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Polyaniline Modified Biochar Anode on the Performance of Microbial Fuel Cell for Treating Ship Oily Water

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Abstract

Conductive polymer modified anode can significantly improve the performance of microbial fuel cell (MFC). This study mainly explored the MFC of polyaniline(PANI) modified almond biochar electrode and applied it to the treatment of oily water in ship engine rooms and the influence on power generation performance. Polyaniline was prepared by chemical synthesis and deposited on the surface of almond biochar. The modified electrodes were loaded into a dual-chamber MFC to measure their degradation and electricity production properties, and the electrodes were characterized to measure their electrochemical properties. It was observed by scanning electron microscopy that the biochar could be modified with polyaniline, and the polyaniline was attached to the surface of the biochar thin layer to form a rod-like nanostructure. In terms of electricity generation performance, the maximum output voltage of the MFC loaded with polyaniline modified almond biochar electrode is the highest, reaching 0.73 V, which is more than 15.8% higher than that of the MFC loaded with blank biochar, and higher than that loaded with blank carbon cloth (CC) by more than 25.9%. The experimental results show that the polyaniline-modified biochar electrode can effectively utilize the advantages of good conductivity and high biocompatibility of polyaniline, and significantly improve the electricity generation and degradation performance of MFC.

Keywords

Microbial Fuel Cell; Ship Oily Water; Biochar; Polyaniline.

1. Introduction

Ship bilge oily water is a mixture of water, oil, and oily sewage from various valves and pipelines in the engine room [1]. The annual oily water of the ship is generally 10% of the total tonnage of the ship, and the volume mass is about 5000 mg·L-1. The composition of oily water is particularly complex. If it enters the ocean due to various leakage accidents , it will cause great harm to the marine ecology [2]. Using traditional physical methods to treat ship bilge oily sewage requires a lot of electric energy, so it is urgent to develop an efficient and non-secondary pollution disposal method.

Microbial fuel cells have received extensive attention in the past 10 years due to their ability to utilize microorganisms as catalysts to convert biomass energy into electricity [3-5].. In recent years, various research institutions are still committed to improving the output power and practical application performance of MFC. The main mechanism of its action is that the microorganisms transfer the electrons generated by metabolism to the external circuit through the attached electrodes to generate electrical signals. Dongle Cheng et al use microbial fuel cell to treat synthetic swine wastewater containing antibiotics successfuly [6]. Payel Choudhury et al get stable power from dairy wastewater using microbial fuel cell [7]. Electrodes serve as a place for microbial attachment and electron transfer, and their electrochemical performance directly affects the performance of the entire battery. Carbon-based materials such as graphite paper, carbon cloth, and carbon cloth are commonly used electrode materials in MFC. On the one hand, they have the characteristics of corrosion resistance, low cost, and easy processing. However, the electrochemical properties of ordinary carbon-based materials are not outstanding among many conductive materials, and even become one of the conditions restricting the power output of MFC. In order to improve the electrochemical performance of carbon-based materials, many strategies for modifying electrodes have been proposed. For example, the biocompatibility of anodes can be improved by adding more oxidized functional groups to the surface of carbon-based materials by electrochemical methods or acid treatment of carbon materials; or by treating carbon materials at high temperature to increase their surface area to improve MFC power output [8]. Among many methods, conductive polymer modified electrodes are generally considered to be an effective means to improve the output power of MFC [9-11].

Elahe Fallah Talookia et al compared the carbon cloth doped with polyaniline and the carbon cloth treated with acid, and obtained that the kinetic activity of PANI/CC was 376 times higher than that of CC anode [12]. Polyaniline has the reputation of synthetic metal. It is a polymer compound with good electrical conductivity and electrochemical properties [13,14]. It is positively charged in the anolyte and can generate electrostatic attraction with negatively charged microorganisms, which is more conducive to the attachment of microorganisms. Good biocompatibility. At the same time, polyaniline also has the advantages of low cost and simple synthesis process [15]. If polyaniline is used for the modification of biochar electrodes, the characteristics of the two materials can be reflected at the same time, and it is possible to obtain electrode materials with more outstanding performance.

