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Enhancing the Power Generation and COD Removal of Microbial Fuel Cell with ZrP-modified Proton Exchange Membrane

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An experimental system consisting of a dual chamber microbial fuel cell was constructed using simulated molasses wastewater as the anode substrate, carbon felt as the electrodes, Nafion membrane or modified Nafion membrane as proton exchange membrane. Zirconium phosphate and α-zirconium phosphate were used to modify the Nafion membrane. By testing and analysis the output voltage and the COD removal rate of the microbial fuel cell, the effects of the zirconium phosphate and α-zirconium phosphate on the performance of MFC were studied. Experimental results show that the power generation and water purification capacity of the MFC were improved significantly by modifying the proton exchange membrane with zirconium phosphate and α-zirconium phosphate, Moreover, α-zirconium phosphate modified exchange membrane has better effect. The steady output voltage of the microbial fuel cell with α-zirconium phosphate is 0.0125V, COD removal is 79.25%. The performance of microbial fuel cell was improved significantly by using zirconium phosphate modified exchange membrane.

Keywords: Microbial fuel cell; nano proton membrane; zirconium phosphate; power generation; wastewater treatment

1. INTRODUCTION

Microbial fuel cell (MFC) is a kind of bioelectrochemical device which converts chemical energy to electrical energy from what would otherwise be considered waste with the help of microorganisms [1]. The MFC technology is one of the most attractive technologies at present for renewable energy production and simultaneous wastewater treatment [2]. It can solve the problems of green energy supply and wastewater management simultaneously [3, 4].

A typical double-chamber MFC is made up of two chambers, i.e. the anode and the cathode.

Usually a proton exchange membrane (PEM) is placed between these two chambers to allow the protons produced at the anode to pass. PEM in MFCs plays an important role on MFC performance. The main duty of PEM is to separate the anode and cathode physically, allow the protons produced at the anode chamber migrate to the cathode and to prevent the migration of the anode electrolyte to the cathode chamber as well as preventing the air from moving to the anode chamber [5]. So far, Nafion is the material that is most often used as exchange membranes in MFCs, and it has become a non-official standard [6]. But there are a number of problems associated with the use of Nafion, including high oxygen permeability, poor thermal stability, biological deposition, serious water loss at high temperature and other issues, and thus restrict the performance of MFCs and further restrict MFCs' popularization and application [7].

The surface modification approach is a simple and powerful method in which a thin layer is deposited on a substrate via intermolecular forces. The modification of Nafion membrane is an effective way to improve the performance of MFCs. Lately, a lot of studies focusing on modifying the PEM using the nano particle technology are reported. Nanoparticles have good hydrophilicity. By modifying the Nafion membrane with adding some inorganic nanoparticles such as SiO_2, TiO_2 or ZrO_2, the performance of MFCs can significantly improve. Some other inorganic proton conductors such as zirconium phosphate (ZrP) are also a kind of multifunctional material that can be developed for membrane modification [8-9]. One dimensional chain of zirconium phosphate has the advantage of structural regularity, designability, higher thermal stability, good acid and alkali resistance; at the same time, it is also a good water retaining material with good electrical conductivity. In recent years, preparing proton exchange composite membranes by doping ZrP into Nafion membranes has been reported, and it is pointed out that ZrP can improve the water holding capacity of the membrane and thus improve the performance of the MFC [10-13]. The two-dimensional layered structure of α-zirconium phosphate (α-ZrP) make it not only keep the regularity and stability of inorganic zirconium phosphate, but also has the designability to introduce interlayer organic compounds [14]. α-ZrP is a good alternative material for the preparation of composite membranes.

In this paper, ZrP and α-ZrP were used to modify the nano TiO_2 and SiO_2 proton exchange membrane respectively, and the effect of these two kinds of inorganic proton conductors on the power generation capacity and the COD removal rate of MFC were tested and analyzed.

