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Effect of Heteropolyacid and Heteropolyacid Salt on the Performance of Nanometer Proton Membrane Microbial Fuel Cell

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To improve the performance of microbial fuel cells, membrane modification of microbial fuel cell with heteropolyacid and heteropolyacid salt is studied. Using lake water and molasses wastewater as the anode substrate and the mixed solution of $K_3[Fe(CN)_6]$ and NaCl as catholyte, the power generation performance and wastewater treatment effect of microbial fuel cells with common Nafion membrane, heteropolyacid modified Nafion membrane and heteropolyacid salt modified Nafion membrane were studied. The experimental results show that the membranes modified by heteropolyacid and heteropolyacid salt have a better water retention capacity than common Nafion membrane, and the microbial fuel cell with modified proton exchange membrane by heteropolyacid salt has better power generation performance and better sewage treatment effect, in addition, the power generating capacity of molasses wastewater is much higher than that of lake water. The water absorption rate of the heteropolyacid nano membrane is 11.59%, and the water absorption rate of heteropolyacid salt nano membrane is 23.26%. The generating ability and the purifying effect of the microbial fuel cell with molasses wastewater as the anode substrate and heteropolyacid salt Nafion membrane as the proton exchange membrane reached the best state, in which the output voltage is 0.0356V and the removal rate of COD is 53.1%.

Keywords: microbial fuel cell; nanometer proton membrane; heteropolyacid; heteropolyacid salt

1. INTRODUCTION

With the rapid growth of population and rapid development of economy, problems of environmental pollution and resources shortage are becoming more and more serious, and it has become a perplex in the development of human beings [1]. Traditional fossil fuels have been overexploited in the past and are gradually becoming exhausted. This situation is potentially a crisis of energy shortage. Meanwhile, in the course of using fossil fuel, large amounts of gas and solid waste will be produced to pollute the environment [2]. So, the development of clean and renewable energy which can replace the fossil energy has become a focus of the whole world [3-5].

Microbial fuel cell (MFC) is a kind of biological reaction device which converts chemical energy to electrical energy from what would otherwise be considered waste with the help of microorganisms. In recent years, the microbial fuel cell has become a focus as a new type of biomass energy source [6, 7]. Microbial fuel cell use organic waste as raw material for power generation, produce electrical energy in wastewater treatment process, and the power generation process does not produce any harmful substances to the environment, and thus it can solve the problems of green energy supply and wastewater management simultaneously, so it is regarded as a kind of sustainable energy which has the advantages of high efficiency, low energy consumption, clean and environmental protection [8-11], and has become a common focus of the two research areas of environment and energy [12-14]. In recent years, researches of microbial fuel cell have received great progress, but its popularization and application is still faced with the problems of low power generation capacity, unstable system, high cost and so on.

In microbial fuel cell, the separator, which is in charge of separating anode and cathode chamber and simultaneously transferring the proton from anode to cathode, is generally considered to be the most critical component to ensure the effective and sustainable development of a microbial fuel cell. Due to its vantage of high conductivity and low internal resistance, proton exchange membrane (PEM) has become the most widely used separator in MFCs [15-18]. The most common used proton exchange membrane in fuel cells is the perfluorosulfonated acid membrane such as the Nafion series membranes produced by DuPont Company. Nafion membranes have the advantages of high proton conductivity, good chemical stability, good mechanical properties and so on [19], but there are still many shortcomings such as high oxygen permeability, poor thermal stability, biological deposition, serious water loss at high temperature and other issues, and thus restrict the performance of microbial fuel cells and further restrict its popularization and application [20].

The modification of Nafion membrane is an effective way to improve the performance of microbial fuel cells. Lately, there are a lot of studies focusing on the improvement of the proton exchange membrane using the nano particle technology [21]. The nanometer material composite membrane is a new type of membrane doped with nano particles such as SiO_2, TiO_2, ZrO_2 and so on [22]. Nanometer material composite membranes improve the water retention capacity due to their nano particle size and large surface area, and they have the advantages of strong proton transfer capability, low price, weak biological deposition, good thermal stability and so on, thus become one of the most promising materials for proton exchange membrane [23-25].