In this study, a chemical method was used to deposit polyaniline on the surface of biochar , and then a low-temperature in-situ polymerization method was used to form polyaniline with fine nanostructures on the outermost layer of the modified material. Finally, the effect of this composite modified carbon cloth anode on MFC was investigated . performance impact. This method can grow polyaniline on the outermost layer of biochar, which effectively utilizes the high biocompatibility of polyaniline and the electrical conductivity of biochar . good feature. The in-situ polymerization methods all have the advantages of rapidity, simplicity and low preparation cost. The polyaniline produced by in-situ polymerization can form relatively ordered nanostructures, and the combination of this method is compared with unmodified biochar and carbon cloth materials in optimizing the output voltage and power density of the battery.

2. Materials and Methods

2.1 Preparation of Almond Biochar

Three-dimensional porous carbon biochar was prepared by high-temperature pyrolysis in a J2361 box muffle furnace after ultrasonic oscillation of the selected almond shell. The specific operation steps are as follows: select Xinjiang natural mature almonds with a size of 4-5 cm, separate the shells of the almonds with an electric saw, and ultrasonically clean the dirt with absolute ethanol and deionized water for 30 minutes respectively. Once the wooden shell was dried in an electric blast drying oven at 60°C for 30 min, until the moisture completely evaporated. In order to prepare three-dimensional porous biochar, the dried almond shells were placed in a ceramic crucible, and the crucible was placed in a vacuum muffle furnace for pyrolysis at a constant temperature of 300°C for 60 min. After the muffle furnace was cooled to room temperature, biochar was prepared, numbered as BD-300, as shown in Fig. 1.

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Fig. 1 Carbonized Badan wood shell (BD-300)

2.2 Preparation of Almond Shell Biochar Modified by Polyaniline Electrode

In this experiment, aniline solution is used as raw material, hydrochloric acid (HCl) as medium acid, ammonium persulfate (APS) as oxidant, and polyaniline is chemically modified on the anode electrode material. The specific methods are as follows:

First, 1 mol/L hydrochloric acid solution was prepared, and then stirred with magnetic stirrer for 30 min to mix evenly. 9.3 g aniline was added into the hydrochloric acid solution, and padanwood shell biochar was added into the solution, and stirred at room temperature 26°C for 2 h. Secondly, the solution mixed evenly above is sealed and stored, and it is placed in the refrigerator to cool to 0-5°C. An appropriate amount of ammonium persulfate (APS) was weighed and quickly added to the solution. The solution was mixed evenly with a magnetic agitator. The solution was placed on an oscillator and shook at a constant speed for 15 h, and the solution changed from light yellow to dark green. Then the paddan wood-shell biochar was removed from the solution and the excess impurities on the surface of the paddan wood-shell electrode were cleaned with deionized water. Finally, put the padan wood-shell biochar into a drying oven heated to 70°C, dry it at 70°C and get it (PANI/BD). Fig. 2 shows the electrode diagram of padan wood shell biochar modified with polyaniline. Naked eyes can clearly see the polyaniline particles attached to the surface of padan wood shell biochar.

Fig. 2 Badan wood biochar modified by PANI

2.3 Setup and Operation of MFC

2.3.1 Bacterial Culture

Use standard LB medium (tryptone 10 g·L-1, sodium chloride 5 g·L-1, yeast powder 5 g·L-1). In a sterile clean bench, weigh Rhodopseudomonas swampis 1 g After adding 100 mL of LB medium, put it into 35°C and shake at 200 r·min-1 for 14-18 h, and control the OD600 value to reach about 4.0 for use in microbial fuel cells.

2.3.2 MFC Assemble

In this experiment, a dual-chamber MFC is used, and its physical diagram is shown in Fig. 3. The anode of MFC uses biochar or carbon cloth electrodes (1 cm×1 cm) with different modification methods, and the cathode uses carbon cloth electrodes (1 cm×1 cm). MFC anolyte was prepared as above 2.3.1 1 mL of bacterial suspension, 45 mL of LB medium was added to provide carbon source

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for microorganisms and 2 mL of marine lubricating oil; the catholyte composition was 50 g/L potassium ferricyanide solution. After the microbial fuel cell was assembled, an external load was connected between the anode and the cathode with a resistance of 1 kΩ, and a data acquisition card was used to record the real-time output voltage of the MFC.

