Research on the Performance of New Microbial Fuel Cell Anodes

Chun Zhao, Shaojun Zhang*, Qianyong Zhang, Rui Sun and Zhirao Yin
School of Shangdong Jiaotong University, Weihai 264200 China
*Corresponding author

Abstract

In recent years, with the vigorous development of the maritime transportation industry, the resulting problem of ship oil pollution has become increasingly prominent. Efficient and thorough treatment of oily wastewater is the key to solving such problems. Microbial fuel cell (MFC) technology is a promising biological treatment method due to its good degradation effect, no secondary pollution, and energy recovery. In this paper, the discarded corn cob materials in nature were selected for high-temperature carbonization at 350°C, and NaOH was used to modify the modified biochar. Then, the coating technology of Ti3C2 MXene, NbC, WC, TaC and other materials was used to modify the surface of biochar, and the biochar anode material was obtained to construct a double-chamber microbial fuel cell device. The properties of the modified anode biochar materials were studied.

Keywords

Microbial Fuel Cells; Modified Biochar; Anode Material.

1. Introduction

As a new type of energy, microbial fuel cell (MFC) has great development space and potential. Microbial fuel cells have two main functions, namely electricity generation and degradation of pollutants in wastewater. The substrate is directly converted into electrical energy, which ensures high energy transfer efficiency, and does not produce toxic and harmful substances, and does not cause environmental pollution, similar to a generator rather than a battery[1]. Its basic working principle is: in the anaerobic environment of the anode chamber, the organic matter decomposes and releases electrons and protons under the action of microorganisms, and the electrons rely on the appropriate electron transfer mediator to effectively transfer between the biological components and the anode, and are transmitted to the cathode through the external circuit to form an electric current, while the protons are transmitted to the cathode through the proton exchange membrane, and the oxidant gets electrons at the cathode to be reduced and combined with protons. The basic working principle is shown in Figure. 1 below.

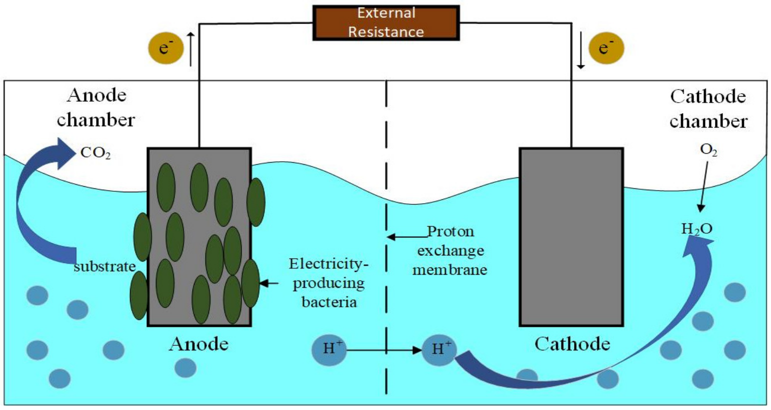


Figure 1. Schematic diagram of the working principle of microbial fuel cells

2. Experiment Preparation

2.1. Preparation of Anode Materials

Biomass materials have a loose and porous structure, and microorganisms can be effectively attached to the surface. According to the experimental results of previous researchers, corn cob has the advantages of high yield, convenient and easy to obtain, and good porosity compared with other biomass materials. Therefore, it is the research object of the anode material in this test. On the basis of the preparation of high-performance biochar from corn cob, the material surface treatment process can optimize the pollution purification and power production capacity of the MFC device. Among them, the surface structure of biochar materials can be changed and the roughness of the materials can be increased by using acid and alkali modification technologies. The rough surface of the electrode is conducive to the attachment and growth of microorganisms, and the rich porous structure and large specific surface area can significantly improve the reaction effect of microorganisms in fuel cells and improve their electrocatalytic performance.

(1) Cut the corn cob into 3 mm thick and 1 cm × 1 cm in size, as shown in Figur. 2. The cut slices were placed in absolute ethanol for 30 min by ultrasonic shaking to remove surface impurities, then ultrasonicated with deionized water for 30 min, and then removed and placed in an electric blast drying oven at 90°C for 2 h for later use. The dried corn cob was put into a box-type resistance furnace and vacuum carbonized at 250°C, 300°C, 350°C and 400°C for 30 min, and then cooled to room temperature with the furnace to take out the sample, so as to prevent the biochar from being oxidized when exposed to air when the temperature is too high[2].