Heteropolyacids (HPAs) are a kind of inorganic proton conducting materials with high proton conductivity at room temperature. The water holding capacity at high temperature and the ability to act as a super acid of such compounds make them good proton conductor [26]. By modifying Nafion membranes using HPAs as conductive material, stable compounds can be produced, and thus the adaptability of the proton exchange membrane to the temperature and humidity can be improved [27].

Higher proton conductivity can be obtained by adding HPAs to membranes modified by nanometer particles. But, HPAs are highly water-soluble substances that will move out from the membranes after long time running, and this will lead to a decline in performance [28]. To solve this kind of problems, HPA is generally converted into Heteropolyacid salt which dissolve difficultly in water and then use for doping modification [29]. By this way, high proton conductivity can be guaranteed, and the water solubility can also be reduced effectively.

In this paper, two kinds of HPAs, silicotungstic acid and phosphomolybdic acid, and two kinds of heteropolyacid salts, phosphomolybdate and silicotungstate, are used to modify nano TiO_2 and SiO_2 proton exchange membrane, and the effects of HPAs and heteropolyacid salt on the power generation performance and water purification of microbial fuel cell was compared.

2. EXPERIMENTAL

2.1 Structure of the experimental system

The experimental system is mainly composed of three parts, which are a dual chamber MFC reactor, an external load and a data acquisition system, as shown in Fig.1.

The double chamber microbial fuel cell mainly consists of a cathode chamber, an anode chamber, a proton exchange membrane, a cathode and an anode. The chamber is made of organic glass. The cathode chamber and the anode chamber are separated by a proton exchange membrane (Nafion 117), and each chamber has the volume of 500 mL. The electrode materials of cathode and anode are carbon cloth (WOS1002), the thickness is 0.36 mm, and the surface area is 6 cm × 7 cm. The electrodes are connected with the external resistance through the copper wire to form a complete closed circuit.

The voltage generated by the microbial fuel cell is collected and transmitted through the USB data acquisition card (MPS-010602), and recorded once every 60 seconds, and stored, processed and displayed by computer.

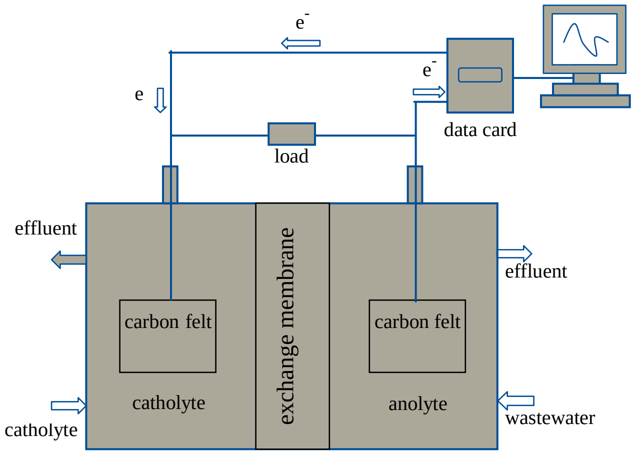

Figure 1. Experimental system of microbial fuel cell

2.2 Preparation of nano TiO_2 and SiO_2 composite membrane

The nano TiO_2 and SiO_2 composite membrane was prepared by following steps: place a Nafion membrane with the size of 10 cm × 10 cm in a methanol solution of 3:1 volume ratio for 1 h to make the membrane surface swelling and thus to provide gaps for the precursor's entry; prepare a mixed solution by mixing with 3.40 g 10 mmol butyl titanate, 2.08 g 10 mmol ethylsilicate and 4.96 g 21.2 mmol KH570; taking the swelling membrane out from the methanol solution and put it into the mixed solution; after 3 h dipping, take it out and put it into a constant temperature drying oven at 60℃ for 24 h. Put the treated composite membrane into a 0.5 mol/L H_2SO_4 solution for 1 h so as to remove the metal ion impurity. After vacuum drying, the composite membrane was dried to constant weight and ready for experimental use.

