

Effect of Modified Carbon Felt Anodes on the Performance of Microbial Fuel Cell

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Abstract: In this paper, phosphoric acid, nitric acid, zinc chloride, ammonia and melamine are used as cheaper activators to modify the carbon felt material, exploring the changes of various activation materials on the power production performance and degradation performance of the device after MFC carbon felt anode treatment, and finding that phosphoric acid-activated carbon felt has the highest output voltage and the best degradation effect on the ship's oily wastewater as a MFC anode device.

Keywords: Microbial Fuel Cell, Oily Wastewater, Phosphoric Acid.

1. Introduction

The anode of microbial fuel cell (MFC) is not only a place for the attachment and growth of electricity-producing microorganisms, but also directly involved in the reaction of catalytic oxidation of organic matter by electricity-producing microorganisms[1]. Therefore, the anode of MFC plays a key role in the efficiency of MFC. Improving the anode material of microbial fuel cell, making it favorable for the attachment of electricity-producing microorganisms and enhancing the electron transfer ability[2], can effectively improve the performance of MFC.

Carbon material not only meets the characteristics of electrical conductivity[3], biocompatibility and chemical stability required for MFC anode materials, but also its low price, is currently the most commonly used anode materials, the surface modification of carbon materials commonly used methods are (1) surface oxidation modification, to increase the content of oxygen-containing functional groups on the surface, commonly used oxidizing agents are nitric acid[4], sulfuric acid, H₂O₂ and O₃, etc., (2) surface reduction modification, to increase the content of surface oxygen-containing alkaline functional groups[5]. the content of oxygenated basic functional groups on the surface, such as ammonia[6] (3) metal-loaded modification to increase the adsorption performance of carbon materials by utilizing the strong bonding between metals or metal ions (Pt, Fe, etc.) and specific adsorbates[7]. In this chapter, carbon mats were selected as anode materials to explore the effects of different chemically activated anodes on the performance of MFCs.

2. Experimental Preparation

2.1. Preparation of MFC anode carbon felt material

The 1cm×1cm carbon felt was cleaned with deionized water and anhydrous ethanol solution and air-dried to make the preactivated electrode. The pre-treated carbon felt was soaked and treated with 80 g/L melamine solution, 5 mol/L dilute nitric acid solution, 80 g/L zinc chloride solution, 7 mol/L ammonia and 50 wt% phosphoric acid solution for 36 h. The carbon felt was rinsed with deionized water and air-dried to obtain five kinds of activated and unactivated carbon cloths and set aside.

2.2. Preparation of MFC cathode solution

In this experiment, the commonly used potassium ferricyanide (K₃[Fe(CN)₆]) was selected as the cathode solution, and a mixture of 90 mM K₃[Fe(CN)₆ and 60 g L⁻¹ KCl was chosen.

2.3. Configuration of oily wastewater from ships

Configuration of artificial seawater: 245.34 g of sodium chloride (NaCl) and 40.94 g of anhydrous sodium sulfate (Na₂SO₄) were dissolved in 8-9 L of distilled water, and 0.200 L of standard solution A and 0.100 L of standard solution B were added slowly with vigorous stirring, diluted to 10 L, and then adjusted the pH to 8.2 with 0.1 mol of sodium hydroxide (NaOH) solution. The formulations of standard solution A and standard solution B are shown in Table 1.

Table 1. Standard solutions A and B formulations

Standard Solution	Chemical Compound	Concentration/ (g·L ⁻¹)
A	MgCl ₂ ·6H ₂ O	555.57
	CaCl ₂	57.94
	SrCl ₂ ·6H ₂ O	2.11
	KCl	69.45
	NaHCO ₃	20.10
B	KBr	10.09
	H ₃ BO ₃	2.71
	NaF	0.31

Add 0# diesel fuel and OP-10 emulsifier to the artificial seawater to configure the simulation of the ship's oily sewage, stirring until transparent, and then add a certain amount of

kaolin used to simulate the turbidity of the sewage, the specific water quality indicators are shown in Table 2.

