

Novel Co/UiO-66 metal organic framework catalyst for oxygen reduction reaction in microbial fuel cells

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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 Co/UiO-66, which derived from pyrolyzing the mixture of $\text{Co}(\text{NO}_3)_2$ as the metal precursor incorporated with $\text{NH}_2\text{-UiO-66}$. It was found that Co/UiO-66 (MOF-900) has been developed as a high-performance electrocatalyst for ORR at a pyrolysis temperature of 900 °C. Therefore, Co/UiO-66 should be a promising oxygen reduction catalyst for application in MFCs. This study provides technical and theoretical validation for the MFC performance improvement by ORR active MOF-derived catalysts modified cathodes.

1 Introduction

Energy shortage and environmental pollution are the most pressing issues that have to be addressed in order to realize the sustainable development of human society. As a new type of energy conversion device, Microbial fuel cells (MFCs) hold great potential to meet both challenges because they could decompose organic waste through biological oxidation and produce electrical energy simultaneously [1-3]. At the anode chamber of MFCs, electrons and protons are produced from the oxidation of organic compounds by microbes, and then transferred to cathode through an external circuit. These electrons are consumed by electron acceptors in cathode. Finally, bioelectricity is generated by the electrochemical process [4, 5]. Among various kinds of MFCs, air-cathode MFC is most widely applied for its simple configuration and direct use of accessible oxygen as electron acceptors [6, 7].

Of all bio-electrochemical process, the cathodic oxygen reduction reaction (ORR) is a key factor for the overall performance and the power output density of MFCs. 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 [8,9]. Platinum (Pt)-based catalysts, possessing excellent ORR catalytic activity, have boosted various novel techniques such as hydrogen production, super capacitor, and have been commonly used in MFCs. But the high cost, scarcity, and sensitivity to poisoning greatly hinder their practical application [10-12]. Therefore, it is urgent to develop efficient and low-cost ORR catalysts to replace Pt.

Up to now, numerous studies have been devoted to fabricate highly active electrocatalysts for ORR. Noble

metal oxides [13-15], carbon-based materials [16-18], transition metal heteroatom doped carbons [19-21] and nitrogen-doped carbonaceous materials [22], have been developed as promising alternatives to replace Pt-based catalysts. In particular, the transition metal heteroatom doped carbons stand out from all other promising candidates owing to their superb ORR electrocatalytic properties. In addition, the intimate contact between the transition metal and carbon shell is critical to influence the structure of composites with the metal active sites, which can significantly affect the electron transmission capability between carbon matrix and metal atoms and the kinetics rate of the ORR. Although the transition metal heteroatom doped carbons have shown outstanding ORR activity, there still exists several technical hurdles of applying these catalysts are existing because of their low surface area, poor porosity structure, corrosion and severe aggregation, all of which deteriorate conductivity and ORR performance of catalysts [23,24]. Nowadays, abiotic non-Pt catalytic materials and biocatalysts are the main approaches to develop MFC cathode catalysts. Carbon material with high durability and the advantages of low price, are considered to be the most promising alternatives, and have been widely studied [25].

In recent years, a new kind of carbon material of metal-organic frameworks (MOFs) has attracted wide attention. MOFs are functional porous materials consisted of metal ion centers coordinated with organic ligands. MOFs have many unique properties, such as unsaturated metal ions in the active site, large specific surface area and pore structure, adjustable make them recently shows potential application in electrocatalysis [26]. It is found that during high-temperature activation, the organic part of MOFs will be converted to conductive carbon which is beneficial for

