International Core Journal of Engineering Volume 8 Issue 11, 2022
ISSN: 2414-1895 DOI: 10.6919/ICJE.202211_8(11).0015

Application of TiO_2/TiC Modified Carbon Cloth Electrode in Microbial Fuel Cells

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Abstract

In order to solve the problem of low output power of microbial fuel cells, a solution method was proposed to prepare TiO_2/TiC-CC composite electrode materials by sol-gel and coating methods. The microscopic morphology and synthesis of the prepared materials were studied and analyzed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and other characterization techniques; the output voltage and cyclic voltammetry characteristic curves of the microbial fuel cell were analyzed by using the battery detection device. and other electrochemical performance tests; use UV spectrophotometer and water quality detector to study the degradation performance of diesel. The results show that the TiO_2/TiC-CC composite has a loose surface and uniform particle distribution, which can effectively ensure the attachment of microorganisms and improve the specific surface area and electrical conductivity of the electrode. Under the synergistic effect of TiO_2 and TiC, the power generation performance of the microbial fuel cell is greatly improved, and the maximum output voltage and maximum output power density can reach 0.52 V and 2261.35 m W/m^2, respectively, compared with the unmodified carbon cloth. It has increased by nearly 24% and 133%; the 7-day degradation rate of diesel oil reaches 86.48%, and the chemical oxygen demand (COD) removal rate is 76.92%, which is higher than that of traditional carbon cloth as MFC anode. and COD removal rate.

Keywords

Microbial Fuel Cell; TiO_2; TiC; Carbon Cloth.

1. Introduction

Microbial fuel cells (MFCs) are bioelectrochemical devices that use the extracellular electron transfer mechanism of electricity-producing microorganisms to directly convert chemical energy in organic matter into electrical energy [1]. The adhesion of electroactive microorganisms to the anode greatly affects the power generation performance of MFCs [2], so the anode material is an important factor restricting the power generation performance of MFCs [3]. As the carrier of electrogenic microorganisms, the anode material not only affects the metabolic activity of the electrogenic microorganisms attached to the anode surface, but also affects the electron transfer efficiency between the electrogenic microorganisms and the anode material [4]. Therefore, the modification of MFCs anodes or the search for cheaper and electrochemically active anode materials has become a popular direction to study the performance of MFCs.

In order to solve the above problems, people are prepared by doping functional materials such as conductive porous carbon [5], carbon nanotubes [6], metal oxides [7], transition metal carbides [8], etc. The biocompatibility of microbial fuel cell electrodes simultaneously provides more

ISSN: 2414-1895
DOI: 10.6919/ICJE.202211_8(11).0015

electrochemical reaction sites. For example, Xia J[9] prepared nitrogen- and sulfur-doped iron carbide nanoparticles by a simple one-step hydrothermal method and used them as anode materials for dielectric-free MFCs, which exhibited a fast start-up time of 2.9 days, a high 636.9 mV and the voltage value and the power density (PD) of 3.86 W/m^2 showed excellent biocompatibility and electrical conductivity. Mohamed HO[10] synthesized WC+rGO/CF anode by urea glass route and reduction-carburization technique, and its surface area, biocompatibility, structural morphology and catalytic activity were improved. Compared with CF anode, WC+rGO/CF exhibited 4.4, 7.6 and 2.1 times higher power density, current density and Coulombic efficiency, respectively.

In this paper, TiO_2/TiC-CC composite electrode materials synthesized by sol-gel method [11] and coating method [12] were used as anode materials for microbial fuel cells. The electrochemical performance of TiO_2/TiC-CC used as anode material for microbial fuel cells and the degradation performance of oily sewage were analyzed by physical and electrochemical characterization.

2. Experimental Section

2.1 Instruments and Reagents

Tetrabutyl titanate, titanium carbide, and isopropanol were all of analytical grade, purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.; 5% nafion solution and N117 proton exchange membrane were purchased from DuPont; hydrochloric acid (36%), absolute ethanol, Anhydrous glacial acetic acid was purchased from Yantai Shuangshuang Chemical Co., Ltd.