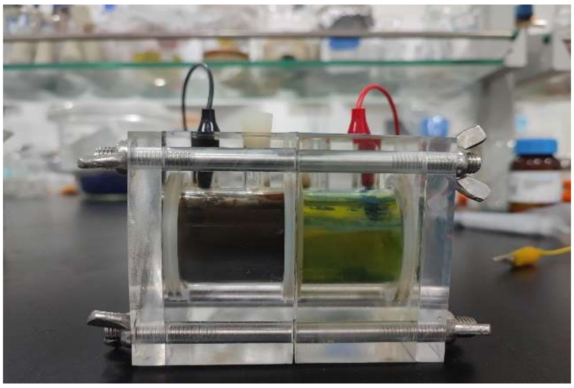

Fig. 3 Physical map of microbial fuel cell reactor

2.3.3 Analysis Method

Scanning electron microscope (SEM, Quanta 250 FEG, FEI, USA) was used to observe the structure and morphology of electrode surface materials. The absorption and reflection spectra of various morphological items were viewed using a Fourier transform infrared spectrometer to measure whether the polyaniline was successfully attached to the surface of the biochar material. The hydrophilic properties of different anode materials were measured using a contact angle meter. Use the MPS-010602 data acquisition card to record the MFC output voltage, record every 5 minutes, and measure the change of the MFC output voltage with time.

3. Results and Discussion

3.1 SEM Structure Characterization

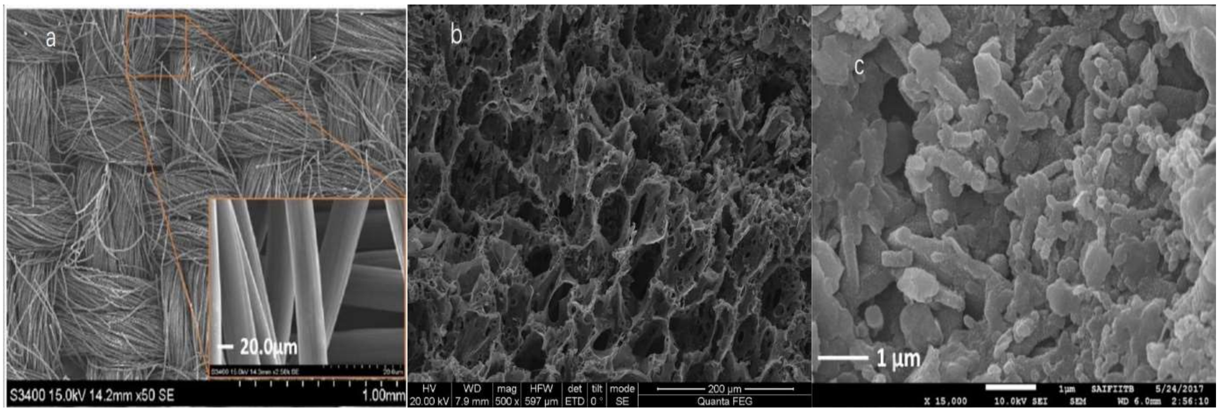

Fig. 4 Electrode microstructure: (a) carbon cloth (b) BD-300 (c) PANI/BD-300

Scanning electron microscope observed the surface structure of the electrode material selected in the experiment. According to Fig. 4 (a) carbon cloth, the surface is smooth and evenly arranged, which is not conducive to the adhesion of a large number of microorganisms. According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), the pore size smaller than 2 nm is called micropore, and the pore size larger than 50 nm is called macropore; the pore size between 2 and 50 nm is called mesopore (or mesopore). As shown in Figure (b) BD-300, it can be seen that BD-300 has a good pore structure, and the area around the pores is relatively dense, which is filled with small hollow spheres. Its large pore in cross section is conducive to the adhesion of a large number of microorganisms. As shown in Figure (C) PANI/BD-300, we can see a rough PANI coating layer

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adhere to the BD-300. A rough and scattered peas like structure can be clearly identified on PANI coated BD-300 which clearly differs from BD-300 surface. Thereby PANI/BD-300 can improve the oil degradation performance and electricity generation performance of the MFC anode chamber.

