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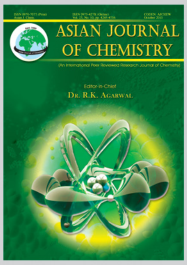

Preparation and Electrochemical Behaviour of a Titanium-Based Lead Dioxide Cathode Used in The Microbial Fuel Cell

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In this paper, the electrochemical behaviours of a titanium-based β-PbO_2 cathode and a carbon cloth electrode used in the microbial fuel cell were studied. Linear sweep voltammetry (LSV) curves and cyclic voltammetry (CV) curves indicated that the electrochemical behaviours measured in a titanium-based β-PbO_2 electrode system was similar to the carbon cloth electrode's, it did not participate in the reaction in the microbial fuel cell, but a titanium-based β-PbO_2 electrode current response values were three times higher than the carbon cloth electrode.Thus it had greater electrochemical activity and could speed up the denitrification reaction in the microbial fuel cell, thereby enhancing its electricity-generation and decontamination performance. Carbon cloth electrode's electrochemical impedance spectroscopy (EIS) patterns showed that its electrochemical activity was poor. The EIS patterns of a titanium-based β-PbO_2 electrode showed that the capacitance arc radius in the beginning of the reaction solution system, was larger than that of the completion of the reaction system with the reduce of interface capacitance value. The results showed that the electrochemical performance of the titanium-based β-PbO_2 cathode was increased in the solution when the microbial fuel cell reaction was stopped. This behaviour of the cathode demonstrated that the start of microbial fuel cell required for a period of time from the mechanism.

Key Words: Microbial fuel cell, Titanium based lead-dioxide cathode, XRD, Electrochemical behaviour.

INTRODUCTION

Utilizing bacterial in microbial fuel cells (MFC) to produce electricity from the degradation of inorganic/organic matter provides an elegant solution for simultaneous wastewater treatment and electricity generation. In the field of wastewater treatment, it is possible to change that the shortcomings of high energy consumption in the existing sewage treatment process. Many papers were reported from the varieties of factors in afecting the electricity-generation properties of the microbial fuel cells[1-5], biological hydrogen production from microbial fuel cells[6,7], microbial fuel cells being used in wastewater treatment[8-10], *etc*.

Research of microbial fuel cells electrode materials is one of the focuses. Currently the anodic electrode material is primarily used by large surface area, easy growing microbial biofilm carbon cloth (without platinum) or graphite and the cathode is generally used by carbon cloth with platinum. Since platinum is expensive and this necessarily limits its application in practical engineering. Choosing platinum alternative materials is the direction of people's efforts. Lead-dioxide electrode has good electrical conductivity similar to metal. In the aqueous solution it has good electro-catalytic properties with high oxygen evolution overpotential. As an insoluble anode it can sometimes replace the platinum electrode. The study of lead dioxide as the electrode material often puts emphasis on their preparation methods, electrochemical behaviour in degradation of organic matter, *etc.*[11-17]. In the microbial fuel cell researchers also use electrochemical means. It mainly studies the electrode performance characteristics or related chemical substances in microbial fuel cell solution[18-23].

There were less reports about the lead dioxide electrodes used in microbial fuel cells. Morris *et al.*[24] studied the lead dioxide electrode as an alternative platinum used in microbial fuel cells. The results showed that the microbial fuel cells with a lead dioxide electrode also had better production electrical properties. But the cost was only 1/17 of platinum electrodes. Our research group made a titanium based β-PbO_2 electrode

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as the cathode of microbial fuel cells and built a single-chamber microbial fuel cell to study the nitrate removal from wastewater and the result was quite good. On the basis, this paper reports the electrochemical behaviours of a titanium-based β-PbO_2 electrode and a carbon cloth electrode in microbial fuel cell reaction solution. We analyzed and compared their electrochemical performance and catalytic mechanism in microbial fuel cells solution.

EXPERIMENTAL

The main instruments used are as follows: X-ray diffraction (RigakuD/Max-rB, Japan Science Electric Co., Ltd.), CHI-660C electrochemical workstation (Shanghai chenhua electrochemical Instrument Factory), pico voltage collector (ADC16; Pico Technologies limited, UK). The chemical reagents used in experiments are analytical reagent and water is didistilled water.

