCs with PNCN and Pt/C, 
based on polynomial fit of polarization curve (R² = 0.9967 and 0.9971, 
respectively), were determined to be 80.5 and 87.9 Ω, respectively. 
Two kinds of MFC reactors had the same configuration, such as anode 
material and electrode distance. The only difference in internal resistance 
between MFCs with PNCN and Pt/C therefore came from the 
diversity of the electrical characteristics, especially the conductivity, 
between the synthesized PNCN and Pt/C. Therefore, the small internal 
resistance of MFC with PNCN can be explained by the high electrical 
conductivity of the synthesized PNCN. Further activation treatment 
of carbonized sample can increase the catalytic surface area and active 
sites significantly. Thus make PNCN perform an excellent catalytic activity 
which is even better than that of Pt/C. In order to study the stable 
performance of MFC with PNCN, the data of voltage for 9 cycles has 
been recorded (Fig. 6). For each cycle, when the fresh substrate was 
added, electricity started to generate and the output voltage of MFC 
rose rapidly until it reached a certain level and then operated in a stable 
status. When the amount of the fuel reduced to a certain extent, the output 
voltsage started to decline. As the voltage dropped to 50 mV, the 
substrate was almost exhausted and this cycle was completed. During a 
long-term operation for more than two months, the voltage variation 
trend and the maximum power density of MFC with PNCN cathode 
keep at the same level. These results show that PNCN has stable performance 
as a catalyst for ORR in a MFC.

In the literature, only few nitrogen-doped carbon materials have 
previously been used as a cost-effective electrocatalyst for ORR in
MFCs, such as nitrogen-doped carbon powders and nitrogen-doped graphene [38,39]. Moreover, the performance of MFCs with nitrogen-doped carbon powders and nitrogen-doped graphene as cathode catalysts for ORR was slightly lower than that of the MFC with Pt/C as cathode catalyst under the same condition. For example, in the study of Feng et al., NG-MFCs produced a maximum power density of 1350 mW m\(^{-2}\), which was 5.19% lower than that of Pt/C-MFCs (1420 mW m\(^{-2}\)); in the study of Shi et al., the ACMFC (air-cathode microbial fuel cells) with NDCP (nitrogen-doped carbon powders) produced a maximum power density of 934.7 mW m\(^{-2}\), which was 4.90% lower than that of ACMFC with Pt/C (980.5 mW m\(^{-2}\)). In contrast to the prior work, the maximum power density of the MFC with PNCN (1159.34 mW m\(^{-2}\)) cathode is 35% higher than that of Pt/C cathode (858.49 mW m\(^{-2}\)). The excellent performance of the MFC with PNCN cathode is attributed to the improvement of the catalytic activity of PNCN catalyst for ORR. In contrast to conventional nitrogen-doped carbon materials, the higher catalytic activity of the PNCN results from its high electrical conductivity and unique structure. The architecture of PNCN, with its high surface area and conductivity, has been demonstrated to be advantageous as catalyst for the electrocatalyst. More importantly, the outstanding structure of PNCN prepared by activation treatment in our study plays an important role in the improvement of the catalytic activity. Due to the redox reaction between KOH and NCN, partial gasification and expansion of the interlayer spacing between graphenes through simultaneous intercalation and deintercalation of the metallic potassium provide a much larger catalyst surface area available for ORR and increase the density of catalytically active site. In addition, oxygen may reach the catalytically active site easily, resulting in the decrease of diffusion resistance, probably due to the special architecture of PNCN.

4. Conclusions

In this study, we provided a simple approach to prepare porous nitrogen-doped carbon material derived from GO–PANI hybrid through carbonization and activation treatment. As a result, the obtained metal free catalyst had high nitrogen content and high surface area, resulting in an excellent electro-catalytic activity for ORR in neutral PBS. Furthermore, the maximum power density of 1159.34 mW m\(^{-2}\) obtained with PNCN catalyst in a MFC was higher than that of Pt/C catalyst (858.49 mW m\(^{-2}\)). The results demonstrated that PNCN was a good alternative cathode catalyst to Pt for ORR in MFCs.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the Heilongjiang Postdoctoral Science-Research Foundation (LBH-Q12118), National Natural Science Foundation of China (No. 51179033), China Postdoctoral Science Foundation (20100480975 and 201104413) and Harbin Special Innovative Talents of science and Technology Research Foundation (2009RFXG204).

References