3.2 Analysis of Water Droplet Contact Angle

The hydrophilicity and hydrophobicity of the used electrode materials were measured by a water droplet contact angle instrument. Under the condition that the electrodes were kept completely dry, the three electrode materials of carbon cloth (CC), BD-300 and PANI -modified BD-300 were tested. As shown in Fig. 5, a is a CF electrode, and its water droplet contact angle θ is 115.655°, indicating that the surface of the carbon cloth has a certain degree of hydrophobicity, which is not conducive to the adsorption of electroactive microorganisms. As shown in Figure 4 b is the BD-300 electrode, and its BD-300 water droplet contact angle θ is 35.515°. After the almond is carbonized, the tar of the almond shell is basically eliminated, and many pores are formed on the surface, indicating that the carbonization The surface wettability and hydrophilicity of almonds are much better than carbon cloth. As shown in Figure 4 c is the PANI/BD-300 electrode, the contact angle θ is 8.860°, after the almond biochar is modified with polyaniline, its surface structure becomes more loose and porous, and part of the surface forms a nano-flower-like structure. The biocompatibility is better, probably because the surface contains a lot of hydrophilic -OH, and the strong interaction between the hydroxyl group and the negative charge of the strain makes it easier for microorganisms to attach. This shows that the hydrophilicity of PANI/BD-300 electrode material is better than that of CF electrode and BD-300 electrode, so it is more suitable for loading in the anode chamber of MFC.

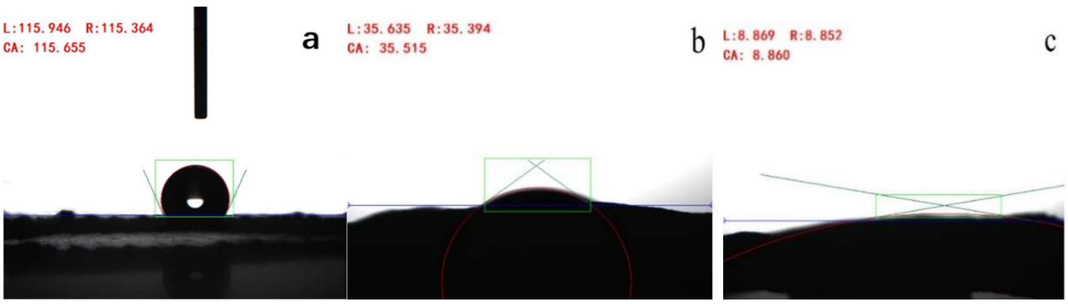

Fig. 5 Droplet contact angle of (a) carbon cloth, (b) biochar, (c) PANI/BD-300

3.3 FTIR Spectral Analysis

Grind 200 mg of potassium bromide powder particles in an agate mortar along one direction to a powder, take the mold and wipe it clean, scoop an appropriate amount of potassium bromide powder with a medicine spoon and evenly put it into the assembled mold to spread. Put the mold on the tablet press, tighten the screw, pressurize it to 1.5 t, hold it for 45 s, and then take it out. Keep a dry environment during the experiment. The light transmittance of the prepared tablet should be more than 75%, and the substrate spectrum is scanned with an infrared spectrometer. The remaining potassium bromide powder was mixed with 1 mg of BD-300 and ground into pellets in the same way. The prepared pellets were placed on a FT-IR spectrometer for average scans at a resolution of 5 cm^{-1} 32 times, Fig. 6 shows the required infrared spectrum.

Analysis of infrared spectroscopy (FTIR) can be seen. Among them, in the range of 4000-500 cm-1, the surface functional groups of almond husk biochar before and after modification changed significantly. Carbonized almond husk biochar, 2 924.1 cm-1 is the absorption vibration peak of C-H, 2351.2 cm-1 is the absorption vibration peak, and 1855.5 cm-1 is the C-H (phenyl) vibration absorption peak. The characteristic peaks in the PANI molecular chain of polyaniline modified almond shell biochar are also reflected in the infrared spectrum. 1444.7 cm-1 is the absorption vibration peak of benzene ring, 1489.0 cm-1 is the absorption vibration peak of phenyl, 1107.6 cm-1 is the absorption vibration peak of -C-N-, 1581.4 cm-1 is the absorption vibration peak of C=C. FTIR analysis proved that PANI was successfully modified on the surface of almond shell biochar.