It can be found from Figure. 2 that the surface and interior of biochar carbonized at 250 °C and 300 °C are reddish-brown, which indicates that the carbonization of corn cob is not complete at this temperature; the internal and external colors of biochar at 350 °C are pure black, and the surface structure is loose flake, indicating that the carbonization of corn cob is relatively thorough; while the soft part of the center of biochar carbonized at 400 °C has shown white ash, and only the charcoal structure at the edge of the material remains, which indicates that the carbonization temperature of corn cob is too high and the yield of biochar generated is low. In summary, 350°C was selected as the carbonization temperature of corn cob biochar.

(a) Uncarbonized Corn Cobs (b) Corn Cob Carbonized at 250°C (c) Corn Cob Carbonized at 300℃

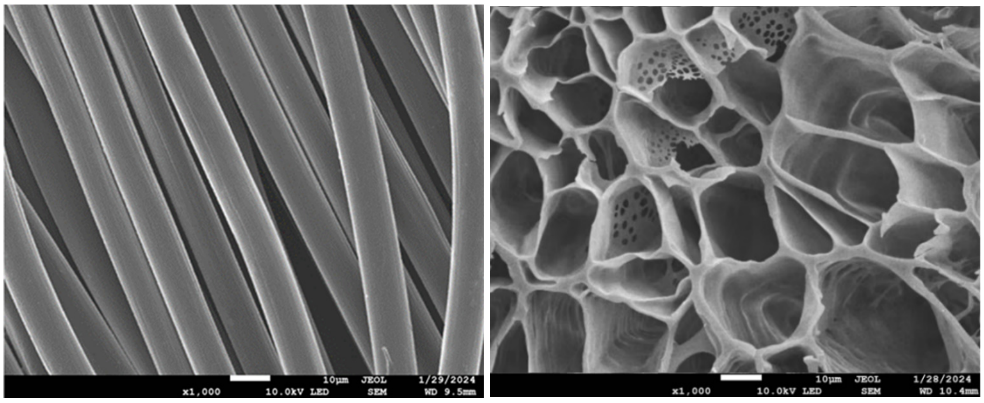
(d) Corn Cob Carbonized at 350℃ (e) Corn Cob Carbonized at 400℃

Figure 2. Morphology of corn cob material

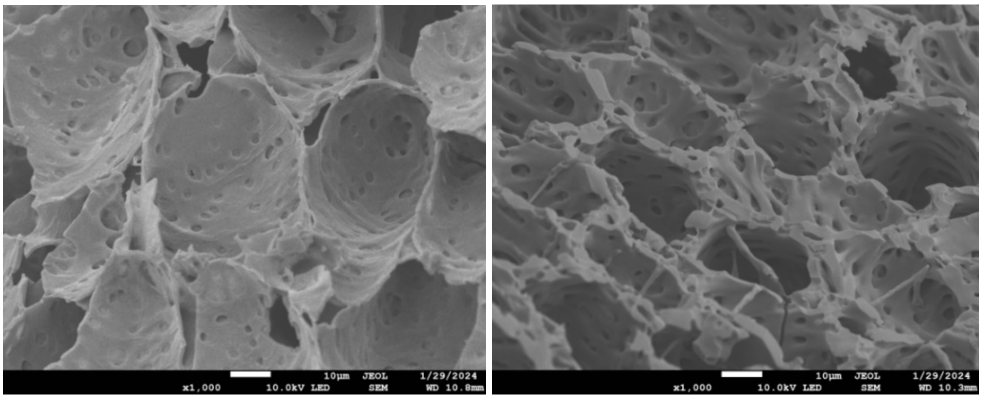
(2) Modification of corn cob biochar

In order to achieve a higher specific surface area of corn cob biochar, it was acidic or alkaline with KOH, NaOH and HCl solutions, respectively. The specific steps are as follows: 2 g of corn cob biochar was placed into KOH, NaOH and HCl solutions at a concentration of 40 g/L, ultrasonic shaking for 30 min and then standing for 12 h, washed to neutral with 1 M H_3PO_4 solution or $NaHCO_3$ solution deionized water, then filtered after ultrasonic shock for 30 min, and the filtered sample was put into a drying oven at 90 °C for 2 h and taken out, and the modified materials were named HCl modified corn cob biochar, KOH modified corn cob biochar and NaOH modified corn cob biochar[3].

