



A novel metal organic framework-derived carbon-based catalyst for oxygen reduction reaction in a microbial fuel cell

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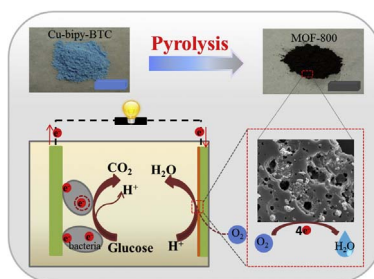
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HIGHLIGHTS

- Novel ORR catalyst MOF-800 is prepared by pyrolyzing ORR active MOF Cu-bipy-BTC.
- Enhanced electrical conductivity and ORR catalytic activity by MOF-800.
- The charge transfer resistance of MOF-800 cathode is 1.38 Ω.
- MOF-800 shows excellent ORR activity through a four-electron pathway.
- A maximum power density of $326 \pm 11.2 \text{ mW m}^{-2}$ is obtained from MOF-800-MFC.

GRAPHICAL ABSTRACT



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ABSTRACT

To improve the power generation of microbial fuel cell (MFC), the cathode is modified to increase its oxygen reduction reaction (ORR) activity by using a Cu, N-incorporated carbon-based material as catalyst, which obtained from pyrolyzing ORR active Cu (II)-based metal organic framework (MOF; Cu-bipy-BTC, bipy = 2,2'-bipyridine, BTC = 1,3,5-tricarboxylate). MOF-800 (the product of pyrolyzing Cu-bipy-BTC at 800 °C) shows porous structure with micropores ranging from 0.5 to 1.3 nm and mesopores ranging from 27 to 46 nm. It also exhibits improved ORR electrocatalytic activity with a higher current density of -3.06 mA cm^{-2} compared to Cu-bipy-BTC. Moreover, the charge transfer resistance of MOF-800 cathode (1.38 Ω) is much smaller than that of Cu-bipy-BTC cathode (176.8 Ω). A maximum power density of $326 \pm 11 \text{ mW m}^{-2}$ is achieved by MOF-800-MFC, which is 2.6 times of that of Cu-bipy-BTC-MFC and comparable with Pt/C-MFC ($402 \pm 17 \text{ mW m}^{-2}$). The results imply the enhancements of ORR catalytic activity and electrical conductivity of MOF-800 are due to the enhanced porous structure and abundant active sites (C–N, Cu–N_x), which result in the improved power generation of MFC. This study provides technical and theoretical validation for the MFC performance improvement by ORR active MOF-derived catalysts modified cathodes.

1. Introduction

As a new type of energy conversion device, microbial fuel cell (MFC)

could decompose organics to generate electricity with the help of bacteria [1–3]. Among various kinds of MFCs, air-cathode MFC is most widely applied for its simple configuration and direct use of accessible

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oxygen as electron acceptors [4,5]. However, oxygen reduction reaction (ORR) in cathode is quite sluggish, so highly efficient catalysts are essential to speed up the rate and reduce the cathode overpotential [5–7]. Platinum (Pt)-based catalysts, possessing excellent catalytic activity, have been commonly used in MFCs. But the high cost, scarcity, and sensitivity to poisoning greatly hinder their practical application [8]. Therefore, it is urgent to develop efficient and low-cost ORR catalysts to replace Pt.

Nowadays, abiotic non-Pt catalysis materials and biocatalysts are the main approaches for the development of MFC cathode catalysts. The former mainly refers to transition metal macrocyclic compounds, metal oxides, electroconductive polymers and carbon-based materials [9]. With the advantages of high durability and low price, carbon-based materials are considered to be the most promising alternatives and have been widely studied [9–11]. Although the electrical conductivity of pristine carbon (such as activated carbon, carbon nanotubes, etc.) is outstanding, its ORR electrocatalytic performances are hardly comparable with Pt/C [11,12]. Previous studies have shown that introducing non-noble transition metal or/and heteroatom can effectively improve their catalytic activities [7,13–15]. In recent years, a kind of emerging carbon-based materials metal organic framework (MOF) has attracted wide attention. MOFs possess many unique characteristics, such as unsaturated metal-ion active sites, large specific surface area and tunable pore structure, which make them shown potential applications in electrocatalysis recently [16]. Cho et al. [17] prepared a composite CuS(28%)/Cu-BTC, and found that the ORR catalyzed by this composite in 0.1 M KOH followed a quasi-four-electron transfer pathway with onset potential of 0.91 V (vs. RHE). Jahan et al. [18] synthesized a graphene oxide (GO)-incorporated Cu-MOF, which showed ORR cathodic peak at -0.23 V (vs. Ag/AgCl) in 0.5 M H₂SO₄ solution, and it was applied to a polymer electrolyte membrane fuel cell with maximum power density of 110.5 mW m⁻².