2. EXPERIMENTAL

2.1 Composition of the experimental system

The experimental system used in the study was a double chamber microbial fuel cell reactor which has an external load and a data acquisition system, as shown in Figure 1. The cathode and anode chambers are mainly made of organic glass. The volume of the cathode and anode chamber is 512 mL, and the cathode and anode chambers are separated by a piece of Nafion 117 membrane. In the reaction process, the anode chamber needs to keep in anaerobic condition, and the cathode chamber needs to keep enough oxygen as electron acceptor. Two pieces of carbon felt are used as cathode electrode and anode electrode, and the thickness of the carbon felt is 0.36 mm (WOS1002), the surface area is 6 cm

× 7 cm. The electrodes are connected with the external resistance through copper wire. In the anaerobic anode chamber, organic matter is degraded as fuel by microorganisms, and the produced electrons are captured by microorganisms and transferred to the anode to form loop current; while the proton reaches the cathode through the exchange membrane and reacts with the electron acceptor to form water. The voltage generated by the MFC is collected and transmitted through the USB data acquisition card (MPS-010602). The voltage values are recorded once every 60 seconds.

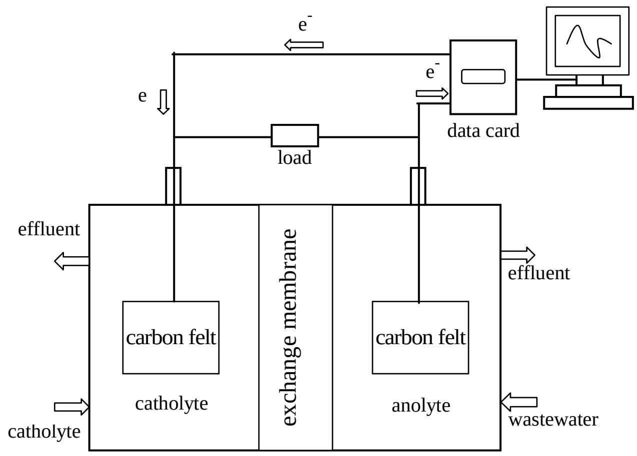

Figure 1. Experimental system of microbial fuel cell

2.2 Pretreatment of Nafion membrane

The proton exchange membrane used in the experiments is a series of Nafion 117 membranes. Before they are used in the experiments, the proton exchange membranes need to be processed to remove impurities from the surface to avoid affecting the performance of MFCs. Firstly, the proton exchange membrane was immersed in H_2O_2 with volume fraction of 5% to boil for an hour, so as to remove the organic impurities in the membrane surface; then took out the boiled membrane, rinsed it with deionized water repeatedly, and then boiled it in H_2SO_4 of 1mol/L for an hour to remove the metal impurities from the surface of the membrane; finally, the membrane was put into the deionized water to boil for an hour to remove the residual H_2SO_4 on the membrane surface, and then was put in the deionized water for later use.

2.3 Sludge cultivation

The sludge used in this study was collected from a campus lake. The appropriate amount of molasses wastewater was mixed with the sludge and then put into the culture bottle; then the closed culture bottle was put into the biochemical incubator for anaerobic cultivation at constant temperature (20℃). When the sludge in the culture bottle is suspended in a flocculent state, it is successful in culture and can be used for experimental study.

2.4 Preparation of anode substrate, catholyte, nano TiO_2 and SiO_2 membrane

In this study, molasses wastewater was used as anode feeding for MFC. Molasses is a byproduct of the sugar production process. This kind of wastewater is acidic and has high color, and is one of the most difficult and unmanageable wastewaters [15]. The mixture of molasses wastewater and the acclimated sludge was used as anolyte for MFC. The mixed solution of $K_3[Fe(CN)_6]$ and NaCl which has good power generation capacity and water purification effect was used as catholyte for MFC, and the preparing method of catholyte is similar to what were described the previous work [16].