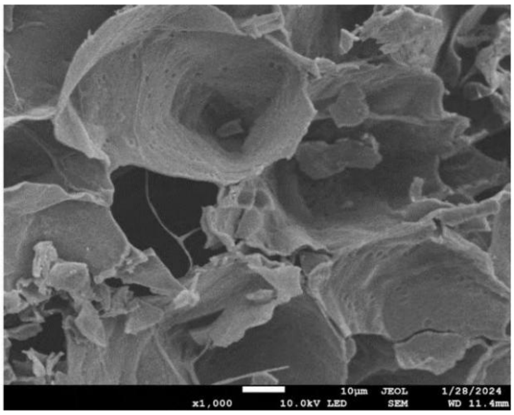
2.2. Scanning Electron Microscopy Analysis of Modified Anode (SEM).



(a) CF (b) Unmodified Corn Cob



(c) KOH Modified Corn Cob (d) NaOH Modified Corn Cob



(e) HCl Modified Corn Cob

Figure 3. SEM images of different anode materials

Acid and alkali modification can change the structural properties of biochar materials, and higher porosity is conducive to the attachment of microorganisms to the electrode materials, but the difference in the properties of acid and alkali substances will affect the formation of biochar surface roughness. Therefore, the selection of suitable modifier is the key to improve the performance of MFC device, and the selection of corn cob anode material modifier in this paper is mainly analyzed by scanning electron microscopy (SEM).

(1) Scanning electron microscopy (SEM) analysis of modified corn cob biochar

Scanning electron microscopy is a method of characterizing the morphology and surface structure of an object by using magnification technology to observe the interaction between electrons and the object to be measured. In order to achieve the purpose of accurate and clear observation of the measured object at high magnification, the material fixed by conductive glue is sprayed with gold, and then the measured object is scanned by different magnifications using an electron microscope to obtain the required structural features of the object.

In order to obtain the morphological changes of corn cob biochar materials modified by acid and alkali more accurately, scanning electron microscopy technology was used to record the morphological characteristics of the materials under microscopic conditions in detail. Figure. 3 shows the SEM images of corn cob biochar modified with traditional carbon felt and different acid and alkali solutions.

As can be seen from the image, the traditional carbon felt material presents a regularly distributed fiber structure as shown in Figure. 3 (a), with a smooth surface and a small specific surface area, which is not conducive to the attachment of microorganisms. Compared with the unmodified biochar, the surface structure of corn cob biochar modified with different acid-base solutions underwent different morphological changes. The unmodified corn cob biochar is shown in Figure (b) with a multi-layer homogeneous flake structure, and the inside of each macroporous pore is relatively flat and smooth, and there is a certain microporous structure in some areas. These micropores are produced due to the decomposition and release of gases and volatile substances inside the corn cob during the high-temperature carbonization process, and the destruction of cellulose and other components. Figure (c) shows that the specific surface area of corn cob biochar modified by KOH increases and the micropore structure gradually increases. This is because the modification and activation of the biochar material by KOH destroys the original surface morphology of the biochar, so that the lignin present on the corn cob is separated, resulting in more porous structure. The corn cob biochar modified by NaOH shown in Figure (d) is a three-dimensional carbonaceous skeleton structure, and the microporous structure on the surface of the macropores is the densest, and the depth of the micropores is large, and the roughness effect is the best. As shown in Figure (e), the biochar under HCl modification shows that the porosity of the biochar is reduced, the skeleton is thinner, and cracks in the structure appear. This is due to the collapse of the edge structure on the surface of the material due to the corrosive effect of HCl, and the specific surface area is reduced. Therefore, the comprehensive analysis shows that the loose and porous structure characteristics of biochar are significantly better than those of carbon felt compared with traditional carbon felt, and the modification of NaOH is more conducive to the construction of the rough structure of biochar materials, which provides a good structural basis for the adhesion of metal compounds on the materials and the efficient propagation of microorganisms in the electrode materials in the follow-up experiments[4].

