Journal of Power Sources 272 (2014) 344–350

Contents lists available at ScienceDirect

Journal of Power Sources

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

# Nitrogen- and boron-co-doped core–shell carbon nanoparticles as efficient metal-free catalysts for oxygen reduction reactions in microbial fuel cells

Shengkui Zhong [a], Lihua Zhou [b, *], Ling Wu [a], Lianfeng Tang [b], Qiyi He [b], Jalal Ahmed [c, **]

[a] Shagang School of Iron and Steel, Soochow University, Suzhou 215021, China
[b] Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China
[c] Department of Bioscience and Biotechnology, Konkuk University, Seoul 143-701, South Korea

## HIGHLIGHTS

- Heteroatoms doped core–shell carbon nanoparticles were prepared for catalyzing ORR.
- The maximum power density of 642 mW m$^{-2}$ was obtained from the carbon nanoparticles cathode.
- The co-existence of N and B could facilitate the ORR kinetics of the carbon nanoparticles.

## ARTICLE INFO

*Article history:*
Received 21 June 2014
Received in revised form
13 August 2014
Accepted 27 August 2014
Available online 4 September 2014

*Keywords:*
Core–shell carbon nanoparticles
Metal-free catalyst
Oxygen reduction reaction
Microbial fuel cell

## ABSTRACT

The most severe bottleneck hindering the widespread application of fuel cell technologies is the difficulty in obtaining an inexpensive and abundant oxygen reduction reaction (ORR) catalyst. The concept of a heteroatom-doped carbon-based metal-free catalyst has recently attracted interest. In this study, a metal-free carbon nanoparticles-based catalyst hybridized with dual nitrogen and boron components was synthesized to catalyze the ORR in microbial fuel cells (MFCs). Multiple physical and chemical characterizations confirmed that the synthetic method enabled the incorporation of both nitrogen and boron dopants. The electrochemical measurements indicated that the co-existence of nitrogen and boron could enhance the ORR kinetics by reducing the overpotential and increasing the current density. The results from the kinetic studies indicated that the nitrogen and boron induced an oxygen adsorption mechanism and a four-electron-dominated reaction pathway for the as-prepared catalyst that was very similar to those induced by Pt/C. The MFC results showed that a maximum power density of ~642 mW m$^{-2}$ was obtained using the as-prepared catalyst, which is comparable to that obtained using expensive Pt catalyst. The prepared nitrogen- and boron-co-doped carbon nanoparticles might be an alternative cathode catalyst for MFC applications if large-scale applications and price are considered.

## 1. Introduction

Microbial fuel cells have attracted considerable attention as a green biotechnology for the efficient extraction of energy from organic matter in pollutants and wastewater [1–3]. Although microbial fuel cells have distinct advantages over other fuel cells, they are not yet commonly considered to be part of an efficient energy portfolio because their ability to produce a substantial amount of power in a cost-effective manner has not yet been fully developed. The low power output of MFCs relative to other types of fuel cells limits their direct commercial and practical applications.

The generation of power in MFCs is often limited by the overpotential of the oxygen reduction reaction at the cathode [4]. The application of a catalyst to the cathode surface is the only way to reduce the cathodic overpotential. The cathode catalysts, however, are largely dependent on highly precious Pt or on unsustainable, environmentally unfriendly ferricyanide. Pt is known to be the most efficient and favorable catalyst, but increasing costs and limited natural reserves prevent its large-scale application in the field of waste treatment. Alarmingly, almost half the capital cost of an MFC is the cost of the cathode [5]. Moreover, the relative

---

* Corresponding author. Tel./fax: +86 20 39323860.
** Corresponding author. Tel./fax: +82 2 4503378.
*E-mail addresses:* qhzhoulh@gdut.edu.cn (L. Zhou), jalalahmed1@gmail.com (J. Ahmed).

http://dx.doi.org/10.1016/j.jpowsour.2014.08.114
0378-7753/

inertness and poisoning of Pt during MFC operating conditions in neutral media also encourage the replacement of Pt in MFC cathodes [6]. Considerable efforts have been directed toward developing inexpensive alternative cathode catalysts, which would substantially reduce MFC operating costs and make this technology sustainable for large-scale commercial waste treatment applications.

A large number of nonprecious metal catalysts have already been reported as MFC cathode catalysts for the ORR [7–9]. Among these catalysts, transition metal macrocyclic complexes have attracted considerable attention from researchers [10]. Although metal macrocyclic catalysts, i.e., phthalocyanine catalysts, outperformed the commercially available Pt catalysts [7,10], most of these catalysts are limited by stability, sustainability and leaching problems. Metal macrocyclic compounds are either soluble or chemically unstable in acidic or alkaline electrolyte solutions [11]; thus, these compounds gradually lose their activity. More importantly, the active sites on M-N4 catalysts are easily attacked by $H_2O_2$, which is a common intermediate in the ORR [12], thereby shortening the life span of the catalyst. Researchers are still searching for new materials to serve as efficient ORR catalysts, particularly metal-free electrocatalysts to overcome the aforementioned activity-related issues and capital costs. Carbon is undoubtedly the best base material of choice due to its abundance of free-flowing $\pi$ electrons [13]. Unfortunately, the $\pi$ electrons in carbon materials are inactive. Therefore, doping with suitable elements has been used to activate these $\pi$ electrons by creating a charge site, which conjugates the $\pi$ electrons and improves the probability of $O_2$ adsorbing on the carbon surface. This doping can be with either electron-deficient B or with electron-rich N components. Previous studies have suggested that integrating both electron-rich N and electron-deficient B components with carbon materials might increase the efficiency of metal-free carbon as an ORR catalyst [14]. Both N and B draw electrons from the carbon atoms, which creates a net positive charge and thus reduces the chemisorption overpotential. The resulting reduced cost and highly efficient ORR catalytic activity have attracted significant interest in catalysts based on N- and B-codoped carbon materials. For instance, Xue et al. employed graphene foams codoped with nitrogen and boron as a catalyst for the ORR and obtained excellent results [15], whereas Shu et al. successfully applied nitrogen–boron dual-self-doped graphene as a cathode catalyst for the ORR in fuel cell applications [16].