2.5 Preparation of ZrP nano TiO_2 and SiO_2 membrane

The preparing method of nano TiO_2 and SiO_2 membrane has been described in our former work [17]. When preparing ZrP nano TiO_2/SiO_2 composite membrane, firstly put the nano TiO_2 and SiO_2 composite membrane into drying cabinet to dry for 1h at 80°C; then, immerse the dried membrane in a mixture of 0.06 $mol \cdot L^{-1}$ $ZrOCl_2 \cdot 8H_2O$ and methanol solution for 0.5 h, and then put the immersed membrane in 8% phosphoric acid solution to soak for 1h [18]. Repeat the above steps for five times, then put the membrane into the drying cabinet to dry for 1 h at 80℃; then, soak the membrane in H_2SO_4 solution of 1.5mol/L for 1 h to finish protonation of the membrane. Finally, rinse the membrane with deionized water repeatedly and then place it in deionized water for putting on standby.

The method for preparing α-ZrP composite membrane is as follows: put 5.5 g zirconium hydroxide into 80 mL of deionized water; then add 5 mL of 37% HCl and 5 mL of 40% HF to the solution, add 46 mL of 85% phosphoric acid to the solution, and then stir for 4d with the magnetic stirring. The product is filtered and washed with deionized water until PH≥5, and the white matter α-ZrP can be obtained by drying the filter at 60℃ for 8 h [19].

Take the prepared α-ZrP from the dring oven and dissolve it in deionized water, and then immerse the nano TiO_2/SiO_2 composite membrane in it. After soaking 3 h, put the membrane into the drying oven again and dry for 24 h at 60℃. Soak the dried membrane in 0.5 mol/L H_2SO_4 solution for 1 h to make the membrane protonated. After washing membrane repeatedly with deionized water, put the membrane in deionized water for later use.

3. RESULTS AND DISSCUSSION

3.1 Effect of ZrP nano TiO_2/SiO_2 composite membrane on MFC

The contrast output voltage curves of MFCs with ordinary Nafion membrane and ZrP-modified nano TiO_2/SiO_2 composite membrane are shown in Figure 2, where ‘ZrP’ denotes ZrP nano TiO_2 and SiO_2 membrane, and ‘Nafion’ denotes ordinary Nafion membrane. Molasses wastewater was used as anolyte of MFC in these contrast experiments.

It can be seen from Figure 2 that the steady state voltage of MFC with common Nafion membrane and ZrP nano TiO_2/SiO_2 composite membrane are 0.0072V and 0.0082V respectively, which means the steady output voltage of MFC with ZrP nano TiO_2/SiO_2 composite membrane has increased by 13.89% compared with that with common Nafion membrane. In addition, the conductivities of common Nafion membrane and ZrP nano TiO_2/SiO_2 composite membrane at 20℃ were measured to be 0.016 S/cm and 0.0206 S/cm, respectively, which mean that the conductivity of the modified ZrP nano TiO_2/SiO_2 composite membrane is 28.75% higher than that of the ordinary Nafion membrane. This is mainly due to the stability and water retention of the membrane are improved by modifying the Nafion membrane with nano SiO_2 particles, and thus the proton conductivity is enhanced; meanwhile, as a kind of inorganic proton conductor material, ZrP has high thermal stability and good acid and alkali resistance, it also has good proton conductivity.

It can also be seen from Figure 2 that the output voltage of the MFC using ZrP nano TiO_2 and SiO_2 membrane as the exchange membrane has a decreasing trend after stability. The main reason for this is that a certain amount of ZrP moved out of the membrane after a certain period of immersion, thus, the proton conductivity of MFC decreased.

