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Modified graphite electrode by polyaniline/tourmaline improves the performance of bio-cathode microbial fuel cell

Hanmin Zhang*, Rong Zhang, Guangyi Zhang, Fenglin Yang, Fan Gao

Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, PR China

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ABSTRACT

Bio-cathode which uses microorganisms as catalyst can reduce MFC cost and sustain similar power output compared to noble metal catalyst. Thereby, looking for a cathode material which is high conductivity, good biocompatibility and even can stimulate and enhance activity of bio-catalyst is of great interest. In this paper, modified electrode by tourmaline and polyaniline (reactor 3) was used as cathode. The output power density was improved by 492.6% and 192.8% compared to reactor 1 (unmodified cathode) and reactor 2 (cathode modified only by polyaniline) (54 mW m^{-2} for reactor 1, 138 mW m^{-2} for reactor 2 and 266 mW m^{-2} for reactor 3, respectively). When the external resistance was 800Ω , output voltages of reactor 1, 2 and 3 were kept at $0.20 \pm 0.005 \text{ V}$, $0.26 \pm 0.005 \text{ V}$ and $0.37 \pm 0.005 \text{ V}$, respectively. Cyclic voltammetry curves showed that reductive current of reactor 3 was higher than those of reactor 1 and 2, indicating that the cathode of reactor 3 had the strongest catalytic activity which was due to that tourmaline could help the interfacial electron transfer, and thereby facilitate the reduction of oxygen at the cathode. Results demonstrated that the tourmaline modified electrode could effectively improve the reduction reaction and enhance the performance of the whole MFC system.

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Introduction

Microbial fuel cell (MFC) has been an attracting technology that can directly produce electricity from biodegradable waste materials [1]. Cathode material plays a key role for oxygen reduction [2]. Oxygen is an inexpensive gas with unlimited availability, whereas its reduction has a high overpotential [3]. The commonly used cathode electrode materials are graphite felt, carbon paper and stainless steel mesh. Previous results

showed that compared with the other two materials graphite felt was the most suitable electrode material for MFC, and exhibited favorable electrochemical performance [4]. Semi-coke and activated carbon was also used as electrode material, producing a maximum power density of 20.1 W m^{-3} and 24.3 W m^{-3} , respectively, compared with 14.1 W m^{-3} and 17.1 W m^{-3} obtained from the MFCs with graphite and carbon felt bio-cathodes, respectively [5]. The bacteria attached to cathode played a major role in oxygen reduction with all the materials investigated. Also, bio-cathode with carbon

* Corresponding author. Tel.: +86 411 84706173; fax: +86 411 84708083.

E-mail addresses: zhanghm@dlut.edu.cn, zhhanmin@126.com (H. Zhang).
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nanotube and chitosan as electrode materials could enhance electricity generation [6].

Bio-cathode MFC using microorganisms as catalyst can achieve the reduction of oxygen and nitrate [7], and the catalytic process by bio-cathode can effectively decrease the overpotential of oxygen reduction. Bio-cathode MFC has a great number of advantages, such as self-regeneration of the catalyst, sustainability, low cost, and great activity at neutral pH [8]. However, the carrier material of biocatalyst and its effects on cathode reduction reaction have been less studied. Here, a novel mineral material of tourmaline, which belongs to the group of silicate minerals called cyclosilicates, was employed to modify electrode. The generalized structural formula of tourmaline can be expressed as $XY_3Z_6 [T_6O_{18}] [BO_3]_3V_3W$, where X—Na, K, Ca or vacancy; Y—Li, Mg, Fe^{2+} , Mn^{2+} , Al, Cr^{3+} , V^{3+} , Fe^{3+} , Ti^{4+} ; Z—Al, Fe^{3+} , Cr^{3+} , V^{3+} , Mg; T—Si, Al, B; V—OH, O; W—OH, F, O [9,10]. Li et al. made use of the method of electrodeposition to deposit the platinum and tourmaline on the glassy carbon disk electrode, as an electrocatalyst for oxidation of methanol, the results showed that Pt/tourmaline catalyst was catalytically more active and stable than platinum-modified glassy carbon electrode [11]. A research indicated that nitrosomonas bacteria and nitrifying bacteria in the control group was significantly less than the experimental group where tourmaline were present in the medium to enrich nitrifying bacteria. The results demonstrated that tourmaline could stimulate the growth of nitrifying bacteria [12]. Moreover, when tourmaline was added into the SBR reactor, aniline and COD concentrations were significantly reduced. The results showed that the added tourmaline improved the microbial activity towards the degradation of aniline [13]. However, so far there has been little understanding about the modified electrode by mineral material and its impacts on electron hop between cells and electrode surface in a bio-cathode MFC.