Herein, we have developed a simple method for synthesizing a metal-free N- and B-codoped carbon nanoparticles (NB-CPs) catalyst that uses dopamine as the nitrogen precursor and 3-aminophenylboronic acid (ABA) as the boron source. *In situ* polymerization was employed to polymerize dopamine, followed by binding to ABA and carbonization to achieve a distribution of nitrogen and boron within the graphitic shell of carbon. One of the most important characteristics of polydopamine (PDA) is that it can be easily adsorbed onto any surface, and the adhesion layer functions as a functionalized self-assembled monolayer to anchor other molecules [17,18]. The self-adhesive characteristic of PDA was employed to encapsulate the carbon particles that successfully anchored boron on the surface. The prepared catalyst exhibited superior electrocatalytic activity toward oxygen reduction in microbial fuel cells.

## 2. Experimental methods

### 2.1. Preparation of N-doped carbon particles

PDA-coated carbon particles (PDA-CPs) were prepared using a method similar to that reported by Liu et al. [19]. Namely, 1.2 g of carbon particles (CPs) was added to 250 mL of tris(hydroxymethyl) aminomethane (Tris) solution (10 mmol $L^{-1}$, pH = 8.5) and dispersed by 10 min of sonication. Then, 1.0 g of dopamine was added, and the mixture was magnetically stirred at room temperature for 24 h. The coated CPs were then obtained by filtering, washing and drying. The PDA-CPs were carbonized in a tube furnace at 900 °C for 2 h by increasing the temperature at a rate of 5 °C $min^{-1}$ under a $N_2$ atmosphere to obtain the N-doped CPs (N-CPs).

### 2.2. Preparation of N,B-doped carbon particles

Next, 0.5 g of the synthesized PDA-CPs was redispersed in phosphate-buffered saline (PBS, pH = 7.4), and then, 0.5 g of 3-aminobenzene boronic acid (ABA) was added to the solution. The mixture was magnetically stirred at room temperature for 5 h. The ABA- and PDA-co-coated CPs (ABA-PDA-CPs) were obtained by filtering, washing and drying. The ABA-PDA-CPs were carbonized at 900 °C for 2 h to produce N,B-codoped CPs (NB-CPs).

### 2.3. Electrochemical measurements

To investigate the ORR activities of the various catalysts, cyclic voltammetry (CV) measurements were performed using a conventional three-electrode system. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Catalysts coated glassy carbon (GC, 5.0 mm diameter) electrodes were used as the working electrodes. To prepare the working electrodes, a mixture with 5 mg functionalized CPs, 1 mL absolute ethanol and 50 μL Nafion (5%, HESEN, China) was prepared under sonication. A 40 μL ink was dropped onto the glassy carbon disk, which was then left to dry in air at room temperature, to yield a catalyst loading of ca. 1.0 mg $cm^{-2}$. An aqueous solution of KOH (0.1 M) was used as the electrolyte for both normal CV and rotating-disk electrode (RDE) voltammetry measurements. Before each test, a proper conditioning gas, which consisted of a $N_2/O_2$ flow, was passed through the electrolyte for at least 30 min. Normal cyclic voltammograms were recorded from 0.1 V to −0.6 V with a sweep rate of 5 mV $s^{-1}$. For the RDE test, the same quantity of catalyst was loaded onto a rotating-disk electrode. The polarization curves for the ORR were obtained using a scan rate of 10 mV $s^{-1}$ with different rotating speeds from 300 to 3000 rpm at 0.2 to −0.8 V (vs. SCE). All of the tests were conducted in triplicate, and the typical curve is presented here.

### 2.4. Preparation of cathodes and MFC operation

An air cathode was constructed as previously reported by Cheng et al. [20] with a waterproof diffusion layer on one side and a catalytic layer coating on another side of a waterproof carbon cloth. The catalytic layer was decorated with either functionalized CPs or Pt/C. The dosage of catalysts on the cathode surface was 5 mg $cm^{-2}$ for the CPs and 0.5 mg $cm^{-2}$ for Pt (10% Pt loading, HESEN, China), and a Nafion binder solution (5%, HESEN, China) was used as the binder. Air-cathode single-chamber MFCs with an inner volume of 12 mL were constructed as previously reported [21]. A cylindrical MFC chamber with a length of 2 cm and a diameter of 3.0 cm was constructed using Plexiglas. The surface areas of both the anode and the cathode were 7 $cm^2$. Non-waterproof carbon cloth (type A) was used as an anode without further treatment. The anode and cathode were placed on opposite sides, with the oxygen catalyst coating layer facing the anode and the polytetrafluoroethylene (PTFE)-coated gas diffusion layer facing air.

The MFC reactors were inoculated with 2.0 mL of activated anaerobic sludge (Liede Sewage Treatment Plant, Guangzhou,