Fourier transform infrared spectroscopy (FTIR) (IRAffinty-1S WL, Shimadzu, Japan) was used to scan the range of 400-4000 cm-1 to characterize the types and approximate contents of functional groups contained in the composites. The morphology of the composites was observed by scanning electron microscope (SEM, JSM7200F). Ultraviolet-visible (UV-vis) spectra were collected using an ultraviolet spectrophotometer (UV-1800, Shimadzu, Japan) to analyze the degradation performance of diesel. HM-U800 water quality multi-parameter detector (Beijing Huamei Water Analytical Instrument Technology Co., Ltd.) was used to determine the chemical oxygen demand in water. SDC-100 contact angle measuring instrument (Dongguan Shengding Precision Instrument Co., Ltd.) was used to observe the different shapes displayed by the water droplets and the size of the tested contact angle, and to characterize the degree of affinity between the electrode surface and the water droplets. The microbial fuel cell was subjected to constant resistance discharge using a battery test system (CT-4008T-5 V 10 mA, Shenzhen Kejingzhida) with a resistance range of 1000-10000 Ω. The instrument used for the cyclic voltammetry (CV) test was the CHI660D electrochemical workstation produced by Shanghai Chenhua Instrument Co., Ltd. The scanning potential range of CV was -0.5 V to +0.8 V, the pulse width was 200 ms, and the scanning rate was 50 mV. /s, amplitude=60 mV, potential increase=6 mV.

2.2 Preparation of TiO_2/TiC Composites

TiO_2/TiC composites were prepared by sol-gel method. Add 6 mL of distilled water to 10 mL of absolute ethanol, add hydrochloric acid dropwise to adjust the pH to 3, and stir vigorously to obtain mixed solution A. Take 10 mL of anhydrous ethanol in a conical flask, slowly drop 1 mL of tetrabutyl titanate into the conical flask under magnetic stirring, and add 0.2 mL of glacial acetic acid dropwise, stir for 10 min to make it evenly mixed, it was slowly added dropwise to solution A with a dropper while stirring continuously for 30 min to obtain a TiO_2 sol solution.

Weigh a certain amount of titanium carbide and add it to the prepared TiO_2 sol solution, stir and disperse it into a suspension, and let it stand for 24 h. The suspension was suction filtered and washed 3-4 times with absolute ethanol, and the solid was collected and dried in a drying oven to constant weight. The composite material was placed in a muffle furnace, heated to 300°C at a rate of 10 $°C\cdot min^{-1}$ at room temperature, kept at a constant temperature for 60 min, and then continued to heat up to 500°C for 2 h. After waiting for the muffle furnace to cool to room temperature naturally, the TiO_2/TiC composite material can be obtained.

2.3 Preparation of TiO_2/TiC-CC Anode Material

First, cut the carbon cloth according to the size of 1×1 cm, and then put it in a beaker and wash it with absolute ethanol and deionized water for 30 min with ultrasonic waves (240 W, 40 KHz), to remove the carbon cloth on it. impurities, and then placed in a 40°C oven to dry for 60 min. The dried carbon cloth was put into a tube furnace and heated at 350°C for 3 h to activate the carbon cloth. Then, the prepared carbon cloths were strung together with titanium wires of appropriate length, and then 2.3 mg of TiO_2/TiC nanomaterials were weighed and placed in a 2 mL centrifuge tube, and 20~30 μL was added to the centrifuge tube. Isopropanol, 14.3 μL of 5% nafion solution and 12.4 μL of deionized water (the amount of solvent can be added in proportion according to the actual situation), shake on a vortex shaker for 30 min, and after mixing uniformly, disperse the solution It was evenly coated on both sides of the previously prepared 1×1 cm carbon cloth. The coated carbon cloth was placed in the air and dried at room temperature overnight to obtain a TiO_2/TiC modified carbon cloth (TiO_2/TiC-CC). In the control group, carbon cloth (CC) was used as the anode material.