Table 2. Water quality indicators for modeling oily wastewater

Water Quality Indicators	Oil (mg/L)	pH	NTU	COD
Numerical Value	2000±0.1	8.2±0.1	10±0.1	3670±0.5

2.4. Configuration of microbial culture solution

The culture medium used in this test is mainly NB liquid medium. Configuration of NB liquid medium: take 18g of NB medium powder, add it into 1L of distilled water, fully stir and dissolve it in a beaker and then divide it into several conical flasks, seal the mouths of the flasks with breathable film and newspaper and then put them into autoclave, after 20min

sterilization, transfer them to a constant temperature incubator of 35°C to continuously cultivate them for 24h, and if the culture medium in the incubator is as clear and transparent as before constant temperature cultivation, then the NB liquid medium is successfully configured and can be used normally. If the culture liquid in the incubator after 24h is as clear and transparent as before the constant temperature incubation, then NB liquid culture medium is successfully configured and can be used normally. The process is shown in Fig 1.

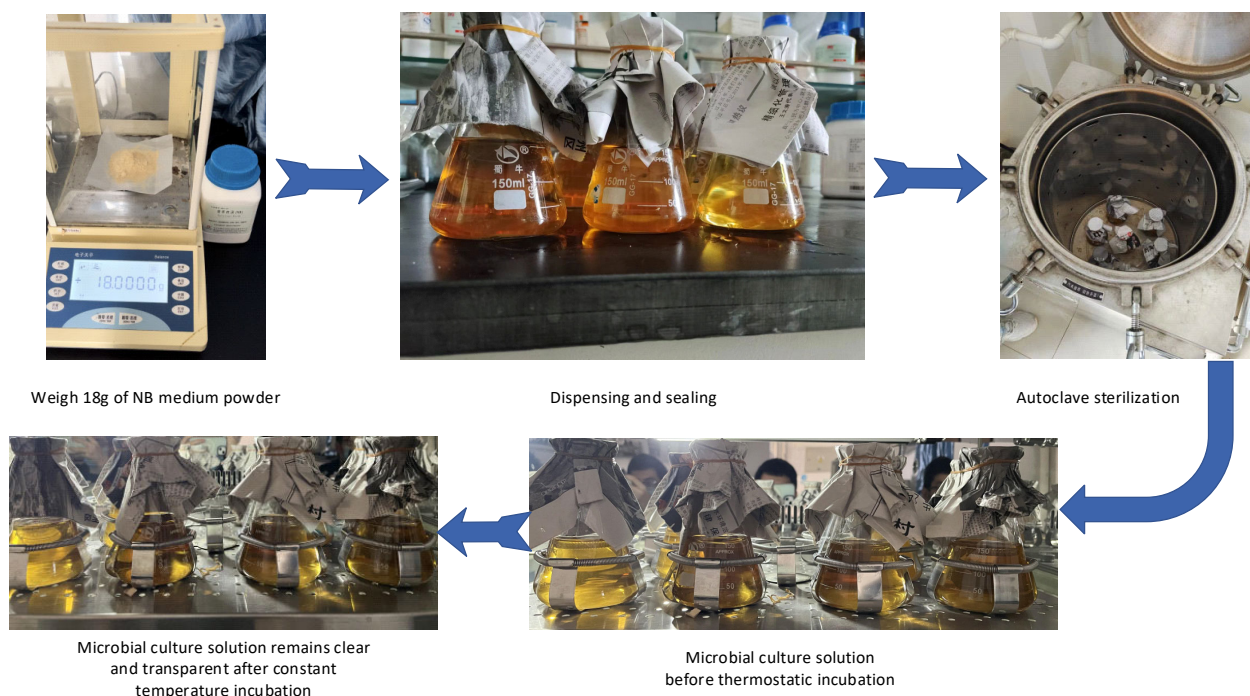


Figure 1. Configuration of NB liquid medium

2.5. Configuration of phosphate buffered saline

PBS can resist the addition of a small amount of acid and alkali[8], and play a role in maintaining the stability of the pH value in the device, and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and NaCl were used to configure the phosphate buffer in this test, as shown in Table 3

Table 3. Phosphate buffered saline (pH=7.2, g/L)

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	NaCl
68.4	31.6	17.6

2.6. Dual chamber MFC reactor design

A Dual Chamber MFC reactor made of Plexiglas was used in this experiment. The overall 3D structure of the unit was first designed and modeled using SolidWorks, As in Fig 2.