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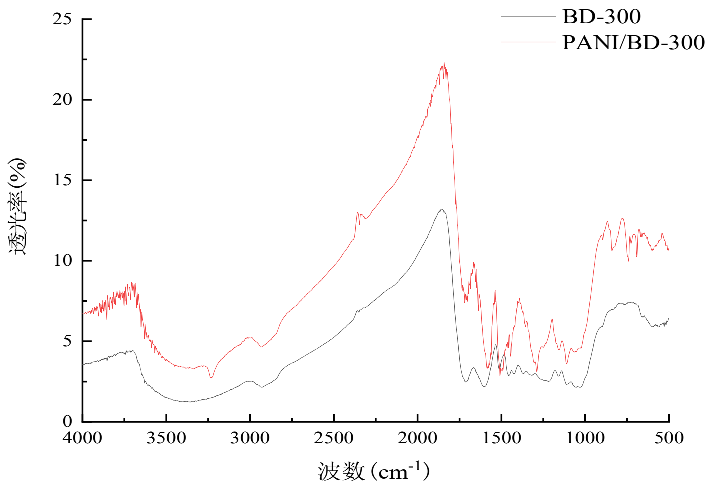

Fig. 6 FTIR spectra of BD-300 and PANI/BD-300

3.4 Output Voltage

The MFC equipped with BD-300 anode and PANI/BD-300 anode operates under a load of 1 KΩ. The curve of the output voltage versus time and the comparison of the maximum output voltage are shown in Fig. 7. When the MFC first started to run, the output voltages of the three groups of MFCs also increased with the increase of time, and began to show a downward trend at 40 h, and the running time was almost the same. The output voltage of MFC with PANI/BD-300 anode is higher than that of MFC with BD-300 anode most of the time, while the output voltage of MFC with BD-300 anode is higher than that of MFC with CC anode most of the time. The voltage is high, and the maximum output voltages of CC anode, BD-300 anode MFC and PANI/BD-300 anode MFC reach 0.58 V, 0.63 V and 0.73 V in turn. The maximum output voltage of PANI/BD-300 anode MFC is 15.87% higher than that of BD-300 anode MFC, which fully shows that the unmodified biochar has more adsorption force for microorganisms than carbon cloth, and the biochar modified with polyaniline is better than the unmodified biochar Charcoal is more adsorptive to microorganisms.

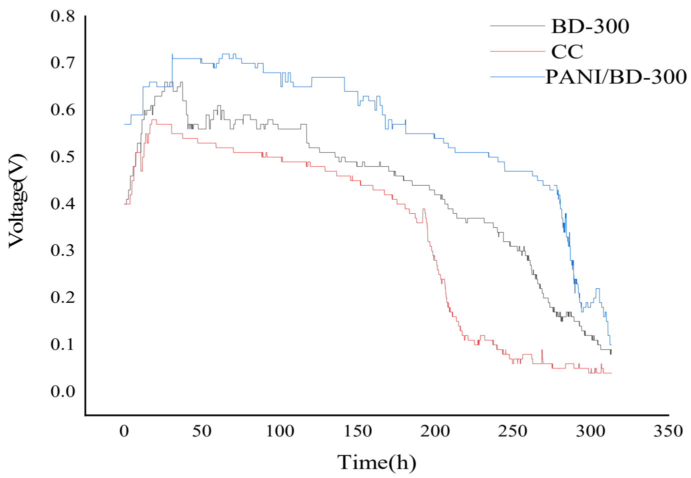

Fig. 7 Output voltage curves of MFC for BD-300 anode, CC anode and BD-300 anode

4. Conclusion

In this paper, polyaniline modified padanwood biochar electrode and its effect on the feasibility of degrading ship oily water by MFC. By observing the oily wastewater before and after the reaction, it can be seen that the oily wastewater has been effectively degraded. In terms of power generation performance, the maximum output voltage of MFC loaded with polyaniline modified electrode reached 0.73 V, which was 15.87% and 25.9% higher than that of the control group without modification of padanwood biochar electrode and common carbon cloth electrode, respectively. The experimental results show that the polyaniline material prepared by in-situ polymerization has good electrochemical performance, and the modified electrode can effectively play the advantages of good electrical conductivity of biochar and high biocompatibility of polyaniline, and can effectively degrade oily sewage from ships and significantly improve the electricity generation performance of MFC.

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