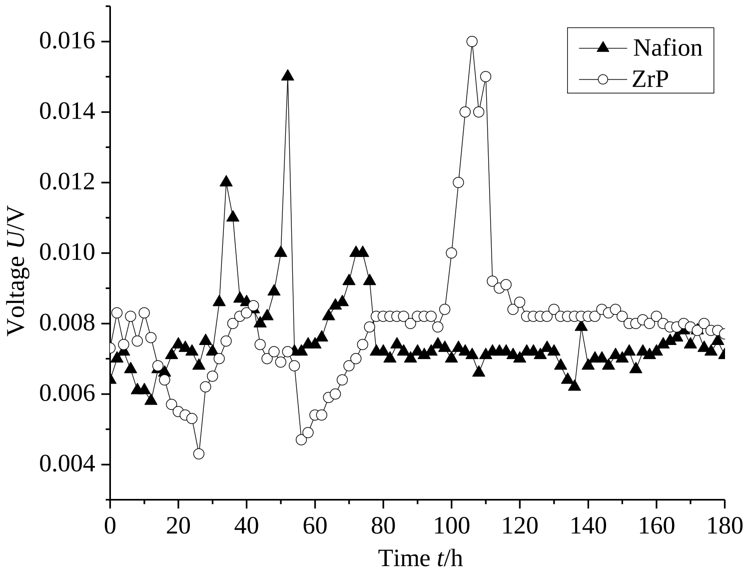

Figure 2. Voltage comparation between ZrP nano membrane and common Nafion membrane

3.2 Effect of α-ZrP nano TiO_2/SiO_2 composite membrane on MFC

The output voltage curves of MFCs with ordinary Nafion membrane and α-ZrP nano TiO_2/SiO_2 composite membrane are shown in Figure 3. It can be seen that the steady-state power generation of the MFC with α-ZrP nano TiO_2 and SiO_2 membrane was significantly higher than that of MFC with normal Nafion membrane. The steady voltage of MFC with α-ZrP nano TiO_2 and SiO_2 membrane is 0.0125V, which is increased by 73.61% compared with that of the Nafion membrane. By comparing Figure 2 and Figure 3, it can also be seen that the output voltage of the MFC with α-ZrP nano TiO_2 and SiO_2 membrane is obviously higher than that of MFC with ZrP nano TiO_2 and SiO_2 membrane, the steady-state output voltage of the former is 52.43% higher than that of the latter; what's more, the steady voltage of MFC with α-ZrP nano TiO_2 and SiO_2 membrane did not decrease significantly. This is because the α-ZrP not only has the same chemical stability and acid and alkali resistance as ZrP, but also has more regular structure. The composite structure formed by ionic bond and hydrogen bond is more regular, and its performance is more stable. So, the modification of proton exchange membrane with α-ZrP has a good effect on improving the power generation capacity of MFC.

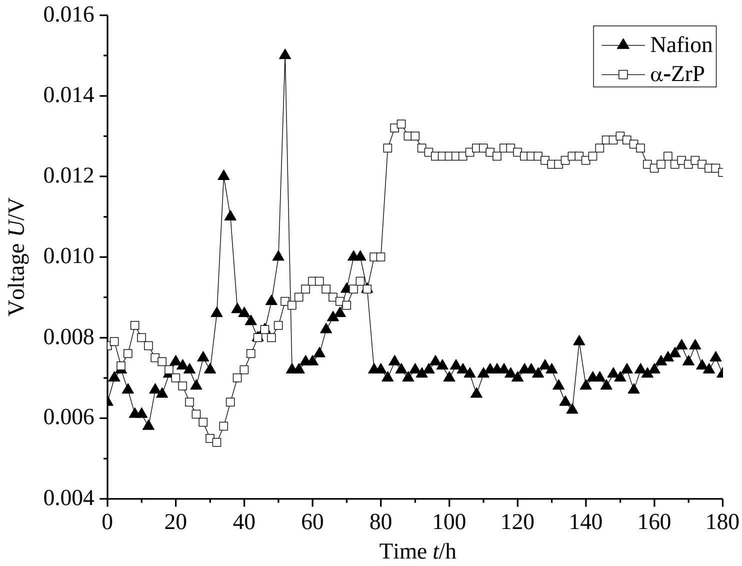

Figure 3. Voltage comparation between α-ZrP nanometer membrane and common Nafion membrane

