



## Short communication

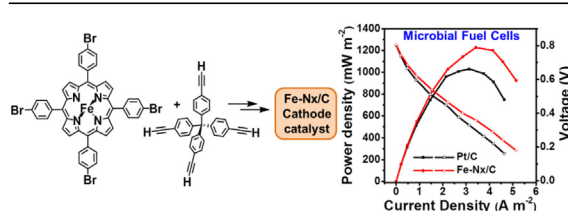
## Iron-rich nanoparticle encapsulated, nitrogen doped porous carbon materials as efficient cathode electrocatalyst for microbial fuel cells

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## HIGHLIGHTS

- A porous N-doped carbon material (Fe-N<sub>x</sub>/C) was prepared from simple building blocks.
- Catalytic performance of Fe-N<sub>x</sub>/C was investigated for oxygen reduction reaction.
- Fe-N<sub>x</sub>/C was applied in microbial fuel cell as an efficient cathode catalyst.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 4 December 2015

Received in revised form

19 February 2016

Accepted 8 March 2016

## Keywords:

Electrocatalyst  
Oxygen reduction reaction  
Microbial fuel cell  
Nitrogen-doped carbon  
Porous organic polymer

## ABSTRACT

Developing efficient, readily available, and sustainable electrocatalysts for oxygen reduction reaction (ORR) in neutral medium is of great importance to practical applications of microbial fuel cells (MFCs). Herein, a porous nitrogen-doped carbon material with encapsulated Fe-based nanoparticles (Fe-N<sub>x</sub>/C) has been developed and utilized as an efficient ORR catalyst in MFCs. The material was obtained through pyrolysis of a highly porous organic polymer containing iron(II) porphyrins. The characterizations of morphology, crystalline structure and elemental composition reveal that Fe-N<sub>x</sub>/C consists of well-dispersed Fe-based nanoparticles coated by N-doped graphitic carbon layer. ORR catalytic performance of Fe-N<sub>x</sub>/C has been evaluated through cyclic voltammetry and rotating ring-disk electrode measurements, and its application as a cathode electrocatalyst in an air-cathode single-chamber MFC has been investigated. Fe-N<sub>x</sub>/C exhibits comparable or better performance in MFCs than 20% Pt/C, displaying higher cell voltage (601 mV vs. 591 mV), maximum power density (1227 mW m<sup>-2</sup> vs. 1031 mW m<sup>-2</sup>) and Coulombic efficiency (50% vs. 31%). These findings indicate that Fe-N<sub>x</sub>/C is more tolerant and durable than Pt/C in a system with bacteria metabolism and thus holds great potential for practical MFC applications.

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## 1. Introduction

Microbial fuel cell (MFC) is a bio-electrochemical technology that converts chemical energy in organic compounds to electricity

by the metabolism of anaerobic bacteria [1]. The bacteria decompose organic fuel in the anode compartment, generating CO<sub>2</sub>, electrons, and protons. Electrons and protons migrate to the cathode to unite with an oxidizing agent, which is oxygen in most cases [2]. Unfortunately, the sluggish kinetics of oxygen reduction reaction (ORR) has become the bottleneck of power generation in MFCs, which function in pH-neutral aqueous electrolyte with lower concentration of H<sup>+</sup> or OH<sup>-</sup>, unlike acidic or alkaline electrolyte in fuel

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cells. Platinum-based catalyst has been considered as the most commonly used ORR catalyst for fuel cells. However, the high cost, scarcity, and limited stability of such precious-metal catalyst have hindered their applications. In addition, it has been reported that Pt/C system is very sensitive to pollutants present naturally in wastewater and easily poisoned [3].

It has attracted broad interest to develop sustainable, efficient, and durable electrocatalysts for ORR. To date, a variety of ORR electrocatalysts have been developed, such as metal-free carbon materials [4–6] and non-precious metal based catalysts [7–14], which are aimed at affordable alternatives in place of Pt-based catalysts. Composites of metal and nitrogen-doped carbon (M-N<sub>x</sub>/C) are a class of non-precious metal ORR catalysts that are often produced by pyrolysis of metallo-porphyrin or -phthalocyanine precursors. Jasinski and coworker first showed ORR activities of Fe-N<sub>x</sub>/C derived from iron(II)-phthalocyanines in fuel cells [15]. Subsequently, various Fe-N<sub>x</sub>/C catalysts have been reported to exhibit comparable or even higher ORR activity than commercial Pt/C system, when they are applied in fuel cells with acidic or alkaline electrolyte [16–19]. The first example of a MFC cathode catalyst based on M-N<sub>x</sub>/C (M = Fe or Co) was reported by Schröder and coworkers, which show a good activity in neutral electrolyte [11]. Since then, development of readily available and sustainable M-N<sub>x</sub>/C catalysts that exhibit good performance in MFC has been an active research area with the goal of replacing currently used expensive and scarce Pt/C system [20–24]. Recently, nitrogen-doped carbon materials derived from pyrolysis of porous polymers have attracted great attention. It has been reported that high porosity can facilitate mass transport, thus is important for M-N<sub>x</sub>/C to function as an efficient ORR catalyst [25]. Given a plethora of organic porous materials with various compositions, we envision that efficient ORR catalyst could be obtained through judicious selection of building blocks. In this work, iron-rich nanoparticle encapsulated, nitrogen doped porous carbon material (Fe-N<sub>x</sub>/C) has been developed as efficient non-precious metal ORR catalyst, through pyrolysis of a porous organic polymer containing iron(II) metallated porphyrins (FePOP). The successful application of such materials as the cathode electrocatalyst in a single-chamber MFC was also demonstrated.