Preparation of Ti-based β-PbO_2 electrode and its XRD characterization: Ti-based β-PbO_2 electrodes were prepared according to the Shen *et al.*[25]. Firstly clean the metal Ti-plate with abrasive paper, after this clean off the grease with hot detergent solution and then treat it in boiling oxalic acid solution (10 %) for 0.5 h, rinse for 3 to 5 times with distilled water after taking out of solution and then move it to clean room for use after drying. Put Ti plate in the mixed solution contaning $Pb(NO_3)_2$ (0.5 mol L^{-1}), $Cu(NO_3)_2$ (0.3 mol L^{-1}), NaF (40 mmol L^{-1}) and HNO_3 (0.1 mol L^{-1}) with voltage 1.6-1.8 V sustained for 0.5 h, a layer of dense PbO_2 was then deposited on the Ti plate surface. An X-ray diffraction instrument was used to characterize the Ti-based β-PbO_2.

Electrochemical tests of Ti-based β-PbO_2 electrode: An electrochemical workstation was used to study Ti-based β-PbO_2 cathode electrochemical behaviour. Three-electrode system was used: the work electrode was a Ti-based β-PbO_2 cathode electrode (exposed area of 1 cm × 1 cm), auxiliary electrode was a large area platinum electrodes (4 cm × 2 cm) and the reference electrode was a saturated calomel electrode. The culture medium and phosphate buffer were used as the electrolyte under anaerobic conditions.The electrolyte had two different types: one was the solution before microbial fuel cells reaction (this solution was called BS for short) and the other was the solution when the microbial fuel cells reaction was over (this solution was called OS for short). The pinciple composition of the solution is Na_2HPO_4 (4.0896 mg L^{-1}); NaH_2PO_4 (2.544 mg L^{-1}), KNO_3 (0.7218 mg L^{-1}). Electrochemical test methods are linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Parameters setting of LSV: the scanning speed was 2 mv/min and the scanning range was from-0.6 v to 1 v. Parameters setting of CV: the scanning speed was 20 mv/s and the scanning range was from-0.5 v to 0.5 v. Parameters setting of EIS: the frequency was from 1 Hz to 105 Hz and the amplitude was 5 mv. A Evolv-Circuit software was used for EIS patterns equivalent circuit analysis.

RESULTS AND DISCUSSION

XRD analysis of Ti-based β-PbO_2: The prepared titanium-based PbO_2 was analyzed by X-ray diffraction. Parameters setting: a Cu anode, graphite monochromator, the tube voltage was 40 kV, the tube current was l00 mA, slit was DSl°, SSl°, RS 0.3 mm, continuous scan mode, scanning speed was 6 °/min and sampling interval was 0.02°. The results were presented in Fig. 1.

The comparison of the XRD patterns of self-made β-PbO_2 with the standard β-PbO_2 showed that the two spectra were quite similar. The main crystal form of our self-made PbO_2 was β-PbO_2 because the 2θ angle (25.68, 32.31, 36.28, 49.36, 52.51, 54.50, 59.13, 60.95, 62.61, 67.41 °) was consistent with that of the standard β-PbO_2.