2.3. Optimization of the Anode

In order to further optimize the modified biochar anode on the basis of the original performance, the metal compound coating technology was used to improve the conductivity of the electrode, reduce the internal resistance and improve the electrochemical performance of the device. The specific test steps are as follows: four different metal compound materials, namely three-dimensional titanium carbide (Ti_3C_2 MXene), niobium carbide (NbC), tungsten carbide (WC), and tantalum carbide (TaC), are prepared, and the optimal ratio of materials and reagents is selected according to the preparation method of Chang Wen's paper. Firstly, the mass of Ti_3C_2 MXene metal compound was weighed 3 mg, it was added to a test tube filled with isopropanol solution, and various components were fully mixed by shaking with a vortex shaker for 20 min, and the obtained mixed solution was coated on the NaOH modified corn cob biochar that had been alkaline to prepare the optimized corn cob biochar, which was denoted as Ti_3C_2 MXene@YMX. The coating methods of the other four metal compounds on corn cob biochar were consistent with those of Ti_3C_2 MXene metal compounds, and the NbC@YMX, WC@YMX and TaC@YMX anode materials were obtained respectively.

2.4. Inoculation and Culture of Electrogenic Strains

The types and characteristics of the strains used for power generation in this experiment are shown in Table 1 below.

Table 1. Types and characteristics of anode microorganisms

Strain Name	Gram Staining	Anaerobic/Aerobic	Yes/No Electricity Production
Clostridium butyrate	Gram-positive	Anaerobic bacteria	Yes
Shewanella	Gram negative	Facultative anaerobes	Yes
Pseudomonas marsh	Gram negative	Facultative anaerobes	Yes
Bacillus subtilis	Gram-positive	Facultative anaerobes	Yes
Active yeast	/	Facultative anaerobes	Yes

Firstly, Clostridium butyricum, Shewanella, Rhodopseudomonas marsh, Bacillus subtilis, and active yeast were activated as single strains, and then the composite culture of five strains was carried out in inorganic salt medium, and the microorganisms were cultured at a constant temperature of 35°C and a rotation speed of 180 r/min for 24 h, so that the microorganisms could multiply and grow rapidly in the culture medium, and form a composite flora as the anode microorganisms of MFC. Figure. 4 shows microbial strains cultivated in a constant temperature shaker[5].

Figure 4. Culture of bacterial strains

2.5. Configuration of the Electrode Fluid

The anode electrolyte used in the test was an emulsified diesel solution prepared with inorganic salt medium. The specific preparation method of the anode solution in this chapter test is as follows: on the sterile workbench, according to the drug ratio in Table 2 below, the inorganic salt medium is prepared, the medium is put into the pressure steam sterilizer at 121 °C for 15 min to kill the bacteria, 2 g of 0# diesel oil and an appropriate amount of Siban 80 emulsifier are injected into the medium, the solution is fixed to 1 L, and the effect of emulsifying diesel is fully stirred with a magnetic stirrer to obtain an anode electrolyte with an oil concentration of 2 g/L. As an excellent electron acceptor, potassium ferricyanide can significantly improve the electrochemical performance of the cathode. Therefore, in this experiment, potassium ferricyanide was fully mixed and dissolved with deionized water to prepare a potassium ferricyanide solution with a solution concentration of 30 mM as the catholyte of MFC.

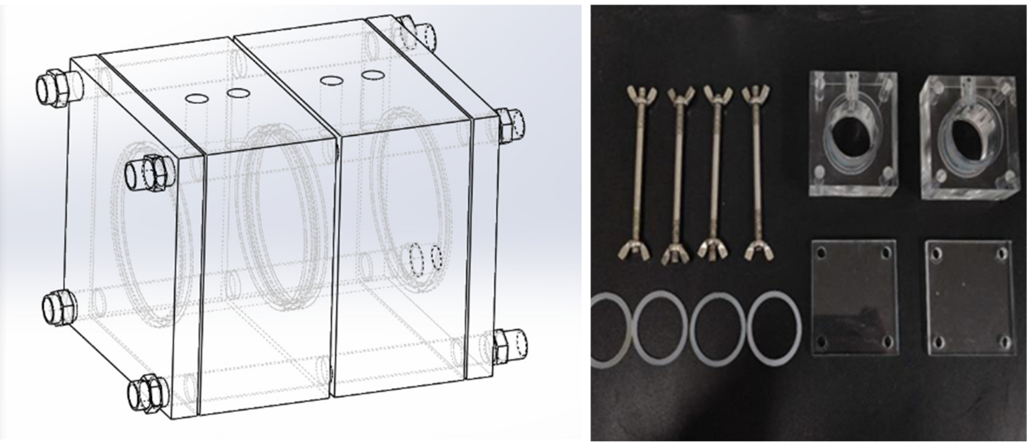
Table 2. Composition And Content of Inorganic Salt Culture Medium