2.3 Preparation of phosphomolybdic heteropolyacid salt

Dissolve 9.03 g 4 mmol phosphomolybdic acid and 2.8 g 8 mmol octadearyl dimethyl ammonium chloride into 40 mL ethanol to react for 2 h at 60℃, and then after inspissation and filtration, dry it for 10 h at 80℃, and then the green powder of phosphomolybdic heteropolyacid salt was received [30, 31].

2.4 Preparation of Silicotungstate heteropolyacid salt

Dissolve 5 g silicotungstic acid into 5 mL deionized water, add about 10 mL 0.1 $mol \cdot L^{-1}$ KOH to the solution for acid-base neutralization, then carry out heating evaporation, crystallization and recrystallization, and then the silicotungstate heteropolyacid salt compounds can be obtained [32].

2.5 Preparation of anode substrate

The anode solutions of MFC used in the experiments are two kinds of raw materials called lake water and molasses wastewater. The lake water was collected from an artificial lake of a campus. The molasses wastewater was prepared according to the following formula: 3.13 g/L $NaHCO_3$, 0.31 g/L NH_4Cl, 6.338 g/L $NaH_2PO_4 \cdot H_2O$, 6.8556 g/L $Na_2HPO_4 \cdot 12H_2O$, 0.13 g/L KCl, 0.2 g/L $MgSO_4 \cdot 7H_2O$, 0.015 g/L $CaCl_2$, 0.01 g/L $MnSO_4 \cdot H_2O$, and 3 g/L brown sugar.

2.6 Microbial cultivation

The microorganisms used in the anode chamber were prepared by the sludge cultivation. The sludge was collected from a campus lake at 0.5 m depth. In conditions of anaerobic, some prepared lake water or molasses wastewater which was used as anode liquor and some nutrient elements necessary for the growth of microorganisms (such as carbon, nitrogen, phosphorus, etc) and the collected sludge were put together into a culture flask, and then were put in the biochemical incubator for acclimatization under the constant temperature of 20℃. Microorganism’s acclimatization is regarded successful when the sludge in the culture flask flocculent suspended.

2.7 Preparation of catholyte

The catholyte for MFC used in this experiment is the mixed solution of $K_3[Fe(CN)_6]$ and NaCl. Dissolve 32.9 g 0.2 $mol\cdot L^{-1}$ ferricyanide with PBS solution, hold it in a 500 mL volumetric flask by PBS solution; prepare a 11.7g 0.4 $mol\cdot L^{-1}$ NaCl solution and hold it in another 500 mL volumetric flask; finally, put the ferricyanide solution and NaCl solution to the microbial fuel cell’s cathode chamber at the ratio of 1:1 to use as the catholyte.

2.8 Preparation of composite membrane

Weigh 1.825 g phosphomolybdic, 2.88 g silicotungstate and 0.496 g KH-570 respectively, make a mixed solution by dissolving and stirring with the right amount of ethanol. Immerge the nano TiO_2 and SiO_2 proton exchange membrane into the mixed solution, maintain the temperature at a constant of 30℃ for 3 minutes; then take it out to air-dry, and then put it in a vacuum drying oven to dry it for 6 h at 60℃. Finally, a heteropolyacid nano composite membrane was finished.

Weigh 1.825 g phosphomolybdic heteropolyacid salt and 2.88 g silicotungstate heteropolyacid salt respectively, make a mixed solution by dissolving and stirring them with the right amount of ethanol. Treating the nano TiO_2 and SiO_2 proton exchange membranes with the same method described above, and finally a heteropolyacid salt nano composite membrane is cranked out.

3. RESULTS AND DISSCUSSION

3.1 Effect of heteropolyacid nano membrane on MFC

The output voltage curves of MFC with ordinary Nafion membrane and nano TiO_2 and SiO_2 heteropolyacid membrane corresponding to lake water or molasses wastewater as anode substrate are shown in Fig.2 and Fig.3 respectively.

It can be seen that the generated voltage of MFC with heteropolyacid nano TiO_2 and SiO_2 membrane is significantly higher than that of ordinary Nafion membrane. The steady voltage of Nafion membrane MFC using lake water as the anode substrate is 0.0054V, but steady state voltage of heteropolyacid nano TiO_2 and SiO_2 membrane MFC is 0.0180V, and is 233.33% higher than the former.