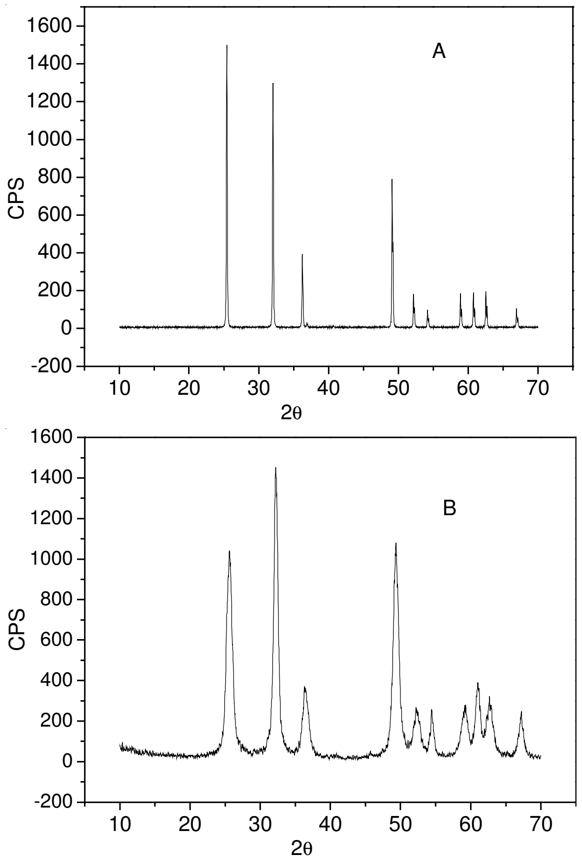

Fig. 1. XRD Patterns of β-PbO_2 (A) standard pattern (B) self-made pattern

Study on the electrochemical behaviour of Ti-based β-PbO_2 electrode: Our group had built a single-chamber microbial fuel cells equiped wirh this titanium-based β-PbO_2 electrode as the cathode, to study the properties of its performance of electricity generation and wastewater degradation[26]. The results showed that the single-chamber microbial fuel cells (under the outer resistance of 1000 Ω), which inoculated with activated sludge, run for 11907 min (about 8 days) and the battery's maximum output voltage was between 500-600 mv with the maximum power density 485 mW m^{-2}. The initial chemical oxygen demand(COD) in the single-chamber microbial fuel cells was 20106 mg L^{-1} and the value was 12102 mg L^{-1} after 8 days' reaction. The COD removal rate was 40 %, the average removal was about 1000.5 mg L^{-1} d^{-1}. Thus, the single-chamber microbial fuel cells had more efficient removal of COD and had an ideal treatment effect on wastewater while producing electricity at the same time. The single chamber microbial fuel cells with a Ti-based β-PbO_2 electrode as a cathode also had a strong performance on the removal of nitrate from wastewater with the average denitrification rate[27] up to 29.3 mg L^{-1} d^{-1}.

To further investigate the catalytic properties and mechanism of the titanium-based β-PbO_2 electrode used in the microbial fuel cells,we had studied the electrochemical properties of this electrode and the commonly used carbon cloth electrodes by an electrochemical workstation. The applied electrochemical methods were: linear sweep voltammetry, cyclic voltammetry and electrochemical impedance spectroscopy.

Linear sweep voltammetry curves: The titanium-based β-PbO_2 electrode and carbon cloth electrodes were tested by linear sweep voltammetry in BS and OS respectively,and the results were presented in Figs. 2 and 3.

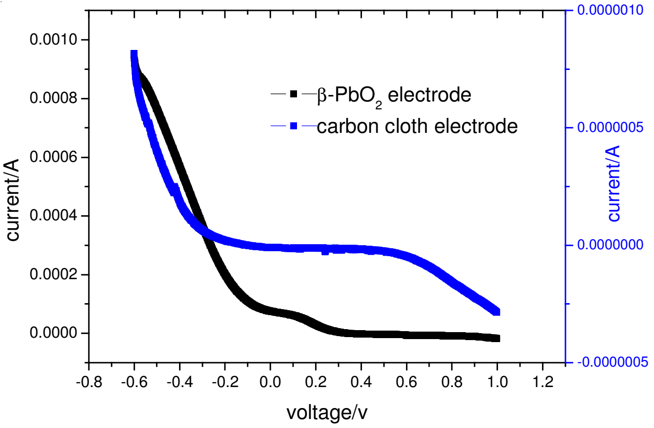

Fig. 2. Linear sweep voltammetry curve of carbon cloth electrode and titanium-based β-PbO_2 electrode in BS

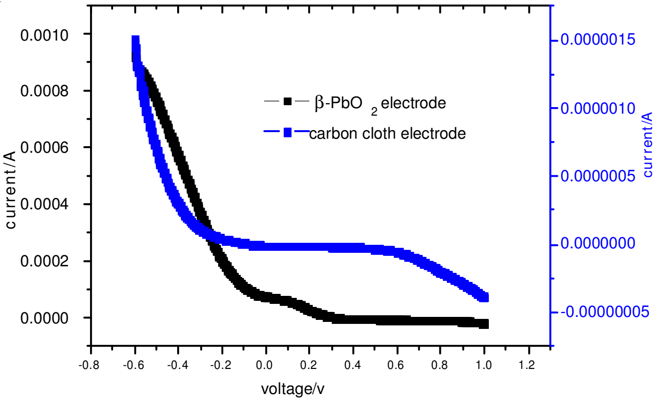

Fig. 3. Linear sweep voltammetry curve of carbon cloth electrode and titanium-based β-PbO_2 electrode in OS