## 2. Experimental

### 2.1. Preparation and pyrolysis of FePOP

To a 100 mL Schlenk tube were added iron (II)-5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin (M1) (100 mg, 0.10 mmol), tetrakis(4-ethynylphenyl)methane (M2) (42 mg, 0.10 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (26 mg, 0.036 mmol) and CuI (4.0 mg, 0.021 mmol), followed by triethylamine (5 mL) and anhydrous DMF (15 mL) as the solvent (Scheme S1). The resulting solution was degassed through three evacuation-nitrogen refill cycles and heated at 100 °C for 2 days under nitrogen atmosphere. It was then cooled to room temperature, and water (10 mL) was added. The mixture was sonicated for 10 min and the solid was filtered. The solid was successively washed with water (2 × 30 mL), ethanol (2 × 30 mL), dichloromethane (2 × 30 mL) and acetone (2 × 30 mL), and dried in vacuo to give the product (FePOP) as a dark solid (100 mg, 91%). Elemental analysis for FePOP: Calculated for (C<sub>77</sub>H<sub>40</sub>N<sub>4</sub>Fe)<sub>n</sub>: C, 85.87%; H, 3.74%; N, 5.20%; Fe, 5.19%; Found: C, 70.43%; H, 3.49%; N 3.91%; Fe, 3.38%. FePOP (50 mg) was pyrolyzed in a furnace under Ar atmosphere at 800 °C [18,26,27], to obtain the pyrolyzed materials (FePOP-800, 43 mg, 86% weight recovery). Then FePOP-800 (40 mg) was ultrasonically leached in 6 M HCl for 6 h to remove Fe element that was not well encapsulated in carbon materials during pyrolysis. Fe-N<sub>x</sub>/C (37 mg) was obtained after filtration and vacuum drying. Based on the raw materials, the cost of Fe-N<sub>x</sub>/C was

estimated to be ~8.6 USD g<sup>-1</sup>, substantially lower than that of Pt/C (150 USD g<sup>-1</sup>) [29].

### 2.2. Material characterization

To characterize the structure of the obtained electrocatalyst, transmission electronic microscopy (TEM) images were obtained with a F-30ST transmission electron microscope (Tecnai, US) on Cu substrate. Powder X-ray diffraction (PXRD) data was obtained with an X-ray diffractometer (Bruke D8 Adv., Germany) equipped with Cu K $\alpha$  source at step scan of 0.02° over the range of 10°–90°. The resulting PXRD data were analyzed with the Powder Diffraction Standard (JCPDS) database. The elemental composition of samples were examined and analyzed by energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, Kratos-Axis UL TRA DLD). The Quantachrome Autosorb ASiQ automated gas sorption analyzer was used to measure N<sub>2</sub> adsorption isotherms. The samples were activated by heating at 120 °C under vacuum for at least 22 h prior to the analysis. Ultrahigh purity grade (99.999% purity) N<sub>2</sub> and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

### 2.3. MFC setup and electrode preparation

Single-chamber MFCs were used in the experiments. The anode was a carbon fiber brush (4 cm in diameter, 2 cm in the length). The cathode was an air-cathode fabricated as described in the literature [28]. The anode and cathode were installed in a plexiglass tube chamber with a length of 4 cm, a diameter of 3 cm and a total volume of 19.8 mL [29,30]. The test cathode of Fe-N<sub>x</sub>/C was prepared by pasting the sonicated mixture of Fe-N<sub>x</sub>/C and carbon black (Vulcan XC-72) in the weight ratio of 1:1 with the assistance of 5% Nafion. The control electrode of Pt/C (20 wt%) was prepared as described by other groups [23,31]. Fe-N<sub>x</sub>/C (2 mg cm<sup>-2</sup>) and Pt (0.5 mg cm<sup>-2</sup>) were used in the electrochemical measurements and MFC experiments, respectively.

All MFCs were inoculated with an effluent obtained from the same MFC reactor, which has been operating for several years in the lab, in order to warrant similar microbial functions. After the inoculation, the MFC was fed with phosphate buffer saline (PBS, 0.1 M, pH = 7.0) containing NaAc (1.0 g L<sup>-1</sup>), KCl (0.13 g L<sup>-1</sup>), and NH<sub>4</sub>Cl (0.31 g L<sup>-1</sup>), and also supplemented with mineral solution (12.5 mL L<sup>-1</sup>) and vitamin solution (5 mL L<sup>-1</sup>) [32]. All tests were carried out at room temperature (around 25 °C). We evaluated the performance of Fe-N<sub>x</sub>/C and Pt/C in two parallel MFC reactors with the same inoculum and anodes but different cathodes (Pt/C cathode or Fe-N<sub>x</sub>/C cathode). The reproducibility of the power output was tested by switching Pt/C cathode and Fe-N<sub>x</sub>/C cathode between the two parallel MFC reactors multiple times. The variation of cell voltages with such a change was all within the experimental error each time, showing almost constant cell voltage for the MFC with Fe-N<sub>x</sub>/C cathode, and also the one with Pt/C cathode. For each trial, the cell voltage of MFC with Fe-N<sub>x</sub>/C cathode was consistently higher than that of the MFC with Pt/C cathode, while the anodes' potentials were almost same for the two MFCs, suggesting the repeatability and reliability of our study. We refilled the nutrient solution every ~50 h, when the voltage dropped below ~100 mV in each reactor.

### 2.4. Electrochemical measurement and calculation

Electrochemical measurements of cyclic voltammetry (CV) were performed using a computer-controlled potentiostat (CHI 850D, Shanghai CH Instrument, China). Rotating ring-disk electrode (RRDE) experiments were performed using a computer-controlled

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