



The excellent performance and mechanism of activated carbon air cathode doped with different type of cobalt for microbial fuel cells



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HIGHLIGHTS

- Two type of cobalt modified AC catalysts were successfully used in air-cathode MFCs.
- The maximum power density of Co/AC was $1420.8 \pm 54 \text{ mW m}^{-2}$, 63.8% higher than control.
- $\text{Co}_3\text{O}_4/\text{AC}$ responded highest i_0 which was 2.6 times higher than the control.
- Co_3O_4 nanosheet formed on the AC with the surface area increased and the R_{ct} reduced.
- The high crystallization resulted in the significant catalytic activity of Co_3O_4 .

ARTICLE INFO

Article history:

Received 9 November 2015

Received in revised form 15 February 2016

Accepted 26 February 2016

Available online 7 March 2016

Keywords:

Cobalt

Electrodeposition

Catalytic activity

Microbial fuel cells

Oxygen reduction reaction

ABSTRACT

A novel cobalt decorated activated carbon (AC) air cathode with facilitated oxygen reduction activity is developed for microbial fuel cells (MFCs). Two kinds of cobalt modified cathodes $\text{Co}(\text{OH})_2/\text{AC}$ and $\text{Co}_3\text{O}_4/\text{AC}$ were prepared via a simple electrodeposition. The electrodeposition process was optimized to achieve high a surface area and pore volume structure. Transmission electron spectroscopy (TEM) analyses confirmed that Co_3O_4 and $\text{Co}(\text{OH})_2$ nanosheets were homogeneously distributed on the AC. Compared to raw AC. Electrochemical evaluation showed that the onset potentials towards oxygen reduction reaction (ORR) of $\text{Co}(\text{OH})_2/\text{AC}$ and $\text{Co}_3\text{O}_4/\text{AC}$ shifted to higher potential and the exchange current densities were increased by 2.6 times and 1.6 times, respectively. The MFCs with $\text{Co}_3\text{O}_4/\text{AC}$ reached a maximum power density of $1420.8 \pm 54 \text{ mW m}^{-2}$, significantly improved performance by 64% in relative raw AC.

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1. Introduction

Microbial fuel cells (MFCs) are particular promising, since they could be used to extract electrons from oxidation of a naturally occurring fuel with high efficiency, such as carbohydrate [1]. To increase energy output and reduce the cost of MFCs, single chamber microbial fuel cells (SCMFCs) containing anode and a single air cathode was widely used [2,3]. But the cost of traditional air cathodes was high due to the use of expensive platinum (Pt) catalyst, Nafion binder, and high grade carbon cloth [4]. Recently, great attention has been paid to using activated carbon (AC) as a cathode catalyst [5,6]. AC powder based cathodes have produced power

densities in MFCs similar to or slightly higher than those made with a platinum catalyst [7]. To further improve the performance for practical application, various approach of modification of AC have been attempted such as doping method. Nitrogen or phosphorus doped AC by acidic pretreatment to introduce functional group and by changing the texture of AC surface have been reported [8,9]. Other approach includes incorporating oxygen reduction reaction (ORR) active materials such as Mn, Fe and Ag [10–16].

Among the non-precious metal electro-catalysts for ORR, cobalt has been widely investigated as alternative catalysts in terms of their low cost, moderate electrical resistance [17]. Cobalt micro- or nano-particles have been reported which are capable of catalyzing ORR with activity comparable to that of Pt catalyst [18,19]. Cobalt macrocyclic complexes such as tetraphenylporphyrin (TPP) [20], tetramethoxyphenylporphyrin (TMPP) [21–23] and phthalocyanine (Pc) [24], which could facilitate ORR, have particularly been investigated for MFCs applications. On top of it, the

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performance of cobalt with iron (II) phthalocyanine (FePc) based oxygen reduction catalysts was studied as cathode materials in MFCs [25,26]. Gong et al. [19] studied a stainless steel mesh/cobalt oxide hybrid electrode (SSM/Co₃O₄) prepared by ammonia-evaporation-induced method to get a similar maximum power density to Pt/C cathode. Li et al. [27,28] indicated that the hybrid binuclear-cobalt-phthalocyanine (Bi-CoPc) and pyrolyzed Bi-CoPc behaved a higher ORR rate. Liu et al. [29] prepared the cobalt porphyrin-based material as methanol tolerant cathode in singer chamber microbial fuel cells. However, the high cost and sophisticated synthesis method of these materials prohibited the use of these cathodes for large scale application. Lefebvre et al. [30] prepared the carbon cloth supported cobalt cathode by plasma sputtering deposition method in MFCs, which generated in average the same power as sputtered-Pt cathodes (0.27 mW cell⁻¹). To our best knowledge, no studies using activated carbon supported cobalt species as air cathode for MFCs have been reported.

Electrochemical deposition is a simple and inexpensive method for the direct growth of metal or metal oxide thin films over AC, which was successful used in previous studies [10,12]. Co(OH)₂ and Co₃O₄ could be electrodeposited on AC surface by different potentials [31,32]. In this study, cathodic and anodic depositions were employed to produce two different cobalt species on AC cathodes and the cathodes were evaluated in MFCs for their electrochemical performance. Furthermore the properties of catalysts were investigated by a series of characterization methods in order to figure out how cobalt influenced on the AC air cathodes in MFCs.