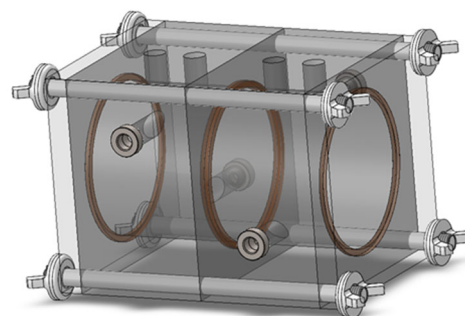


Figure 2. Dual chamber MFC SolidWorks modeling drawing

The physical composition of this experiment is shown in Fig. 3. The anode chamber and cathode chamber are 8.0cm×8.0cm×4.0cm rectangular structures with 4.0cm

diameter holes inside, which are separated by a proton exchange membrane and have a volume of about 50.27 ml. In order to facilitate the injection of electrode liquid and the installation of electrodes, four holes with a diameter of 1.0cm are drilled at the top of the electrode chamber, and four holes with a diameter of 1.0cm are reserved at the side for the inflow of oily wastewater and the replacement of cathode liquid. Four 1.0 cm diameter holes were drilled at the top of the electrode chamber and four 1.0 cm diameter holes were reserved at the side to facilitate the inflow of oily wastewater and the replacement of the cathode liquid. The left and right sides of the MFC reactor were equipped with two baffle plates with a length and width of 8.0 cm×8.0 cm and a thickness of 1.0 cm, which were mainly used for sealing the MFC reactor. In order to ensure the airtightness of the device and prevent the anode liquid and cathode liquid from mixing with each other, rubber seals were designed between the baffle plate of the anode chamber and the anode chamber, the anode chamber and the cathode chamber, and the cathode chamber and the cathode chamber baffle plate, and there were four holes with a diameter of 1.0 cm drilled on the four corners of the whole MFC reactor, which were used to secure the MFC device as a whole through the insertion of four long screws with a diameter of 8 mm and four M8 bolts.

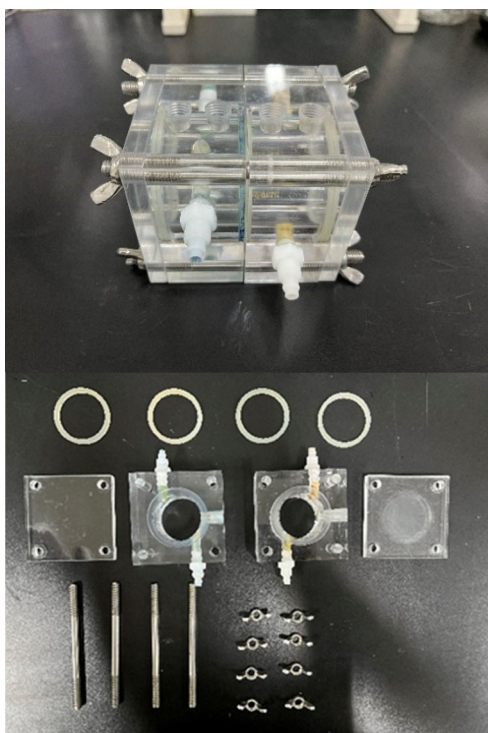


Figure 3. Dual chamber MFC concrete figure

3. MFC Performance Testing

3.1. MFC Output Voltage Test

The variation of output voltage with time in the operating state of the MFC device is shown in Fig. 4. At the beginning of the device reaction, the voltage increases rapidly, which is due to the rapid propagation and growth of the inoculated microorganisms in the anode liquid, and a large number of them attach to the anode material, which makes the cell conductivity enhanced and the voltage increased. When the MFC device runs for a period of time, the output voltage reaches the peak, in which the output voltage using