Serial Number	Name of the reagent	Content g/L
1	Disodium ethylenediaminetetraacetic acid	0.01
2	Potassium monobasic phosphate	3
3	Dipotassium phosphate	1.5
4	ammonium nitrate	2
5	Anhydrous calcium chloride	0.01
6	distilled water	100
7	Magnesium sulfate heptahydrate	0.1
8	pH	7.5

2.6. Construction of a Two-Chamber MFC

The whole process of setting up the plant is carried out in a sterile environment on the workbench. After the MFC battery case was sterilized by ultraviolet light for 2 h, 50 mL of anode solution and 50 mL of catholyte were injected into the two electrode chambers, respectively, and 1 mL of composite microbial culture medium was added to the anolyte. The prepared 1 cm ×1 cm modified biochar was immersed in anodic solution as an anode electrode. For the cathode, a carbon rod with a diameter of 0.5 cm and a length of 15 cm is used as the cathode electrode. Two small holes at the upper end of the anode chamber, one for placing the anode electrode and the other for silica plugging, ensure that the microorganisms work in an oxygen-free environment. The small hole in the cathode chamber is used as the cathode electrode by placing carbon rods on one side, and the other is connected to the atmosphere to ensure that electrons, protons and oxygen from the outside world in the cathode chamber can be effectively combined to ensure the smooth oxidation reaction.

The battery type used in this test is a square double-chamber MFC, and the device is designed by SolidWorks, and the three-dimensional drawing of the device assembly and the style of each component are shown in Figure. 5. The double-chamber MFC is composed of two polycarbonate materials with dimensions of 8 cm×8 cm × 4 cm, which are respectively used as the cathode and anode electrode chambers of the device, the internal volume of the chamber is 50 mL, and two small holes with a diameter of 1 cm are respectively opened at the upper end of the electrode chamber for the installation of electrode liquid and the placement of electrodes, and the two ends of the electrode chamber are provided with cover plates, and rubber gaskets are arranged between the cover plate and the electrode chamber and between the two electrode chambers to play the role of sealing solution and air isolation, and the diameter used between the two electrode chambers is 4 The circular nation-117 proton exchange membrane is separated by four stainless steel fully threaded screws of M8×12 specifications through all electrode chambers and end caps, and fastened with M8 ingots nuts to assemble a complete set of double-chamber microbial fuel cell devices[6].



(a) Three-dimensional installation drawing (b) Dismantling diagram of the physical installation

Figure 5. Configuration diagram of a dual chamber MFC reactor

3. MFC Performance Test

3.1. The Effect of the Anode Electrode on the Performance of Electricity Production

3.1.1. MFC Output Voltage Test

In this test, the output voltage test is an important indicator to measure the power generation capacity of the MFC device. During the test process, the CT4008 battery detection system is used to connect the MFC device to 1000 Ω resistors at both ends, and the time detection interval is set in the system to collect the obtained voltage, and the collected data will be automatically saved to the system. According to Ohm's law (Equation 1), the current in the circuit can be calculated:

$$I = \frac{U}{R} \tag{1}$$

wherein, I is the circuit current; U is the voltage at both ends of the MFC device; R is the external resistor at both ends of the MFC device.

The output voltage of the MFC is shown in Figure. 6 under continuous operation. Subsequently, the voltage rises rapidly, because at the beginning of the device reaction, the inoculated microorganisms multiply and grow rapidly in the anode solution, and attach a large number of people to the anode material, which makes the conductivity of the battery increase and the voltage increases. When the MFC runs for about 10 h, the output voltage of the device reaches its peak, and the maximum voltage of Ti_3C_2 MXene@YMX is 698 mV, and the voltage of CF is 527 mV. Over time, the voltage trend varies significantly depending on the anode material. When the device is operated to 70~80 h, the output voltage decreases significantly, mainly because the nutrients for microbial degradation are reduced in the fuel cell at this stage, which limits the growth of microbial communities. In terms of overall performance, the output voltages of MFCs loaded with different anode materials are in descending order of Ti_3C_2 MXene@YMX > WC@YMX > NbC@YMX > TaC@YMX > uncoated modified corn cob > CF. The power production performance of corn cob anode modified by metal compound is significantly higher than that of carbon felt materials, and the power production performance of Ti_3C_2 MXene@YMX is higher than that of other materials in terms of peak voltage and overall stable operation trend. This indicates that Ti_3C_2 has a significant MXene@YMX modification effect, and its excellent conductivity and biocompatibility make the MFC device battery internal resistance smaller and the output voltage higher.