As can be seen from the figures, in BS, the open circuit potential of carbon cloth electrode was 0.524 v, activation potential was -0.171 v (the corresponding current was 1.1×10^{-7} A) and the open circuit potential of titanium-based β-PbO_2 electrode was 1.006 v, activation potential was 0.241 v (the corresponding current was 1.5×10^{-4} A); in OS, the open circuit potential of carbon cloth electrode was 0.609 v, activation potential was -0.230 v (the corresponding current was 2.2×10^{-7} A) and the open circuit potential of titanium-based β-PbO_2 electrode was 1.006 v, activation potential was 0.251 v (the corresponding current was 1.1×10^{-4} A), which showed that the polarization degree of the carbon cloth electrode was stronger than that of the titanium-based β-PbO_2 electrode. The polarization curves of these two kinds of electrodes were both flat, indicating that their role in the reaction mechanism of microbial fuel cells solution was the same.The characteristics of carbon cloth as an inert electrode were also reflected in the lead dioxide electrode, but the current value corresponding to the activation potential had a difference of three orders of magnitude, indicating that the electrochemical activity of the titanium-based β-PbO_2 electrode was stronger than that of the carbon cloth electrode.

Cyclic voltammetry curves: Cyclic voltammetry was used to study the electrochemical activity of these two kinds of electrodes in the microbial fuel cells solution. The titanium-based β-PbO_2 electrode and carbon cloth electrodes were tested by cyclic voltammetry in BS and OS respectively and the results were presented in Figs. 4 and 5.

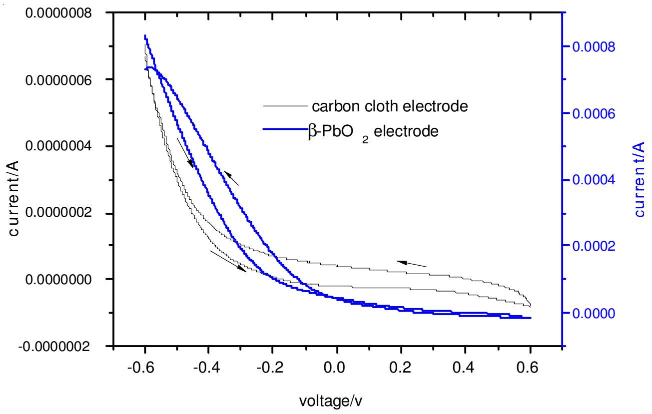

Fig. 4. Cyclic voltammetry curve of carbon cloth electrode and titanium-based β-PbO_2 electrode in BS

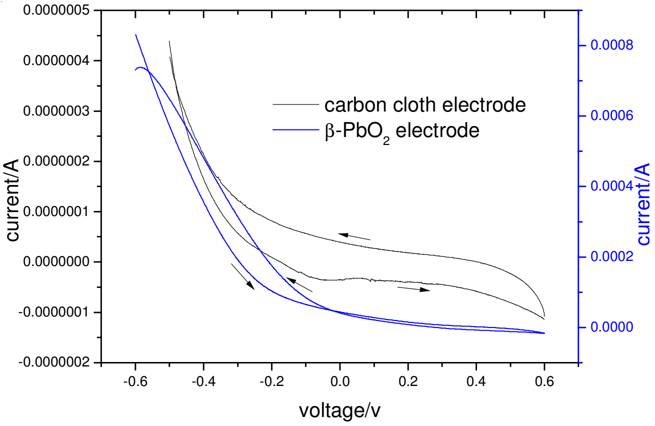

Fig. 5. Cyclic voltammetry curve of carbon cloth electrode and titanium-based β-PbO_2 electrode in OS

It can be seen from the figures that the cyclic voltammetry curves of the two electrodes are similar. Two systems, the current of titanium-based β-PbO_2 electrode was three orders of magnitude higher than that of the carbon cloth electrode, indicating that its catalytic properties was stronger than that of the carbon cloth electrode. But the oxidation reaction peak on the cyclic voltammetry curve was not obvious, indicating the catalytic properties of titanium-based β-PbO_2 electrode in microbial fuel cells was stronger not because of its metal properties. The