phosphoric acid-activated (P) carbon felts is the highest at 676 mV, and the voltage using inactivated (B) carbon felts is the lowest at 539 mV. With the growth of time, the voltage change tendency according to the difference of anode materials shows obvious differences. The output voltage decreased significantly when the device was operated for 10,000 s, mainly because the nutrients available for microbial degradation were reduced in the fuel cell at this stage, limiting the growth of the bacterial population. In terms of overall performance, the output voltages of MFCs loaded with different anode materials were in the order of phosphoric acid-activated (P) carbon felts > melamine-activated (S) carbon felts > ammonia-activated (N) carbon felts > zinc chloride-activated (Zn) carbon felts > nitric acid-activated (O) carbon felts > inactivated (B) carbon felts in the order of high to low. The electroproduction performance of the chemically activated carbon felt anode was significantly higher than that of the inactivated carbon felt material, in which the phosphoric acid-activated (P) carbon felt had a better electroproduction performance both in terms of the peak voltage and the overall trend of stable operation, while the voltage of the inactivated (B) felt dropped faster and the voltage was less stable because it was less susceptible to microbial adhesion, and had a poorer capacity for electroproduction.

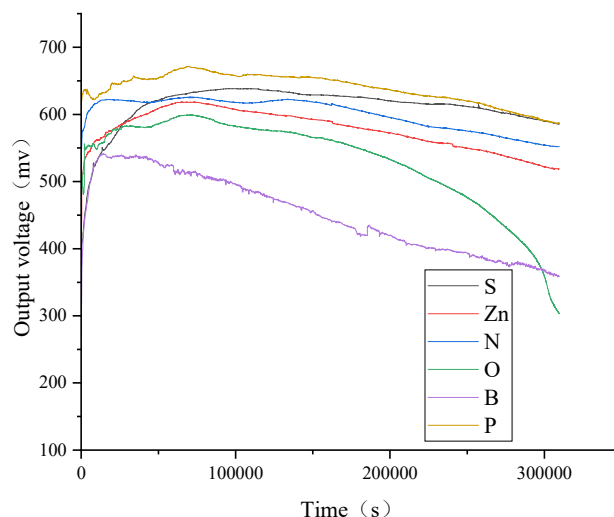


Figure 4. Output voltage of different anode materials for MFC device

3.2. MFC Degradation Performance Test

3.2.1. Determination of oil content

In this test, the oil degradation rate of MFC is calculated by comparing the pollutant concentration before and after treatment. In order to obtain the oil content of the oily wastewater before and after treatment by the MFC system, this test used the "Detection of Oil - Ultraviolet Spectrophotometry SL93-1994" as the test standard, and utilized a UV-visible spectrophotometer to test its absorbance. Using pure petroleum ether as the extractant, the emulsified diesel oil was diluted several times to make the concentration of 1, 5, 10, 30, 50, 80, 100mg / L of the standard oil, respectively, to measure its wavelength at 256 nm, and the standard surrogate oil concentration as the horizontal coordinates, absorbance as the vertical coordinates of the standard fitting curve of the sample UV absorption, Fig. 5 is

the standard curve of UV absorbance after the completion of the drawing of oil samples, its fitting curve and the fitted curve and the UV-Visible spectrophotometer. Figure 5 shows the UV absorbance standard curve of the oil samples after the completion of the drawing, and the fitting curve and the fitting coefficient are $y=0.0191+0.0228x$ and $R^2=0.9998$, respectively, with a high degree of fitting, which can be used for further calculating the degradation rate of oily wastewater from ships.