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the electrical conductivity [27]. Hereby, MOFs have been served as pyrolytic precursor to prepare non-noble metal or/and heteroatom doped carbon-based materials with ORR catalytic activity [28]. 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 [29]. Chen et al. found that the efficient MOF-derived coralline-like catalyst favored four-electron ORR process and achieved low overpotential for ORR comparable to benchmark Pt/C [30]. Tang et al. reported that Co-MOF-derived dual metal and nitrogen heteroatom doped carbons displayed exceptional ORR property and high stability with onset potential of 0.347 V in pH-neutral electrolyte [31]. Meanwhile, You et al. found that MOF-derived porous nitrogen doped electrocatalyst favored the efficient four-electron pathway for ORR in MFC and the MFC achieved the maximum power density of 1665 mW/m², which was 39.8% higher than that for Pt/C catalysts [32]. Fu et al. found that novel PeN-carbons could be synthesized using MOF UiO66-NH₂ as precursor through calcination. The product has showed excellent catalytic activity for ORR which can be comparable to Pt/C catalysts [33]. The customized functionalization and thermal conversion of MOFs can adjust the electronic structure of carbon layers and harvest more active sites for oxygen catalysis, providing an efficient synthetic route for the exploration of superior ORR electrocatalysts. The MOF-derived carbonaceous composites can inherit unique features of corresponding MOFs to fabricate non-noble metal heteroatom doped carbonaceous electrocatalyst with remarkable ORR performance, conductivity and stability. MOF-derived composites can not only possess the host-guest synergistic effects between carbon and metal ion center, but also contain uniform alignment of metal ion centers in carbon matrix. The latter is favorable to build up adjustable 3D ordered network structure to mitigate the mass transfer barrier and aggregation of carbon. Therefore, it can be expected to enhance the electrical conductivity of ORR catalytic active MOFs and maintain/improve its catalytic activity through pyrolysis.

Consequently, in this study, NH₂-UiO-66 was synthesized by hydrothermal method, and Co/UiO-66 were prepared via pyrolyzing the mixture of NH₂-UiO-66 and Co(NO₃)₂ at different high temperature under the protection of nitrogen. Then cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were adopted to evaluate the electrocatalytic activities of the as-prepared catalysts.

2 Experiment

2.1. Synthesis of Catalysts

0.181g 2-aminoterephthalic acid and 0.233 g ZrCl₄ were dispensed in 50 mL N, N-dimethylformamide (DMF). Then, the mixed solution was transferred into a 100 mL Teflon lined steel autoclave and hydrothermally reaction at 120 °C for 48 h. The solid NH₂-UiO-66 products were filtered and rinsed with DMF and methanol for several times, and then dried under the vacuum for 24 h at 80 °C.

The Co(NO₃)₂ as the metal precursor was incorporated with NH₂-UiO-66 to prepare Co/UiO66 composites by impregnation method and calcination. 0.6 mM Co(NO₃)₂ and 2 g NH₂-UiO-66 were mixed in 15 mL methanol and the solution was stirred for 24 h at 40 °C by a magnetic stir bar to ensure complete loading of cobalt metal in NH₂-UiO-66. Subsequently, the mixture was centrifuged and washed with methanol, followed by drying at 80 °C under vacuum. Finally, the Co/UiO66 products was pyrolyzed under protection of N₂ between 700 °C, 800 °C and 900 °C for 2 h in programmable furnace with a rate of 5 °C min⁻¹. For simplicity, these samples were termed as MOF-T (i.e., MOF-700, MOF-800, MOF-900), where T represented the pyrolysis temperature.

2.2 Electrochemical Measurement

The electrochemical measurements were conducted on electrochemical workstation (PalmSens4C, PalmSens BV, Netherlands) in a conventional three-electrode cell mode with Ag/AgCl as the reference electrode, platinum wire plate as the counter electrode and glassy carbon electrode (5 mm diameter) as the working electrode. To prepare the working electrode, 3 mg of Co/UiO66 electrocatalysts were dispersed in 0.5 mL isopropanol and 0.5 mL deionized water contacting 20 µL Nafion (5 %) solution in an ultrasonic bath for 10 min to produce the catalyst ink. 7.6 µL suspension was dropped onto glass carbon electrode and dried at room temperature to form a uniform film. The cyclic voltammetry (CV) measurements was tested by electrochemical workstation in both nitrogen and oxygen saturated 0.1 M KOH electrolyte from -0.8 to 0.2 V at a scan rate of 50 mVs⁻¹. Rotating disk electrode (RDE) tests were carried out at the various rotation speeds from 250 to 2500 rpm with a scanning rate of 10 mVs⁻¹ in O₂-saturated alkaline and neutral electrolytes.