The power generation capacity of the MFC with α-ZrP nanometer membrane can be compared with some other MFCs. Mokhtarian *et al.* use a Nafion112-polyaniline composite membrane in MFC, by which the maximum power density was 124.03mW/ m^2 [20]; Ghasemi *et al.* fabricated self-made Nafion and activated CNF(ACNF)/Nafion nanocomposite membranes in MFC, and its maximum power density was 57.6mW/m^2 [21]; Zhang *et al*. use PVAc-g-PVDF-coated cotton fabric membrane to enhance performance of MFC, and the highest power of this MFC were about 400 mW/m^2 [22]. The power density curves of MFC with α-ZrP nanometer membrane are shown in Figure 4. It can be seen that the steady power density of MFC with the proposed α-ZrP nanometer membrane was about 745mW/m^2, which was obviously higher than the maximum power of most general MFCs. This shows that the α-ZrP modified membrane can play a good role in improving the power generation performance of MFC.

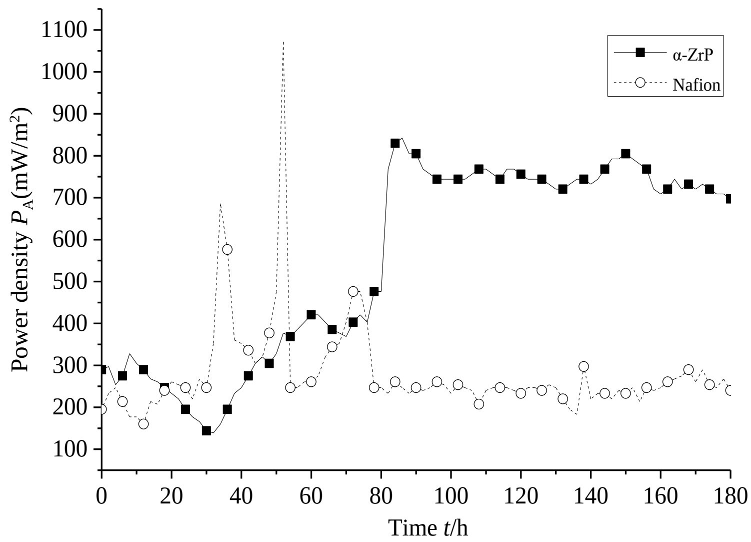

Figure 4. Power density curves of MFC with α-ZrP nano membrane and Nifion membrane

3.3 Analysis of the cathode and anode pH value

Microbial metabolic decomposition in MFCs will lead to changes in pH values in the cathode and anode chambers. The normal operation of the MFC can be judged by the change of the pH value in the cathode and anode chambers. Figures 5 and 6 are the pH curves of anode and cathode chambers for MFC with ZrP and α-ZrP nano membranes. No matter which of these two membranes are used, the anode pH value of the MFC has always increased with the reaction process, but the anode pH value of the MFC with ZrP nano membranes was lower while the anode pH value of the MFC with α-ZrP nano membranes approached to 7. This means that the anolyte of MFC with α-ZrP nano membranes gradually becomes neutral with the output voltage gradually stabilized.