The purpose of this article is to improve the electrical properties of the MFC by preparing a new type of electrode material with tourmaline/polyaniline coated on graphite electrode, where polyaniline was used as binder to join tourmaline with graphite electrode. The tourmaline-based bio-cathode MFC was examined in terms of microstructure and morphology of electrode, electrochemical performance and effects on catholyte chemistry.

Materials and methods

MFC construction and operation

In our study, Polyaniline as the binder was chosen to bind tourmaline to graphite electrode because of its conductivity and biocompatibility. Polyaniline and tourmaline co-adhered to graphite rod as the cathode electrode, designated as reactor 3, and polyaniline modified graphite for reactor 2 and the unmodified graphite rod for reactor 1. All the reactors and chambers had the same size, the volume of each anode or cathode was 100 ml (4 cm [L] × 5 [W] × 5 [H]). The graphite fibers (thickness of 5 mm, Beijing Sanye Co., Ltd. pretreatment in the solution of nitric acid and sulfuric acid [4]) acted as anode electrode material. Anode and cathode were linked with cooper

wire through an external resistor of 800 Ω . Proton exchange membrane (Nafion 117 PEM) was used as the diaphragm to separate the anode and cathode chambers. The membrane pretreatment was carried out sequentially by boiling in deionized water, H_2O_2 (30% V/V), deionized water, 0.5 M H_2SO_4 , and then deionized water, each step was carried out for 1 h [14]. The effective area of the proton exchange membrane was 16 cm^2 . The effective area of the cathodes was 15.7 cm^2 .

The anode medium contained $C_6H_{12}O_6$ -1.0 $g L^{-1}$, NH_4Cl -0.31 $g L^{-1}$, KCl -0.13 $g L^{-1}$, $CaCl_2$ -0.015 $g L^{-1}$, $MgSO_4$ -0.059 $g L^{-1}$, KH_2PO_4 -4.4 $g L^{-1}$, $K_2HPO_4 \cdot 3H_2O$ -3.4 $g L^{-1}$ and 1 $ml L^{-1}$ of trace elements solution [15]. The cathodic medium was same as anode expect carbon source, with 1.0 $g L^{-1}$ $NaHCO_3$ instead of $C_6H_{12}O_6$. The anode electrolyte was replaced when the voltage dropped below 50 mV, and cathode electrolyte was done every 3 days. Each MFC was purged with air all the time in order to supply electron acceptor (oxygen) in the cathodes. All reactors were operated under the exactly identical conditions. The temperature was controlled at $(25 \pm 2 \text{ } ^\circ C)$.

Inoculating sludge and tourmaline properties

The inoculating sludge was collected from Lingshui wastewater treatment plant (Dalian, China). Tourmaline was purchased from Wuhua Co., Ltd (Inner Mongolia, Chifeng, China). The characteristics of the used tourmaline were examined and shown in Table 1, and the average particle diameter was 43 μm .

Electrode preparation

Graphite electrode to be modified was used as working electrode, calomel electrode as reference electrode and Pt electrode (Tianjin, aida Co., Ltd.) as counter electrode. Mixed proton acid consisted of sulfuric acid (1.0 $mol L^{-1}$) and aniline (0.1 $mol L^{-1}$). Graphite electrode was deposited in the electrolyte at a constant voltage of 0.8 V for 30 min to prepare polyaniline electrode as control (reactor 2), and then washed with deionized water to remove residual aniline on the electrode surface. Finally, the electrode was dried at room temperature for 24 h. The way to prepare tourmaline/polyaniline modified graphite electrodes were same as above except that 1.0 g tourmaline was added and the electrolyte was always stirred to evenly mix during the preparation. In this case, tourmaline particles would be embedded or wrapped in the polymer, forming the tourmaline/polyaniline electrode.

Analysis and calculations

The morphologies of the tourmaline/polyaniline composites (cathode) were observed using scanning electron microscope (SEM), equipped with X-ray energy dispersive analysis (EDS)

Table 1 – Components analysis of tourmaline.

Content	Mass (%)	Content	Mass (%)
NaO ₂	1.19	CaO	1.18
MgO	8.05	TiO ₂	0.44
Cr ₂ O ₃	0.22	B ₂ O ₃	10.16
SiO ₂	37.05	FeO	8.33
K ₂ O	0.09	Al ₂ O ₃	29.8

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