When using molasses wastewater as anode substrate, the steady state voltage of Nafion membrane MFC is 0.0072V, the steady voltage of heteropolyacid nano TiO2 and SiO2 membrane MFC is 0.0220V, and the output voltage of the latter is increased by 205.56% than that of the former. The introduction of nano SiO2 particles into the Nafion membrane improved the stability and water retention of the membrane, and thus proton conductivity was improved [33]. Meanwhile, heteropolyacid itself is a good proton conductor, its involvement further improve the proton conductivity of the exchange membrane [34-35]. Contrast of voltage values between the lake water and the molasses wastewater show that the generating capacity of molasses wastewater is higher than the lake water, this is mainly due to the high concentration organic of molasses wastewater gives better potential for biomass power. Further measurement displays that the conductivity of the heteropolyacid nano TiO2 and SiO2 membrane is 0.0224 S/cm at 20℃, which is apparently higher than that of the existing silicotungstic acid organic-inorganic composite membrane with the conductivity of 0.0014 S/cm at 20℃[36].

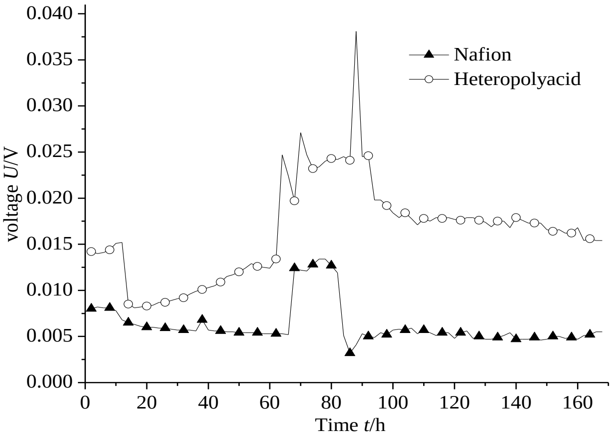

Figure 2. Voltage of MFC with heteropolyacid nanometer membrane and Nafion membrane when anode substrate is lake water

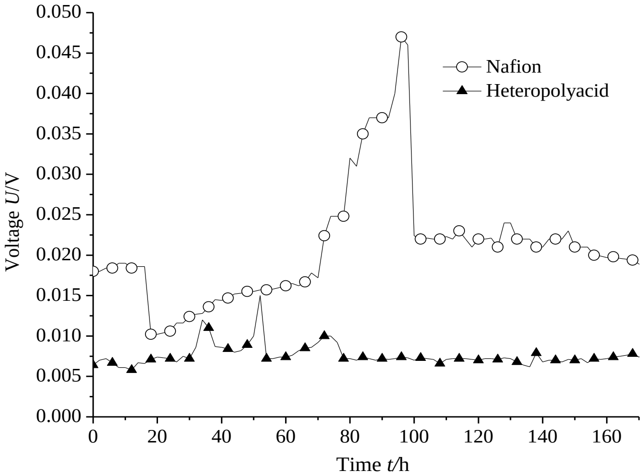

Figure 3. Voltage of MFC with heteropolyacid nanometer membrane and Nafion membrane when anode substrate is molasses wastewater

It can also be seen from Fig.2 and Fig.3 that the output voltage of MFC with heteropolyacid nano TiO_2 and SiO_2 membrane decreased after stabilization. This is because the heteropolyacid is soluble in water, after long time soaking, the heteropolyacid moved out from the membrane, the proton conductivity decreased, and then cause the late output voltage not to keep stable but to show a downward trend.

3.2 Effect of heteropolyacid salt nano membrane on MFC

Contrast voltage curves of MFC with heteropolyacid salt nano membrane and Nafion membrane are shown in Fig.4 and Fig.5. It can be seen that, when the lake water is used as the anode substrate, the steady voltage of MFC with heteropolyacid salt nano membrane is 0.0272V, and is increased by 403.7% than that of Nafion membrane; when the molasses wastewater is used anode substrate, the steady voltage of MFC with heteropolyacid salt nano membrane is 0.0356V, and is increased by 406.9% than that of Nafion membrane.