2.4 Assembly and Start-up of the MFC Device

The working principle of MFC is shown in Figure 1. The MFC device consists of an anode chamber and a cathode chamber, which are separated by a proton membrane. In the anode chamber, TiO_2/TiC-CC is used as the anode, and the anolyte in the anode chamber of the MFC device is the activated bacteria solution (mainly Rhodopseudomonas swampis, Clostridium butyricum and yeast), and the simulated oily sewage is used as the anode solution. Basal medium with sole carbon source and 80 μmol/L neutral red. A carbon brush was used as the cathode in the cathode chamber, and the catholyte was 20 mmol/L $K_3[FeCN)_6]$ solution. The two electrodes are led out by wires and connected to the battery detection device to form a complete circuit, the anode chamber is sealed and maintained in an anaerobic environment, the cathode chamber is continuously aerated to maintain the dissolved oxygen concentration, and a proton exchange membrane is sandwiched between the two chambers. The battery is started by a spontaneous electrochemical reaction.

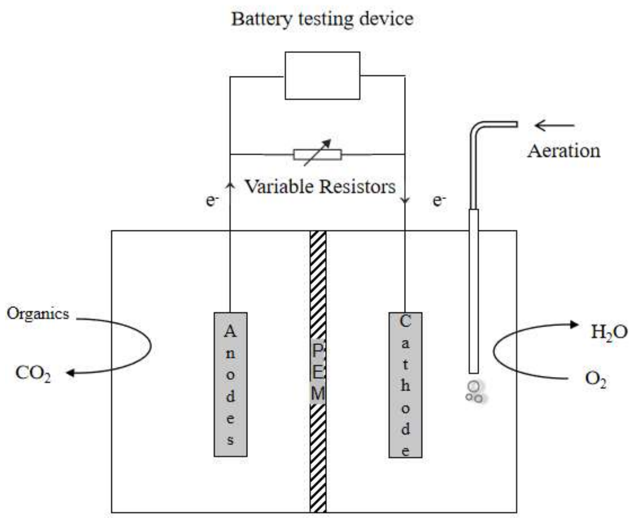

Fig. 1 MFC unit reaction schematic diagram

2.5 Degradation Rate of Marine Diesel Fuel by Microbial Fuel Cells

1) Draw the diesel standard curve

The diesel medium was extracted with petroleum ether and diluted to an appropriate concentration, and a full-wavelength scan was performed using an ultraviolet spectrophotometer UV-1800 to determine the optimal absorption wavelength. A series of diesel standard solutions with mass concentrations of 1, 5, 10, 20, 30, 50, 80, and 100 mg/L were prepared, and the absorbance was read at the optimum wavelength, and a standard curve was drawn.

ISSN: 2414-1895
DOI: 10.6919/ICJE.202211_8(11).0015

2) Determination of diesel degradation rate

The activated bacterial solution with a volume fraction of 2% was inoculated into the anode chamber of the microbial fuel cell, and cultured on a shaker for 7 d at 37℃ and 180 r/min. The blank diesel medium without strains was used as the control group. Set the centrifugation temperature of the fermentation broth to 4℃, and centrifuge at 9000 r/min for 20 min; take 20 mL of petroleum ether to extract the centrifuged supernatant, ultrasonically shake for 15 min, and then let stand for stratification, and recover the upper organic phase. After dehydration with sodium sulfate, it was added to a 50 mL volumetric flask, and the volume was fixed and stored for testing. Based on the drawn standard curve, calculate the concentration of residual oil in the sample. its degradation rate.

$$\eta=\frac{C_0-C}{C_0}\times 100\% \tag{1}$$

where: is the degradation rate, %; C_0 is the initial crude oil concentration, mg/L; C is the oil concentration after treatment, mg/L.

2.6 Removal Rate of Diesel COD by Microbial Fuel Cell

In this paper, the COD was determined by the rapid digestion spectrophotometric method "HJT 399-2007 Determination of Water Chemical Oxygen Demand Rapid Digestion Spectrophotometric Method". Company), the COD removal rate is calculated according to the formula (2) based on the difference between the chemical oxygen demand of the incoming and outgoing water.

$$\text{COD removal rate}=\frac{(COD_0-COD_1)}{COD_0}\times 100\% \tag{2}$$

In the formula: COD_0 is the total amount of COD influent, and COD_1 is the total amount of COD effluent.