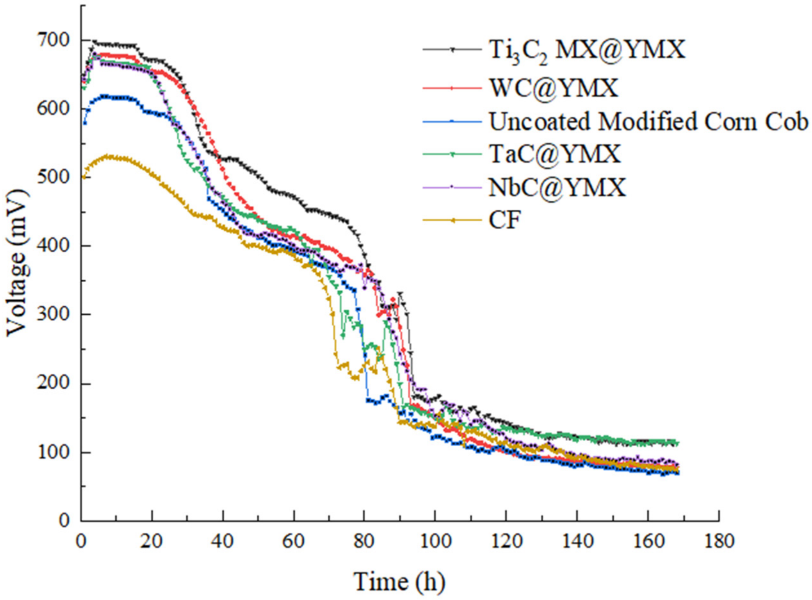


Figure 6. Output voltage of different anode materials

The initial voltage of the MFC loaded with biochar electrodes was not much different, all of which were above 600 mV, but the output voltage of CF was lower at 500 mV, as shown in Table 3 .

Table 3. MFC output voltage of different anode materials

Serial Number	Name	Initial voltage(mV)	Peak voltage(mV)
1	Ti_3C_2 MXene@YMX	649	698
2	NbC@YMX	643	679
3	WC@YMX	640	678
4	TaC@YMX	631	676
5	Uncoated Modified Corn Cob	580	618
6	CF	500	527

3.1.2. Power Density Test of MFC

Power density refers to the relationship between the anode electric maximum and the generated power of the battery system, and is an indicator to measure the power production capacity of the battery. The test method can be calculated according to Equation (2):

$$P = \frac{U^2}{RA} \tag{2}$$

wherein, I is the circuit current; U is the voltage at both ends of the MFC device; R is the external resistor at both ends of the MFC device; A is the projection area of the anode electrode of the MFC device; P is the power density of the MFC device[7].

The power density of different anode materials was tested, and the resulting power curves are shown in Figure. 7. It can be seen from the figure that the curve slope of the corn cob biochar anode modified by metal compounds is much larger than that of the traditional carbon felt material. The maximum power density of the Ti_3C_2 MXene modified biochar anode is 2577 mW/m^2 and the maximum current density is 3601 mA/m^2, while the power density of the carbon felt is only 898 mW/m^2, and the power density of the biochar electrode is 1.87 times that of the carbon felt.