TABLE-1
IMPEDANCE PARAMETERS OBTAINED OF THE EQUIVALANT CIRCUIT BY FITTING EIS IN Fig. 6

R1/Ω	R2/Ω	C1/μF	C2/μF	C3/μF	C4/μF	CPE1/$Ω^{-1}$
6.6 × 10^2	5.8 × 10^3	2.3 × 10^{-6}	9.7 × 10^{-4}	9.9 × 10^{-4}	4.9 × 10^{-6}	2.4 × 10^{-5}
n = 0.42						

TABLE-2
IMPEDANCE PARAMETERS OBTAINED OF THE EQUIVALANT CIRCUIT BY FITTING EIS IN Fig. 7

R1/Ω	R2/Ω	R3/Ω	C1/μF	C2/μF	CPE1/$Ω^{-1}$
6.5 × 10^2	4.5 × 10^2	6.5 × 10^2	1.3 × 10^{-7}	2.2 × 10^{-8}	2.2 × 10^{-8}
n = 0.53					

cyclic voltammetry curves also confirmed that the titanium-based β-PbO_2 electrode itself was not involved in microbial fuel cells denitrification reaction, simply because of its high current responsivity, which made the electrons produced from the anode chamber in microbial fuel cells be quickly accepted when transferred to the cathode to give the denitrification. And this could speed up COD decomposition process by the bacteria in the anode chamber and effectively improve the ability of nitrogen removal and decontamination of microbial fuel cells.

Electrochemical impedance spectra: Electrode impedance method is an important method to study the catalytic properties of electrodes. Nyquist plot is the most common representation of impedance data. Under the open circuit potential, the titanium-based β-PbO_2 electrode and carbon cloth electrodes were tested by EIS in BS and OS and the results were presented in Figs. 6-8.

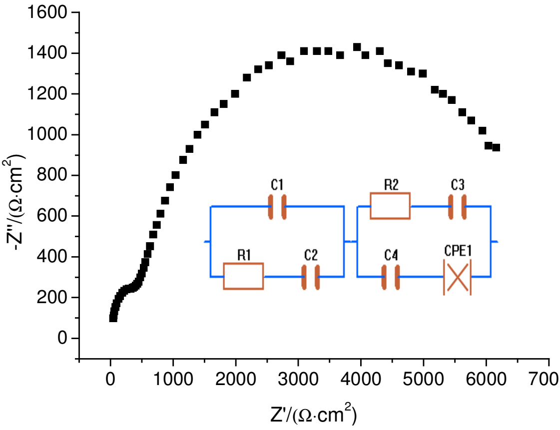

Fig. 6. EIS spectra of titanium-based starting Ti-based β-PbO_2 electrode in BS and its equivalent circuit

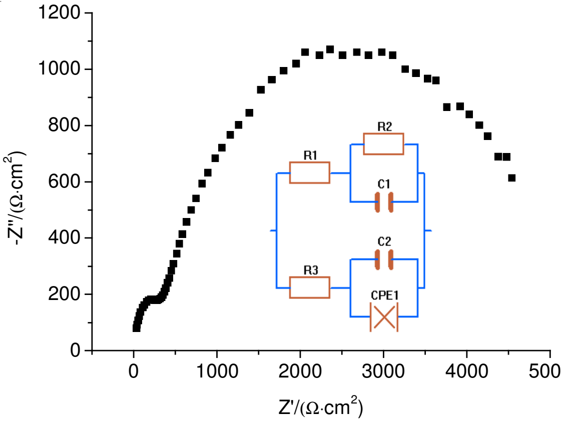

Fig. 7. EIS spectra of titanium-based starting Ti-based β-PbO_2 electrode in OS and its equivalent circuit