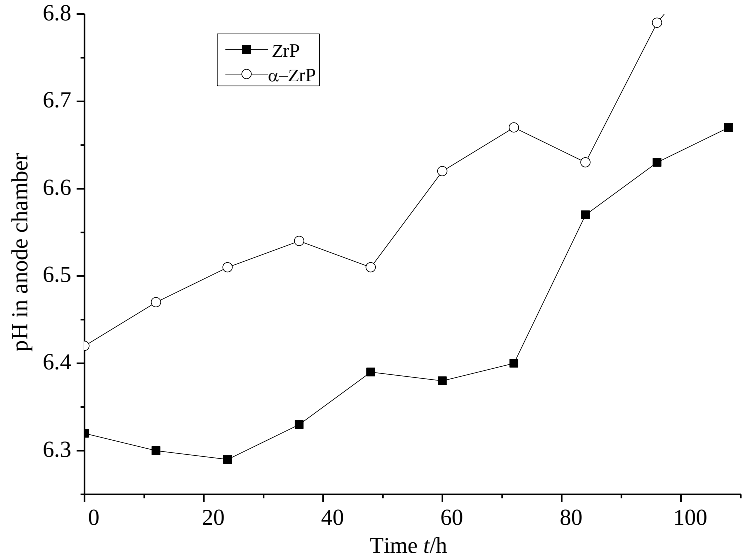

Figure 5. Anode pH comparation between ZrP nano membrane and α-ZrP nano membrane

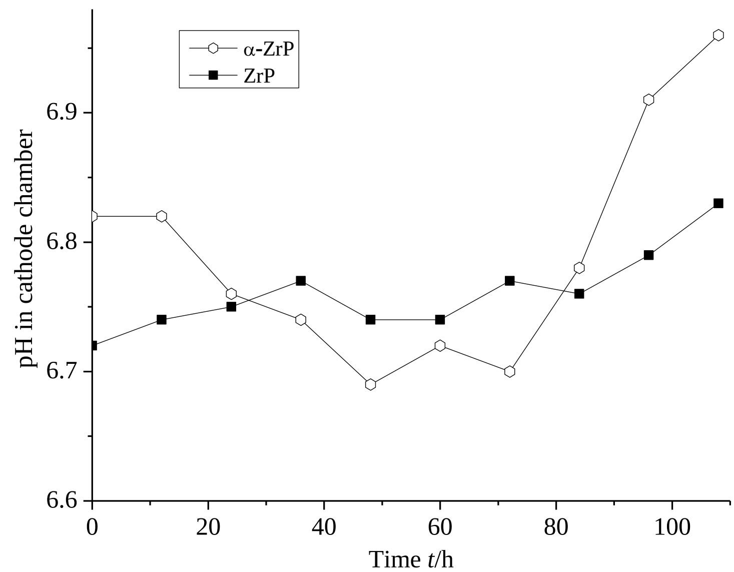

Figure 6. Cathode pH comparation between ZrP nano membrane and α-ZrP nano membrane

Compared Figure 5 with Figure 6, it can be seen that the hydrogen ion concentration on both sides of the α-ZrP nano TiO_2 and SiO_2 membranes varies greatly, while the hydrogen ion concentration on both sides of the ZrP nano TiO_2 and SiO_2 membranes is slightly different. This shows that in the process of proton transfer, α-ZrP nano TiO_2 and SiO_2 membrane is more conductive to the transfer of proton, and the conductivity is better.

3.4 Analysis of water absorptivity of the membrane

The water absorptivity of the proton exchange membrane will directly affect the power generation performance of MFCs. The higher the water absorptivity of the membrane, the better its conductivity. In order to compare the water absorption properties of ZrP nano TiO_2 and SiO_2 membrane and α-ZrP nano TiO_2 and SiO_2 membrane, the water absorption rate of two kinds of membranes were calculated and the results are shown in Table 1.

It can be seen from Table 1 that the water absorptivity of ZrP nano TiO_2 and SiO_2 membrane is 29.91%, the water absorption of the α-ZrP nano membrane is 52.88%, the water absorption of α-ZrP nano TiO_2 and SiO_2 membrane is about 2 times of that of ZrP nano membrane. It is further explained that the conductivity of α-ZrP TiO_2 and SiO_2 proton membrane is better than that of ZrP nano TiO_2 and SiO_2 membrane.