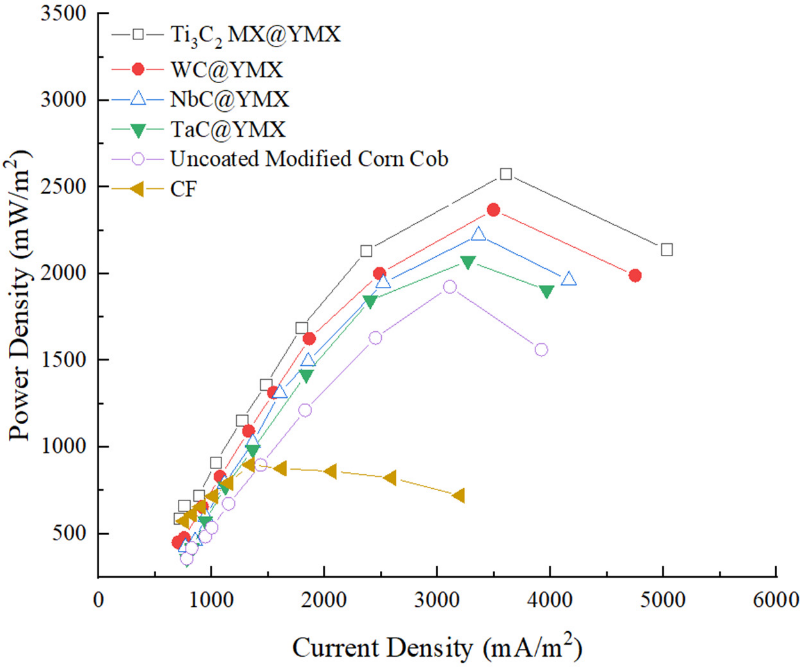


Figure 7. Power density of different anode materials

Table 4. MFC power density of different anode materials

Serial Number	Name	Peak power density (mW/m^2)	Peak current density(mA/m^2)
1	Ti_3C_2 MXene@YMX	2577	3601
2	WC@YMX	2368	3493
3	NbC@YMX	2222	3360
4	TaC@YMX	2074	3267
5	Uncoated Modified Corn Cob	1924	3108
6	CF	898	1340

This indicates that the Ti_3C_2 MXene@YMX is more biocompatible than the carbon felt anode, and the charge is transferred through the anode electrode more efficiently, thus increasing the power generation capacity of the MFC device per unit area of the anode material. The power density of biochar anodes coated with similar metal compounds is relatively similar, which is higher than that of uncoated corn cobs, as shown in Table 4. The results show that the metal compounds have excellent electrical conductivity, and the use of their coating and modification technology is one of the feasible methods to reduce the internal resistance of the battery and increase the power generation efficiency of MFC.

3.2. Effect of COD Removal Rate of Anode Electrode

The indicators of MFC device for purifying ship oily sewage mainly include the degradation rate of sewage oil and water and the removal rate of COD.

Chemical oxygen demand (COD) is an important indicator to measure the oxygen content of reducing substances in water samples during the oxidation process. It is usually used to analyze the amount of organic pollutants in water samples, higher COD indicates greater levels of contaminants in water samples. In this experiment, the water samples were first digested by HM-12 multi-function digestion instrument, and then the COD content of water samples was detected by HM-U800 ultraviolet water quality multi-parameter comprehensive detector. According to equation (3), the removal effect of the MFC device on the COD in the sewage water sample can be calculated.

$$COD \quad \text{Removal rate} = \frac{(COD_0 - COD_1)}{COD_0} \times 100\% \qquad (3)$$

Among them, COD_0 is the content of chemical oxygen demand in the water sample before the degradation of oily wastewater. COD_1 is the content of chemical oxygen demand in the water sample after the degradation of oily wastewater.

The COD removal rate was measured for 7 days on the MFC device loaded with different biochar anodes, and the specific experimental data measured are shown in Figure. 8.