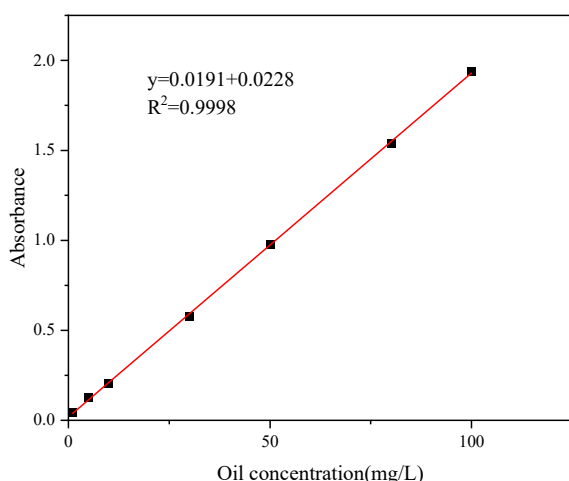


Figure 5. Emulsified diesel standard curve

Calculation of degradation rate of emulsified diesel was carried out. First, 5 mL of petroleum ether and 0.6 g NaCl were added to the decomposed 10 mL water sample and shaken at a rate of 120 times per minute for 30 min, followed by 20 min of ultrasonic shaking and ultimately a 10-minute centrifugation process to remove the bacilli and flocculent material and to extract the residual oil. The resulting upper organic phase was transferred to anhydrous Na_2SO_4 for 1 h of standing, followed by a filtration operation and the filtrate was recovered into a 10 mL volumetric flask and petroleum ether was added to a constant volume. The wavelength at 256 nm was measured by UV-visible spectrophotometer, and the oil content could be calculated according to the plotted standard curve of the oil sample. In this paper, the degradation rate of the MFC plant for treating oily wastewater was calculated using Equation 1. η_1 is the oil degradation rate, %; C_0 is the initial concentration of the oil sample treated, $\text{mg}\cdot\text{L}^{-1}$; C_1 is the concentration of the oil sample after treatment, $\text{mg}\cdot\text{L}^{-1}$.

$$\eta_1 = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

3.2.2. MFC Degradation Performance Test

After 7 days of degradation test, it can be found by comparing six groups of MFC devices with different anodes that the chemically modified anodes all help to improve the degradation efficiency of the MFC device, as shown in Fig. 6, in which the first-stage MFC degradation of using phosphoric acid-activated (P) carbon felts, nitric acid-activated (O) carbon felts, ammonia-activated (N) carbon felts, melamine-activated (S) carbon felts, and zinc chloride-activated (Zn) carbon felts as anodes in the device. The degradation efficiencies of emulsified diesel in the pool were 80.23%, 74.39%, 75.75%, 78.19% and 76.74%, respectively. Through

comparative analysis, it was found that the carbon felt electrode activated by phosphoric acid (P) had increased lipophilic functional groups and had excellent microbial adsorption capacity on the surface, which would promote the attachment and growth of microorganisms on the anode carbon felt surface, accelerate the initiation of MFC, and improve the overall MFC degradation effect.

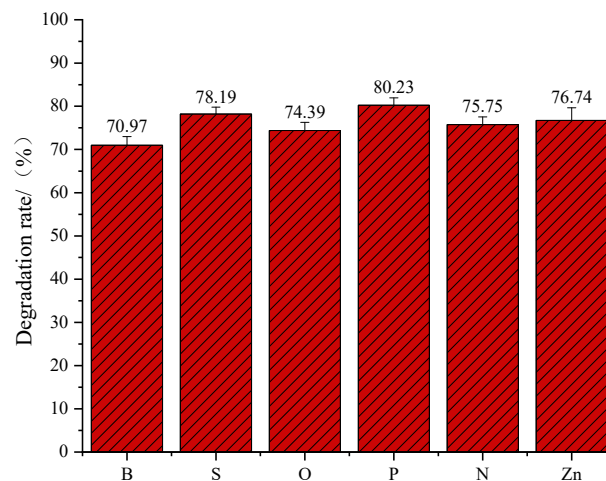


Figure 6. Seven-day degradation rate of different anode materials

4. Conclusion

The electroproduction performance of the chemically activated carbon felt anode was significantly higher than that of the inactivated carbon felt material, in which the phosphoric acid-activated (P) carbon felt had a better electroproduction performance both in the peak voltage and in the overall stable operation trend. Moreover, the lipophilic functional groups of the phosphoric acid-activated carbon felt electrode were increased, and the surface possessed an excellent microbial adsorption capacity, which would promote the attachment and growth of microorganisms on the surface of the carbon felt anode. This will promote the attachment and growth of microorganisms on the anode carbon felt surface, accelerate the initiation of MFC, and improve the overall MFC degradation effect.

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