2. Materials and methods

2.1. Air-cathode preparation

All the air-cathodes were made by rolling-press method according to procedures described by previous study [5]. Air-cathodes were consisted of a stainless steel mesh (SSM) with a gas diffusion layer (GDL) and a catalyst layer (CL). The amount of activated carbon (AC) used in each CL was about 0.25 g and PTFE with a mass ratio of 1:6. The method of making the cathodes was same as us previous study [12]. The gas diffusion layer was prepared by the same procedure of catalyst layer, but only include Carbon black (Jin qiu shi chemistry Co. Ltd., Tianjin, China) and PTFE with a mass ratio of 3:7. The electrodeposition cell used in this study is a conventional three-electrode cell with the AC air cathode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt ribbon as the auxiliary electrode. The electrodeposition was carried out using a Corrtest CS120 model electrochemical workstation (Wuhan, China) from a electrolyte solution of 100 mM Co(CH₃COO)₂·4H₂O. Co(OH)₂ and Co₃O₄ were electrodeposited on the surface of AC with potentiostatic polarization potentials of -1 V/SCE and 1 V/SCE for the cathodic and anodic depositions were employed, with named sample as Co(OH)₂/AC-x and Co₃O₄/AC-x with the postfix number for the deposition time, respectively. Control sample (Raw-AC) was also prepared without any deposition. The electrodeposition samples were washed in running distilled water three times before putting it into the MFCs.

2.2. MFCs setup and operation

The single-chamber MFC has an inner cylindrical chamber with diameter of 3 cm and total volume of MFCs is of 28 mL. The anode was made of a round shape carbon felt and placed in the center of the inner cylinder. The distance of anode and cathode was keep as 4 cm, and a titanium wire was chosen to form external circuit. Domestic wastewater was employed as the inoculums. In the first 3–4 cycles cell cultivation, 50 mM phosphate-buffered saline (PBS)

containing sodium acetate (1 g L⁻¹), NH₄Cl (0.31 g L⁻¹), KCl (0.13 g L⁻¹), NaH₂PO₄·2H₂O (3.321 g L⁻¹), Na₂HPO₄·12H₂O (10.305 g L⁻¹), trace mineral (12.5 mL L⁻¹), and vitamin (5 mL L⁻¹) were added. The cell was incubated at 30 °C and the voltages of MFCs were recorded every minute by a data acquisition card (Morpheus Electronic Co. Ltd, Beijing, China).

2.3. Electrochemical and material analysis

Polarization curves and power density curves were obtained by varying the external resistance from 9000 Ω to 70 Ω. Each resistor was tested for fixed time (about 30 min) to ensure a stable voltage. Cathode and anode potentials during polarization were measured using SCE as a reference electrode. Linear sweep voltammetry (LSV) of all the cathodes were tested by a potentiostat (CHI600E, ChenHua Instruments Co. Ltd., Shanghai, China). LSV was conducted from open circuit potential (OCP) to -0.3 V with a scan rate of 0.1 mV s⁻¹. Ag/AgCl (saturated KCl) was used as reference electrode and platinum sheet (1 cm²) was used as counter electrode. The voltages in the text were measured with Ag/AgCl as reference voltage. These two electrodes were both fixed with 0.5 cm spacing from the working electrode. Before the tests, the cathodes should be immersed in 50 mM PBS for about 24 h. Electrochemical impedance spectroscopy (EIS) of all the cathodes was performed over a frequency range of 100–100 mHz at open circuit potential using a potentiostat (VersaSTAT 3, Princeton Applied Research, USA). Exchange current density (*i*₀, A cm⁻²) was calculated based on Tafel plots, with overpotential of 0–100 mV, the *y*-axis intercept in Tafel plots was the logarithm of the exchange current density based on simplified Butler–Volmer equation [33].

$$\lg\left(\frac{i}{i_0}\right) = \frac{\beta F \eta_{cathode}}{2.303RT} \quad (1)$$

To characterize the crystal structure of the catalysts, X-ray diffraction (XRD) was carried out with a D/max-2500 X-ray generator. The X-ray intensity was measured over a diffraction 2-theta angle from 10 to 80 with a velocity of 0.02 step⁻¹ and 2 min⁻¹. The morphologies of cathodes were examined by Hitachi S-3500N scanning electron microscope (SEM) and JSM-ARM200F field emission transmission electron microscope (FE-TEM). Specific surface area determination of the cathodes' CL was performed using the BET method with an adsorption meter (ASAP2460, Micromeritics, USA). Temperature programmed reduction (TPR) profile of the catalysts were recorded using a Micromeritics 2900 system, equipped with a thermal conductivity detector. The catalyst samples were first purged in flow of argon at 100 °C to remove traces of water, and then cooled to 25 °C. The TPR of 40 mg of each sample was performed using 5% hydrogen in argon gas mixture with a flow rate of 50 cm³ min⁻¹. The samples were heated from 25 °C to 850 °C with a heating rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) was employed to obtain the oxidation state information of deposited cobalt species on a XPS spectrometer (K-Aepna, Thermo Fisher scientific Inc., USA).

3. Results and discussion

3.1. Electrochemical characterization

Fig. 1 shows the result of the LSV for the AC air-cathode with different electrodeposition time of cobalt. Fig. 1A is the cathodic deposition for 150 s, 300 s and 600 s, respectively. When potential was -0.1 V, the current density of Co(OH)₂-300s was higher than that of Co(OH)₂-150 s and Co(OH)₂-600 s. The current density of the ORR at the AC air cathode with cobalt deposition time of 300 s was 6 mA cm⁻², which was 1.83 times higher than that

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