3. Results and Discussion

3.1 Anode Material Characterization and Analysis

The synthesis process principle of TiO_2/TiC-CC anode material is shown in Figure 2. The TiO_2/TiC composite material was prepared by the sol-gel method at high temperature, and then the TiO_2/TiC-CC composite electrode material synthesized by the coating method was used for microbial fuel cells.

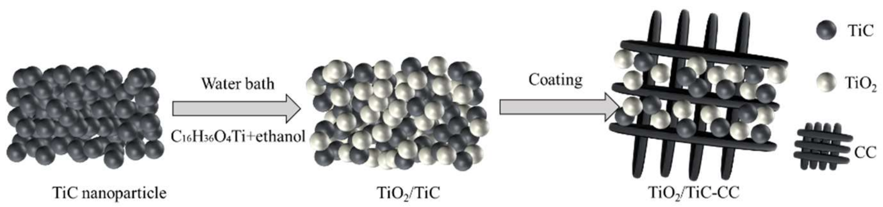

Fig. 2 Schematic diagram of the preparation process of TiO_2/TiC-CC composites

The SEM images of CC, TiO_2/TiC, TiO_2/TiC-CC and TiO_2/TiC-CC with attached bacteria are shown in Fig. 3. Figure 3(a) is the SEM image of bare carbon cloth (CC), which is composed of smooth carbon fibers with uniform thickness, and Figure 3(b) is the SEM image of TiO_2/TiC. It can be observed that after high temperature sintering, the large TiC surface There are obvious coatings and small particles, which indicates that the TiO_2/TiC composite can be successfully prepared by the sol-gel method. Figure 3(c) is the scanning electron microscope after coating the TiO_2/TiC nanomaterial on the surface of the carbon cloth. The topography below shows that the TiO_2/TiC nanoparticles are

ISSN: 2414-1895 DOI: 10.6919/ICJE.202211_8(11).0015

uniformly dispersed on the surface of the carbon cloth. Figure 3(d) shows the adhesion of microorganisms on the surface of the anode electrode after CC is modified by TiO_2/TiC nanomaterials. It can be clearly seen that a layer of biofilm has been formed on the surface, and the surface of the anode has been completely covered. This shows that TiO_2/TiC nanomaterials have good biocompatibility, which can promote the rapid enrichment of microorganisms on the electrode surface, which is conducive to the rapid start-up of microbial fuel cells.