To further investigate the ORR performance of electrocatalysts, the rotating ring disk electrode (RRDE) measurements were carried out rotation speed controller (Pine, AFMSRCE 421701, USA) with 1600 rpm rotating speed in O₂-saturated 0.1 M KOH solution. The electron transfer number (n) and the hydrogen peroxide yield (H₂O₂ %) can be calculated by the equations based on disk current (I_{disk}) and ring current (I_{ring}) of RRDE test.

$$n = (4I_{disk}) / (I_{disk} + I_{ring}/N) \quad (1)$$

$$H_2O_2 = (200 * I_{ring}/N) / (I_{disk} + I_{ring}/N) \quad (2)$$

Where I_{ring}, I_{disk} and N are the ring current, disk current and collection efficiency (N=0.37), respectively for the employed RRDE.

3 Result and Discussion

To evaluate the oxygen reduction reaction (ORR) activity of catalysts of MOF-900, Cyclic voltammetry (CV) combined with The linear sweep voltammetry (LSV) was performed on RDE in PBS solution because they were desired to be used as electrocatalysts in real MFCs. From Fig. 1(a), clear peaks of the oxygen reduction reaction

appear in the O₂-saturated solution for MOF-900, and almost disappear in the N₂-saturated solution, revealing that it was associated with ORR activity.

Fig. 1(b) shows the LSV results of the MOF-800 catalysts. The current density of MOF-800 keeps increasing along with the rotational speed from 250 to 2500 rpm min⁻¹. When the current density of the ORR is between -0.35 V and -0.80 V, a stable limit diffusion current region appears. This indicates that the progress of the oxygen reduction reaction is affected by the diffusion rate of the material oxygen to the catalyst surface, and the kinetic process of this system is generally described by the Koutecky Levich equation (K-L).

$$1/J = (1/J_K) + (1/J_L) = (1/J_K) + (1/(B\omega^{1/2})) \quad (3)$$

$$B = 0.62nFAD_0^{2/3}\nu^{-1/6}C_0 \quad (4)$$

The LSV of all samples measured in O₂-saturated solution at 1600 rpm min⁻¹ are shown in Fig. 1(c); it is clear that MOF-900 exhibits a more positive onset potential, half-wave potential, and bigger current density (at -0.6 V) than the rest. The details were calculated and are listed in Table 1, indicating that the difference in ORR catalytic activity between MOFs is strongly dependent on the degree of graphitization and the content of different nitrogen species. Different heat treatment temperatures may also produce this change. In particular, a suitable high pyrolysis temperature facilitates the formation of high levels of graphite. Then the high graphitization can further enhance the electrical conductivity of the carbon shell and reduce the thermodynamic barrier of the ORR. Therefore, the significant ORR performance of MOF-900 is attributed to high graphitization, nitrogen doping, great pore structure, and synergistic interactions between carbon atoms and metal centers.

The oxygen reduction reaction is usually carried out by a 2e-(H₂O₂) or 4e-(H₂O) mechanism. To further research the pathway of the ORR of the MOF(s) catalysts, the corresponding limiting current density and the rotational speed at different voltages in the LSV curve were selected to Construct K-L curve equation. From Fig. 1(d), the kinetic process of the oxygen reduction reaction with the MOF(s) catalysts can be fitted well by the K-L equation, illustrating the occurrence of ORR is