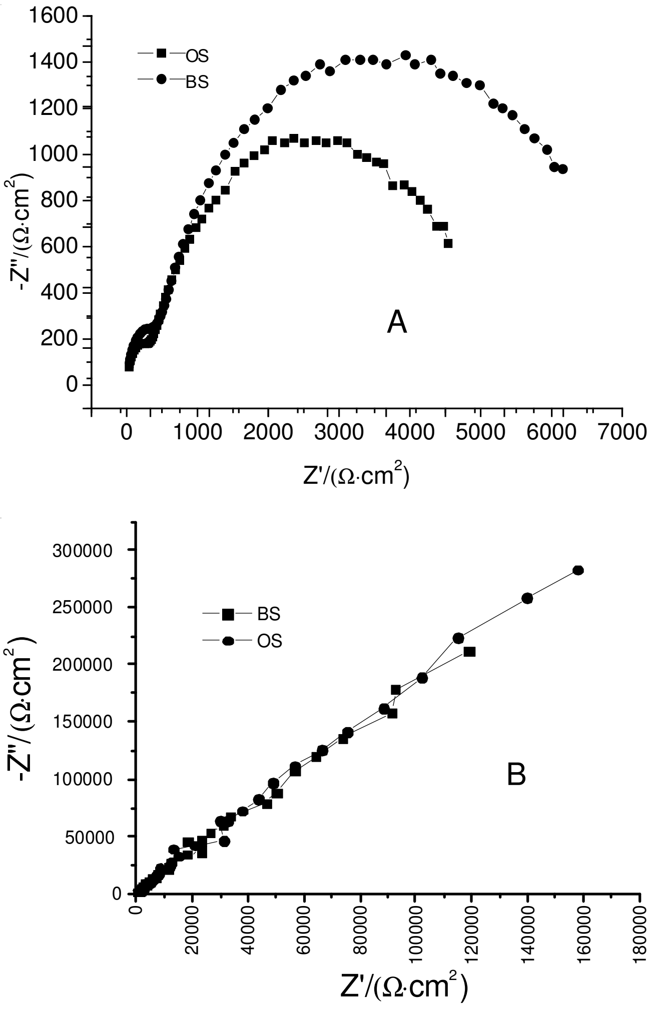

Fig. 8. EIS spectra of titanium-based β-PbO_2 electrode (A) and carbon cloth electrode (B) in BS and OS

In Nyquist plots, capacitance arc did not appear on the carbon cloth electrode (Fig. 8B), indicating that it was mainly Warburg impedance in solution and its electrochemical activity was poor when used as an electrode in microbial fuel cells. Electrochemical impedance spectra patterns of Ti-based β-PbO_2 electrode had a capacitance arc in high-frequency band (Figs. 6 and 7), the equivalent circuit component values were relatively close, indicating that the reaction mechanism of the electrode had not been changed before and after reaction. From Tables 1 and 2, we found that the interface capacitance value decreased in OS. Comparing the electrochemical impedance spectra patterns of titanium-based β-PbO_2 electrode (Fig. 8A), we could find that in OS, the radius of capacitance arc in high-frequency band became smaller, the solution impedance charge-transfer resistance value depends on the size of the capacitance arc radius, the radius of the capacitance arc became larger, indicating that its resistance value was greater and the electrode polarization resistance Rct on the surface increased. These results suggested that the electrochemical reaction activity of the titanium-based β-PbO_2 electrode in microbial fuel cells increased over a period of reaction time. Usually microbial fuel cells took some start-up time in order to obtain a stable voltage output, which was often thought for bacteria to hang biofilm on the carbon cloth electrode. This study showed that the electrochemical activity of titanium-based β-PbO_2 enhanced after the microbial fuel cells running for some time, thus explained this phenomenon from the mechanism.

Conclusion

(1) A titanium-based β-PbO_2 electrode was preparated by electrodeposition and applied as the cathode of a single-chamber microbial fuel cells.The results showed that the microbial fuel cells had a good performance in both electricity generation and a strong capacity to remove nitrate from waste-water.

(2) A variety of electrochemical methods were used to analyze catalytic properties of the electrode and its mechanism. Linear sweep voltammetry curves and cyclic voltammetry curves indicate that the electrochemical behaviour of β-PbO_2 electrode similar to the carbon cloth electrode. They have similar mechanism in microbial fuel cells. Microbial fuel cells with a titanium-based β-PbO_2 electrode has a high capacity electrical properties and higher COD removal rate, which is dued to titanium-based β-PbO_2 electrode's high catalytic performance. And this high catalytic performance can accelerate electrons reaction in the cathode, which thus can speed up the bacteria on the anode chamber of COD degradation rate and enhance the performance of microbial fuel cells. Electrochemical impedance spectra show that the titanium-based β-PbO_2 has stronger catalytic properties than the carbon cloth electrode and from the mechanism it also proves that microbial fuel cells often require a longer start period before the formal operation.

(3)Titanium-based β-PbO_2 electrode does not change microbial fuel cells unique biological battery characteristics. As a cheap alternative to platinum electrodes, with great research significance and application value, it will be one of important non-platinum electrode materials of microbial fuel cells.

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