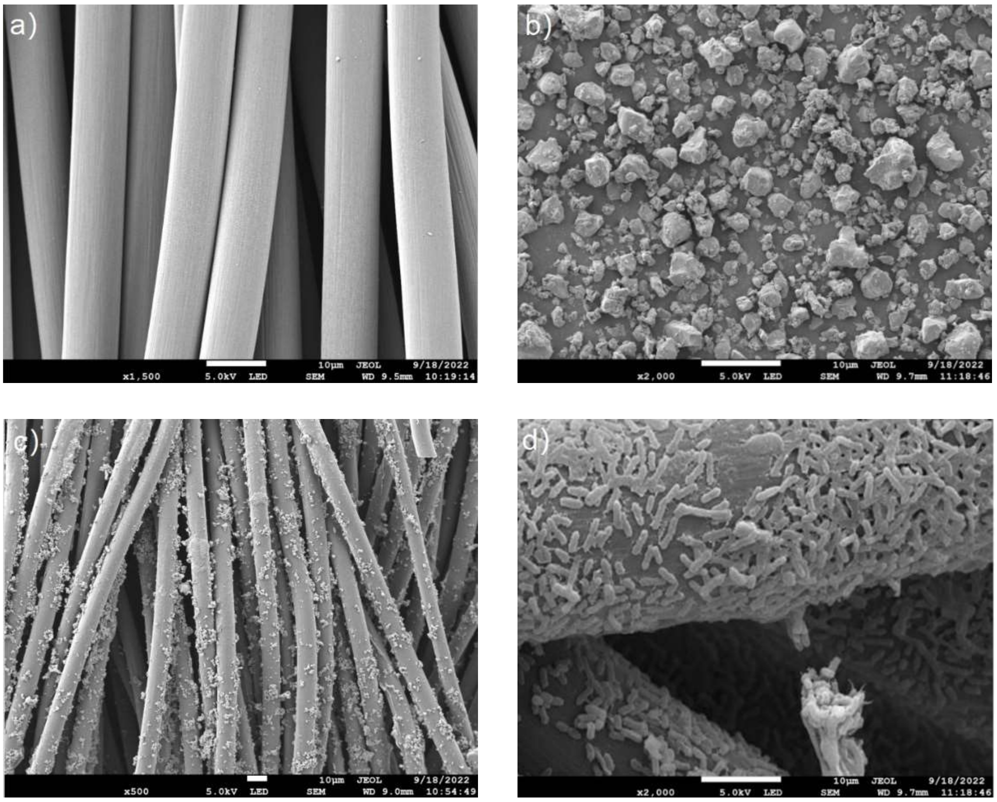

Fig. 3 CC, TiO_2/TiC, TiO_2/TiC-CC and attached bacteria TiO_2/TiC-CC SEM. (a) CC, (b) TiO_2/TiC, (c) TiO_2/TiC-CC, (d) attached bacteria TiO_2/TiC-CC

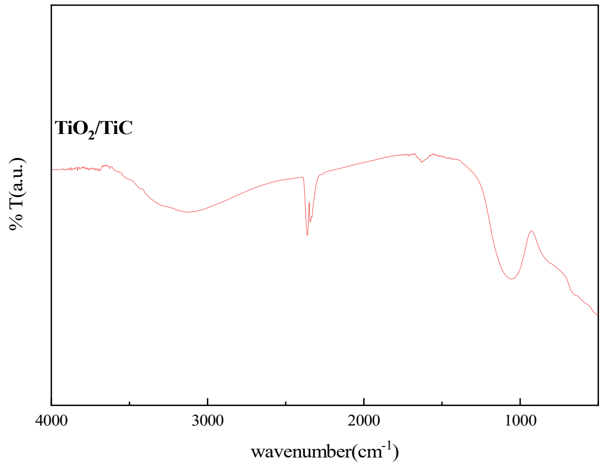

Fig. 4 Infrared spectra of TiO_2/TiC

The infrared spectrum of TiO_2/TiC is shown in Fig. 4. It can be seen that the curve has a characteristic absorption peak of TiO_2 at 939 cm^{-1}, because there is a Ti-O bond on the surface of TiO_2, which causes vibration. There is a TiC absorption peak at 1051 cm^{-1}, mainly due to the stretching vibration caused by Ti-C bond. The existence of these functional groups indicates that the structure in the composite matrix is intact.

3.2 Surface Wettability Analysis

Through the test of the contact angle, the hydrophilicity of the material can be characterized. The more hydrophilic the surface of the anode material, the more favorable it is for bacteria to attach to its surface. The contact angle was measured by the water drop test (when the electrode was completely dry), and the contact angle measurement of different anode materials is shown in Figure 5. Fig. 5(a) is the contact angle of the smooth bare carbon cloth, its size is 136.9° , Fig. 5(b) is the contact angle of the carbon cloth after being modified by TiO_2/TiC, and its hydrophilicity is obviously improved, from 136.9° decreased to 113.6° , which is also consistent with the scanning electron microscope results after the microorganisms were attached to the anode surface. The improvement of hydrophilicity can promote the adhesion of bacteria on the anode to a certain extent, and it is easier to obtain nutrients to accelerate the growth. Breeding to provide feasibility for improving the power generation performance of MFC.

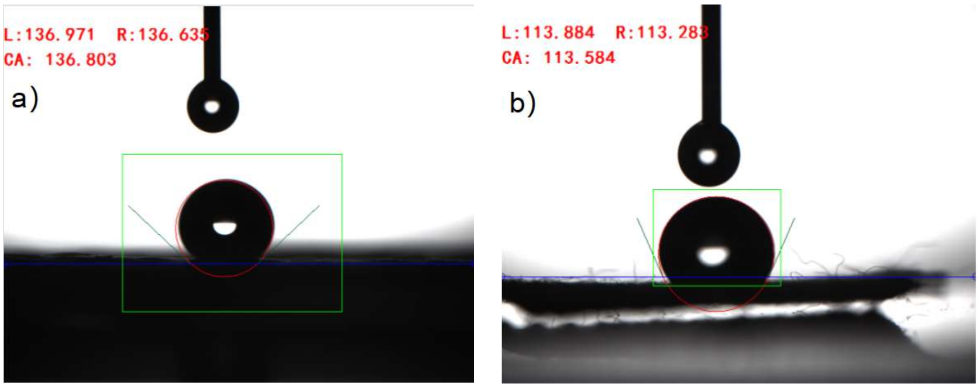

Fig. 5 Contact angle determination of different anode materials (a) CC; (b) TiO_2/TiC-CC