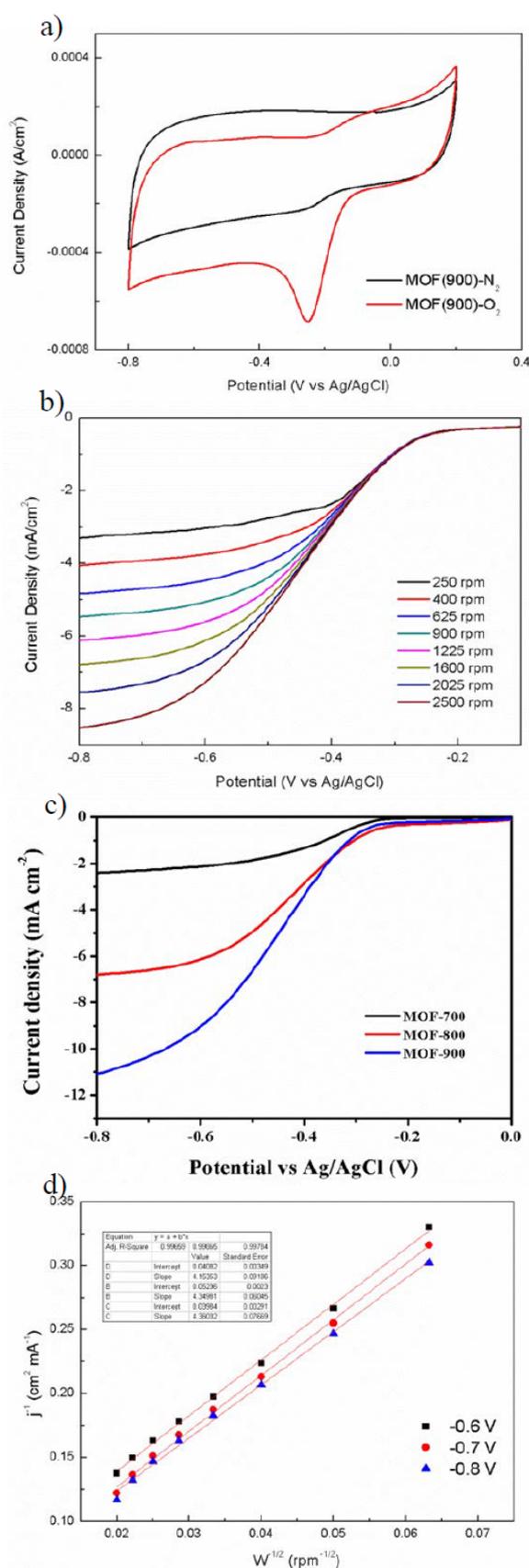


Fig. 1. (a) CV plots of MOF-900 in O₂-saturated (red line) and N₂-saturated (black line) PBS electrolyte. (b) LSV plots of MOF-800 under different rotation speeds (250–2500 rpm min⁻¹). (c) LSV plots of various catalysts in O₂-saturated electrolyte at 1600 rpm. (d) Koutecky–Levich plots of MOF-900 at different potentials.

Table 1. Electrochemical results of different catalysts for ORR

	MOF-700	MOF-800	MOF-900
On-set potential (V)	0.02	0.03	0.04
Half-wave potential (V)	-0.39	-0.43	-0.475
Current density (mA cm ⁻²)	-2.125	-6.130	-9.027

based on the first-order reaction kinetics of dissolved oxygen. Moreover, the K-L curves give the electron transfer number (3.5) for MOF-900, indicating that it favors a 4e- ORR process, which is same with Pt/C (3.99). Thus, the oxygen reduction reaction with the MOF-900 catalyst is a very efficient catalytic process. To sum up, the catalysts of MOF-900 may have potential to be an effective, high-conductivity, low-cost, and environmentally friendly cathode catalyst for MFCs.

4 Conclusions

In summary, the results suggest that Co/UiO-66 (MOF-900) exhibits remarkable ORR electrocatalytic activity, it should be a high-performance electrocatalyst for ORR. Co/UiO-66 could be a promising oxygen reduction catalyst for application in MFCs.

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