Table 1. Water absorption of the two different membrane

	ZrP nano TiO_2 and SiO_2	α-ZrP nano TiO_2 and SiO_2
wet weight W_1 (g)	5.95	5.58
dry weight W_0 (g)	4.58	3.65
water absorption rate (%)	29.91%	52.88%

3.5 Analysis of water quality

MFCs using wastewater as fuel can not only produce electricity by degrading the organic compounds, but also can purify the wastewater effectively. Table 2 shows the influent and effluent COD values of MFCs with the three different proton exchange membranes. It can be seen that all the effluent COD values of MFCs with the three different proton exchange membranes are significantly decreased compared with the influent wastewater, but the MFC with α-ZrP nano TiO_2 and SiO_2 membrane have best purifying effect. The COD removal rate of MFCs with Nafion membrane, ZrP nano TiO_2 and SiO_2 membrane and α-ZrP nano TiO_2 and SiO_2 membrane are 38.1%, 70.98%, 79.25%, respectively. The removal rate of COD from molasses wastewater by MFC with ZrP or α-ZrP modified membrane was significantly higher than that of MFC with conventional Nafion membrane. Compared with the three kinds of MFC with three different membranes, MFC with α-ZrP nano TiO_2 and SiO_2 membrane not only has the best power generation capacity, but also has the best water purification effect.

The COD removal of this MFC can be compared with the former experimental results. In the early stage of work, the research group had studied treating molasses wastewater by MFC with MnO_2-modified electrode. Corresponding to the three cases of unmodified carbon cloth cathode, MnO_2-

loaded carbon cloth cathode and MnO_2-loaded carbon felt cathode, the stability values of COD removal rates of MFC treating molasses wastewater were 24.15%, 24.91%, and 35.53%, respectively [23]. Compared with the COD removal rate of the same size MFC with MnO_2-Modified Cathode, the MFC with ZrP or α-ZrP nano TiO_2 and SiO_2 membrane give better water purification effect. This indicates that the method of modifying proton exchange membrane is more effective than the method of modifying electrode in improving the water purification effect of MFCs, and this also indicates that the proton exchange membrane plays an important role in the process of generating power and treating wastewater by MFC.

Table 2. COD of MFC with different membrane

	Nafion	ZrP nano TiO_2 and SiO_2	α-ZrP nano TiO_2 and SiO_2
influent COD（mg/L）	13300	13300	13300
effluent COD（mg/L）	8220	3860	2760
COD removal rate (%)	38.1%	70.98%,	79.25%

The COD removal of this MFC can also be compared with some frequently-used treatment methods of molasses wastewater. The COD removal rate of molasses wastewater by the anaerobic pond were about 46.0% [24]; the COD removal rate of molasses wastewater by the combined process of EGSB-MFCBAF reached 53.2% [25]; and the highest COD removal efficiencies of molasses wastewater of the SBR system is 65.2±2.5% [26]. After comparison, it is found that the MFC with ZrP modified membrane has better effect on COD removal than the conventional molasses wastewater treatment method.

4. CONCLUSIONS

The membrane modification technology can effectively improve the power generation capacity and COD removal rate of MFCs. ZrP has excellent water retention and good electrical conductivity. By using ZrP and α-ZrP to modify the nano TiO_2 and SiO_2 proton membrane, the power generation capacity and COD removal rate of MFC can be significantly improved. Among them, the performance of MFC with α-ZrP modified nano TiO_2 and SiO_2 proton membrane is the best. The steady-state power generation voltage of MFC with α-ZrP modified membrane is 0.0125V, which is 73.61% higher than that of MFC with common Nafion membrane, and 52.44% higher than that of MFC with ZrP modified membrane. The COD removal rate of MFC with α-ZrP modified proton membrane can reach 79.25%, which is 41.15% higher than that of MFC with common Nafion membrane, and 8.27% higher than that of MFC with ZrP modified membrane. The modification of proton exchange membrane with zirconium phosphate has good effect on the performance improvement of microbial fuel cell.

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