3.3 Degradation Rate of Diesel Oil

3.3.1 UV Absorption Standard Curve for Diesel Fuel

The sample was scanned at full wavelength for petroleum ethers dissolved in petroleum hydrocarbons. 256 nm was taken as the test wavelength as there was a clear absorption peak at 256 nm. The standard curve was fitted using the sample volume concentration as the x-axis and the corresponding absorbance as the y-axis. The equation of the standard curve for diesel oil was calculated as Y=0.0189x-0.0188. The concentration of diesel oil and the absorbance showed good correlation with the correlation coefficient R^2=0.9998. The fit was good and suitable for the analysis of the concentration of the tested oil.

3.3.2 Calculation of Degradation Rates

The residual oil in the MFC device after 7 d treatment with microbial strains was calculated by UV spectrophotometer and standard curve fitting equation for emulsified oil. The degradation rate of marine emulsified oil was determined by two different anode materials separately, and three parallel groups were set up for each test. The degradation rates of the MFC devices with carbon cloth and TiO_2/TiC modified carbon cloth anodes were calculated to be 68.20% and 86.48% respectively for 7 d. The degradation rate of the TiO_2/TiC modified carbon cloth anode MFC device was 1.26 times higher than that of the carbon cloth anode. TiO_2/TiC modified carbon cloth anode has good adsorption capacity, which can effectively increase the number of microorganisms on the anode surface and improve the biodegradation of diesel fuel by MFC.

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DOI: 10.6919/ICJE.202211_8(11).0015

3.4 COD Removal From Diesel

COD is an important indicator of water quality condition, the higher the COD, the more organic pollutants in the water and the more serious the pollution. In this study, the COD removal rate of diesel fuel by the MFC device was determined using a rapid elimination spectrophotometric method, with three parallel groups set up for each test. As shown in Figure 6, the COD removal rate of diesel fuel by MFC loaded with TiO_2/TiC modified carbon cloth anode was 76.92%, and the COD removal rate of carbon cloth anode loaded with carbon cloth anode was 52.20% respectively, which proved that the TiO_2/TiC modified carbon cloth anode has better adsorption performance and biocompatibility, which can effectively increase the number of microorganisms on the surface of the anode and improve the COD removal effect of MFC on diesel fuel.

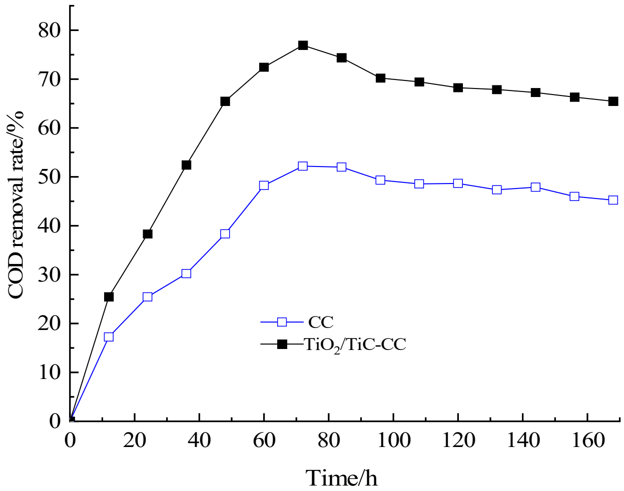

Fig. 6 Cyclic voltammetry curves of composite electrode materials with different scan rates