Despite that MOFs have potential application in ORR electrocatalysis, they are typically electrical insulators [17], and not suitable for the application of the electrochemical fields. Thus, it is necessary to take measures to enhance the electrical conductivity of MOFs and simultaneously maintain its ORR catalytic activity to improve its electrocatalysis performances. Previous studies have demonstrated that conductive substances (such as CuS [17], GO [18]) can enhance the electrical conductivity of MOFs, however, the ORR performances of the composites are still lower than that of commercial Pt/C and the stability of the composites need to be further studied. It is found that during high-temperature activation, the organic part of MOFs will be converted to conductive carbon which is beneficial for the electrical conductivity [19]. Hereby, MOFs have been served as pyrolytic precursor to prepare non-noble metal or/and heteroatom doped carbon-based materials with ORR catalytic activity [20–22]. After pyrolysis, the characteristics associated with electrocatalysis of MOFs, such as intrinsic ligand heteroatoms and metal centers, specific surface area and pore structures, will be retained to some extent or even be enhanced [19,23]. Therefore, it can be expected to enhance the electrical conductivity of ORR catalytic active MOFs and maintain/improve its catalytic activity through pyrolysis.

Cu-bipy-BTC (bipy = 2,2'-bipyridine, BTC = 1,3,5-tricarboxylate) is one kind of typical water-stable MOF, which copper ion as metal center and 2,2'-bipyridine and 1,3,5-tricarboxylate as organic ligands [24]. It has been extensively studied in electrochemistry, such as electro-synthesis of dimethyl carbonate [25], and detection of hydrogen peroxide [26], and electrode material for highly capacitive pseudocapacitors [27], etc. Mao [28] found that Cu-bipy-BTC was able to effectively catalyze the ORR in phosphate buffer (pH = 6), and the ORR nearly followed a 4e⁻ pathway with electron transfer number of 3.8. MFC is generally operated in a pH-neutral environment [29]. Thus, it is feasible to modify MFC cathode with excellent pH-neutral ORR catalyst Cu-bipy-BTC. The major problem is to improve its electrical conductivity [26]. This study intended to enhance the electrical

conductivity of Cu-bipy-BTC by direct pyrolysis, and use the pyrolysis derivatives to modify MFC cathode to improve the ORR performance and consequently boost MFC electricity generation performance. Although starting from MOF's structural features and chemical compositions, MOFs have been served as pyrolytic precursor to prepare ORR electrocatalysts [21,22], to our knowledge, there is no report on the study of ORR catalytic active MOF as pyrolysis precursor. Therefore, it is necessary to study the ORR performances of Cu-bipy-BTC pyrolysis derivatives. Moreover, an elucidation of Cu-bipy-BTC derivatives in enhancing the electrical conductivity and cathodic oxygen reduction in MFC is interesting and valuable.

In this study, Cu-bipy-BTC was synthesized by hydrothermal method, and its derivatives were prepared via pyrolyzing Cu-bipy-BTC at different high temperature under the protection of nitrogen. Field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) were conducted to observe the morphologies of the pyrolysis derivatives. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and nitrogen sorption isotherm were used to characterize the structures and chemical compositions of the pyrolysis derivatives. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were adopted to evaluate the electrocatalytic activities of the as-prepared catalysts. Moreover, single chamber air-cathode MFCs were constructed with Cu-bipy-BTC and its derivatives as cathode catalysts. The performances of the as-prepared catalysts modified cathode MFCs were discussed by power densities, polarization behaviors and electrochemical impedance spectroscopy (EIS), and compared with plain cathode (no catalyst modified) MFC and classic Pt/C modified MFC. This study was expected to comprehend the improvement of MFC performance by ORR active MOF-derived catalysts modified cathodes.

2. Materials and methods

2.1. Preparation of Cu-bipy-BTC and derivatives

Cu-bipy-BTC was synthesized as described by Song et al. [24]. The MOF derivatives (denoted as MOF-T) were prepared by temperature programmed pyrolysis of the MOFs in N₂ atmosphere. Briefly, a certain amount of as-prepared Cu-bipy-BTC was added into a porcelain boat and then placed in a tube furnace, under flowing N₂ for 30 min to exclude air, and heated at target temperature (T = 600, 700, 800, 900 °C) for 2 h with a ramp rate of 5 °C min⁻¹ under the protection of N₂. After the furnace was cooled to room temperature naturally, the catalysts MOF-T (MOF-600, MOF-700, MOF-800 and MOF-900) were obtained.

2.2. Characterization of Cu-bipy-BTC and derivatives

The crystal structures of Cu-bipy-BTC and derivatives were characterized by a powder X-ray diffractometer (Model D8 Advance, Bruker) with Cu K α radiation ($\lambda = 1.54$ Å) at step scan of 0.02°. FTIR spectra of the samples were obtained on an FTIR spectrometer (Nicolet Continuum) using a Vector 33 with KBr discs from 4000 to 400 cm⁻¹. The morphologies of the catalysts were observed using a Zeiss Merlin instrument equipped with an energy-dispersive spectroscopy (EDS) device. TEM and HRTEM observations were made on a TEM system (Tecnai G2 F20, FEI) at 200 kV. The surface chemical composition of the samples was investigated by an ESCALAB 250 spectrometer with monochromatic Al K α X-ray source. XPS data were fitted with the software "XPSPEAK" (version 4.1). Nitrogen sorption measurements were taken on a micromeritics 3Flex gas sorption analyzer to evaluate the specific surface area and porosity of the catalysts. Before testing, Cu-bipy-BTC was degassed at 50 °C for 8 h, and MOF-T was degassed at 200 °C for 2 h.

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