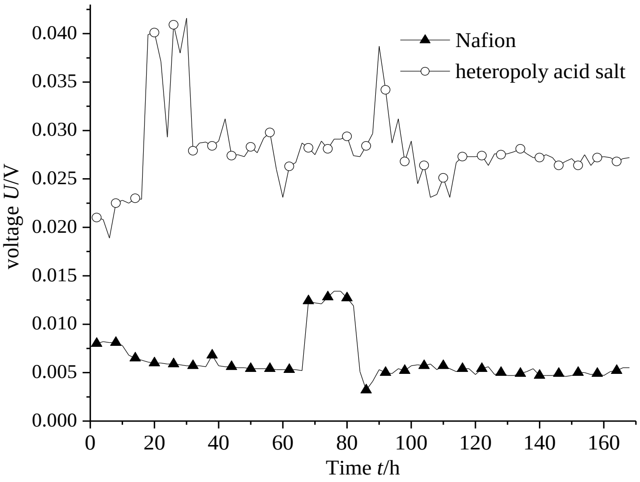

Figure 4. Voltage of MFC with heteropolyacid salt nanometer membrane and Nafion membrane when anode substrate is lake water

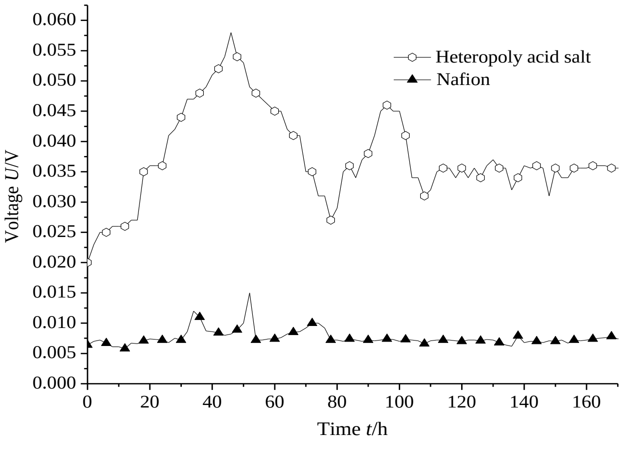

Figure 5. Voltage of MFC with heteropolyacid salt nano membrane and Nafion membrane when anode substrate is molasses wastewater

Heteropolyacid salt has better water retention properties, so the water absorption capacity improved, and the proton conductivity enhanced. In addition, the introduction of metal materials is also useful for improving the conductive properties. On the other hand, it can be seen from Fig.4 and Fig.5, the voltage of MFC with heteropolyacid salt nano membrane presents no downward trend once it has reached steady state. This is because the heteropolyacid salt is not as easy to dissolve in water as the heteropolyacid, so the heteropolyacid salt cannot move out from the membrane abundantly after long time soaking, and thus the conductive performance will not be caused to decline.

By comparing Fig.2 with Fig.4 and Fig.3 with Fig.5, it can be seen that the power generating capacity of MFC with heteropolyacid salt nano membrane is better than that of heteropolyacid nano membrane. When the anode substrate is the lake water, the steady output voltage of MFC with heteropolyacid salt nano membrane is increased by 51.1% compared with that of heteropoly acid nano membrane, and when the anode substrate is molasses wastewater, this index is increased by 61.8%.

3.3 Analysis of water absorption of the membrane

The water absorption of the membrane will directly affect the power generation performance of microbial fuel cells. When the water content of the membrane is higher, the migration coefficient of protons is higher than that of water, and its electrical conductivity is higher. The higher the water absorption performance of the membrane, the better the conductive performance of the membrane. In order to compare the water absorption properties of nano TiO_2 and SiO_2 heteropolyacid membrane and heteropolyacid salt nano TiO_2 and SiO_2 membrane, water absorption of the two kinds of membrane were calculated. The water absorption of a membrane can be determined by measuring the weight change of the membrane before and after the hydration [37]. First, baking the membrane in the oven at 80℃ for 24h, then take out the membrane and weigh it after it has be cooled to room temperature, and record this weight of the dry membrane is W_0; then placed the membrane in the deionized water to soak for 24h at room temperature, take out the membrane and weigh it, and record this weight of the wet membrane is W_1, then the water absorption of the membrane is