3.5 Output Voltages for Different Anode MFCs

One of the important indicators of MFC performance is the power production capability, and the process of MFC voltage generation is more complicated than that of chemical fuel cells. The comparison of MFC output voltage performance of different anodes is shown in Table 1. The maximum output voltages of both are 520 mV and 430 mV, and the stabilization time, running voltage time and maximum output voltage of TiO_2/TiC modified carbon cloth anode are higher than those of unmodified carbon cloth anode, while the voltage output is mainly affected by the electrode surface area, the number of microbial load and internal resistance, etc. It indicates that the modified electrode plays the dual role of electrochemical reactant and conductor, which promotes the migration of π electron migration speed between C=C bonds, improve the conductivity and catalytic activity of the composite, electron can be rapidly transferred between TiO_2/TiC and carbon cloth, reduce the resistance value has a stronger ability to output electrons, good voltage characteristics, and has better synergistic catalytic effect.

Table 1. Output performance of MFCs with different anodes under 1000 Ω load

Anode type	Voltage stabilization time(min)	Running voltage time(min)	Maximum output voltage(mV)
TiO_2/TiC-CC	3100	7105	520
CC	1120	4021	430

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3.6 Power Density Curves of MFC with Different Anodes

The specific case of power density, which is one of the criteria for weighing the efficiency of MFC capacity, is shown in Figure 7. From the figure, it can be seen that the MFC power density increases rapidly with the increase of current density to the maximum value. The maximum MFC power density of the loaded carbon cloth anode, walnut shell biochar anode and TiO_2/TiC modified carbon cloth anode are 415.95 mW/m^2 and 2261.35 mW/m^2, respectively. the maximum MFC power density of the modified carbon cloth anode is 5.43 times higher than that of the pre-modified carbon cloth anode, which is probably due to the good conductive network built by TiO_2 and TiC on the carbon cloth surface, thus improving the electron transfer efficiency of the MFC. network on the surface of carbon cloth, thus improving the electron transfer efficiency of the MFC.

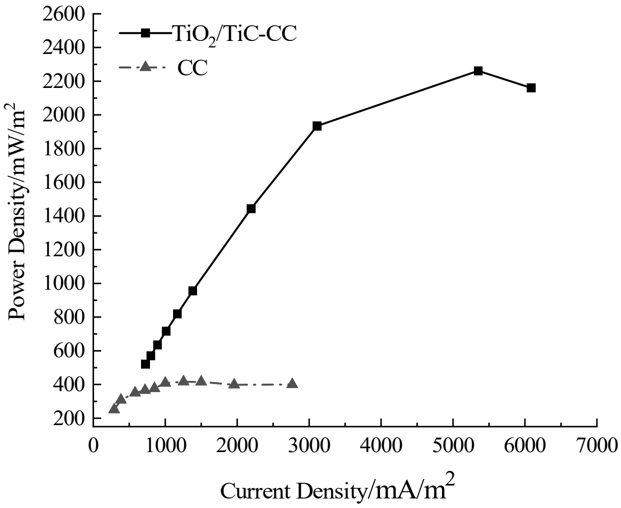

Fig. 7 Power density curves of different anode materials

4. Conclusion

1) The TiO_2/TiC-CC composite anode material was synthesized by sol-gel method and coating method. SEM images showed that the TiO_2/TiC-CC composite anode can effectively increase the number of microorganisms on the anode surface, has good biocompatibility and adsorption properties, and can significantly improve the degradation effect of MFC on diesel fuel.

2) The 7-d degradation rate of diesel fuel was 86.48% for the MFC loaded with TiO_2/TiC-CC composite anode and 68.20% for the MFC loaded with conventional carbon cloth anode. The COD removal rate of diesel fuel was 76.92% for the MFC loaded with TiO_2/TiC-CC composite anode and 52.20% for the microbial fuel cell loaded with carbon cloth anode.

3) The TiO_2/TiC modified carbon cloth anode resulted in increased anode bioadhesion, enhanced electrical conductivity, and reduced charge transfer resistance, thus providing favorable conditions for increasing the anode electron yield and electron transfer rate, which in turn significantly improved the electrical production performance of MFC.

Acknowledgments

This work was funded by; Introduction and Education Plan of Young Creative Talents in Universities of Shandong Province (500076); Demonstration Base of Joint Cultivation of Graduate Students in Shandong Province; Shandong Provincial Higher Educational Science and Technology Foundation, China (KJ2018BBA015).

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