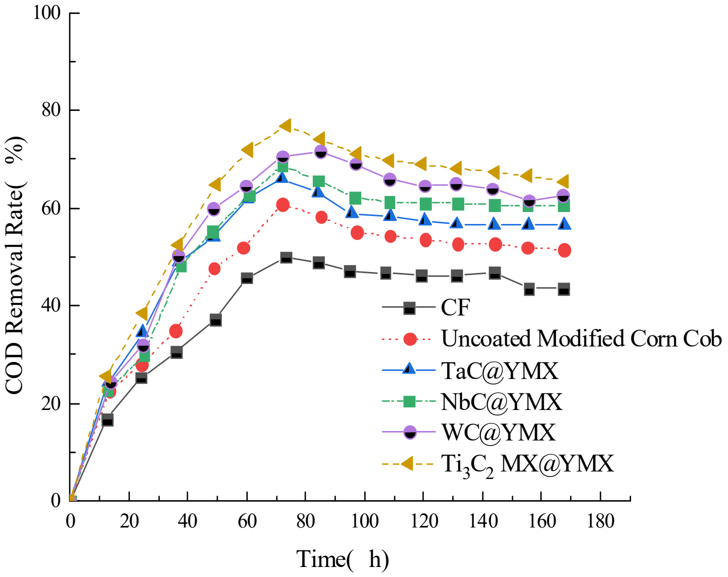


Figure 8. COD removal rate of MFC with different anode materials

After 20 h, the COD degradation effect of CF and uncoated modified corn cob was significantly lower than that of other metal compound materials, and the COD removal rate of each device reached the highest at about 80 h, and gradually stabilized in the later stage of operation. The COD removal rates of the six anode materials Ti_3C_2 MXene@YMX, WC@YMX, NbC@YMX, TaC@YMX, uncoated modified corn cob and CF were 76.87%, 71.71%, 68.72%, 65.97%, 60.81% and 49.9%, respectively. According to the analysis of COD removal rate, the microorganisms on the anode material attached to the anode material in the early stage of degradation and multiplied rapidly to form biofilms, and the removal rate at this stage was about the same and the removal effect increased rapidly. When microorganisms multiply to a certain stage, due to the different properties of anode materials, materials with larger specific surface area and better biocompatibility have significant advantages in purifying pollutants, and the surface of these materials can attach and reproduce more microorganisms, and obtain survival nutrients by decomposing a large number of organic pollutants, which greatly improves the COD removal efficiency in the battery. The anode material with the best microbial catalytic activity was Ti_3C_2 MXene@YMX, while the carbon felt material had the lowest degradation rate due to its poor hydrophilic properties and limited affinity for microorganisms[8].

4. Conclusion

In this experiment, a microbial fuel cell device was built that can treat oily sewage from ships. In order to improve the output performance of the device more effectively, according to the mechanism of degradation and power generation of the MFC device and the performance characteristics of the biochar material, the waste corn cob biochar was selected for modification and modification, and a new type of MFC anode electrode was prepared, and the performance test of MFC was passed. The results of the trial were as follows:

(1) SolidWorks software is used to design the MFC device with a double-chamber square structure. In the anode chamber, the inorganic salt medium with diesel emulsion as the pollutant was used as the anode solution, and the composite flora of five strains of Clostridium butyricum, Shewanella, Rhopseudomonas marsh, Bacillus subtilis and active yeast were used as the degrading microorganisms in the anode solution, and the new biochar material Ti_3C_2 MXene@YMX was used as the anode electrode. Potassium ferricyanide solution is used as the catholyte in the cathode chamber, and the carbon rod is used as the cathode electrode, and the MFC device with excellent sewage treatment performance is assembled.

(2) Optimize the prepared anode electrode material. The corn cob was carbonized at 250°C, 300°C, 350°C and 400°C to obtain the best corn cob biochar at 350°C. The modified biochar was obtained by KOH, NaOH and HCl modification technologies, respectively. The differences between the modified biochar and CF were compared, and the NaOH-modified biochar had the best performance by physical characterization, which had the advantages of high roughness, large specific surface area, good hydrophilicity, strong wettability, and conducive to microbial adhesion. The biochar materials were modified by Ti_3C_2 MXene, NbC, WC and TaC coating technologies, and the biochar anode materials such as Ti_3C_2 MXene@YMX, NbC@YMX, WC@YMX and TaC@YMX were obtained, respectively.

(3) Test the properties of the anode material. Equipped with a biochar anode modified with metal carbide, four sets of MFC devices and an MFC with CF were assembled to test the performance of each item. Tests have shown that MFCs loaded with Ti_3C_2 MXene@YMX have the best performance among the tested devices. Among them, the maximum output voltage of the MFC with Ti_3C_2 MXene@YMX is 698 mV, which is 32.4% higher than that of the MFC with CF. The maximum power density was 2577 mW/m^2, which was 1.87 times higher than that of CF-loaded MFC, and the COD removal rate was 76.87%, which was 27% higher than that of CF-loaded MFC. The performance of the MFCs of the other groups equipped with biochar anodes was similar to that of the Ti_3C_2 MXene@YMX, and they were all higher than those of the CF loaded devices, but the comprehensive analysis showed that the operation effect of the Ti_3C_2 MXene@YMX was the best.

The above experimental results show that the new material Ti_3C_2 MXene@YMX prepared in this paper is used as an anode electrode for MFC device in the treatment of ship oily sewage, which has excellent power generation performance and outstanding oil treatment effect.

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