$$\Delta W(\%)=\frac{W_1-W_0}{W_0}\times 100\% \qquad (1)$$

The water absorption test data for the two kinds of different membranes are shown in Table 1. The water absorption rate of the heteropolyacid salt nano membrane is 23.26%, and the water absorption rate of heteropolyacid nano membrane is 11.59%.

Table 1. Water absorption of different membrane

	heteropolyacid	heteropolyacid salt
wet weight W_1 (g)	3.66	3.55
dry weight W_0 (g)	3.28	2.88
water absorption rate ΔW (%)	11.59	23.26

The water absorption rate of heteropolyacid salt nanomembrane is about two times of the water absorption rate of heteropolyacid nano membrane. This is a strong support for the experimental result which shows the conductive performance of heteropolyacid salt nano membrane is better than that of the heteropolyacid nano membrane.

Water absorption rate of heteropolyacid salt nano membrane is also higher than some other composite membrane. Data displays that the water absorption rate of composite membrane deposited with Chitosan (CS)/silicotungstic acid (SiWA) is lower than 10% at the usual temperature (25℃) [38].

3.4 Water quality analysis

Tables 2 shows the influent and effluent COD corresponding to the three kinds of different exchange membranes, where the anode influent is lake water, and Table 3 shows the influent and effluent COD in which the anode influent is molasses wastewater. It can be seen from table 2, when the lake water is anode influent, the effluent COD of MFC with Nafion membrane is slightly lower than the influent COD, but the effluent COD of MFC with heteropolyacid membrane is significantly higher than the influent COD. This is because the heteropolyacid is easily soluble in water. After long time soaking, the heteropolyacid moved out from the membrane and pollute the anode solution, thus made the effluent COD increased. When heteropolyacid salt was used as the exchange membrane of the MFC, the effluent COD is slightly higher than the influent, which is mainly because the heteropolyacid salt can also move out from the membrane, but the amount of outmigration was significantly reduced compared with heteropolyacid, and did not cause too much pollution on the anode solution. Another reason for the low COD removal rate of MFC using lake water as fuel is that the COD content of the lake water itself is low, an thus degradable organic matter is very little.

When use the molasses wastewater as fuel, the effluent CODs were all declined after the reaction, as it can be seen from Table 3. The COD removal rate of MFC with Nafion membrane is 38.1%, the COD removal rate of MFC with heteropolyacid membrane is 46.2%, and the COD removal rate of MFC with heteropolyacid salt membrane is 53.1%. By analysis of experimental data, we can know that the MFC with heteropolyacid salt nano membrane has a better effect of wastewater treatment.

Molasses wastewater belongs to high-concentration organic wastewater. The existing main treatment methods of molasses wastewater are some terminal degradation methods, by which the COD removal rate are usually low. For example, chemical oxidation with ozone can provide as much as 15-25% COD reduction, while the COD removal efficiencies by a factual anaerobic pond were about 46.0% [39]. So, MFC is an alternative method for molasses wastewater treatment.

Table 2. Influent and effluent COD of MFC using molasses wastewater as anode substrate

	Nafion	heteropolyacid	heteropolyacid salt
influent (mg/L)	530	530	530
effluent (mg/L)	510	925	553

Table 3. Influent and effluent COD of MFC using lake water as anode substrate

	Nafion	heteropolyacid	heteropolyacid salt
Influent (mg/L)	13300	13300	13300
Effluent (mg/L)	8220	7143	6240
COD removal rate (%)	38.1%	46.2%	53.1%

4. CONCLUSIONS

Microbial fuel cells using heteropolyacid nano TiO_2 and SiO_2 membrane and heteropolyacid salt nano TiO_2 and SiO_2 membrane as exchange membrane have better power generation performance than that of using common Nafion membrane as exchange membrane. Especially when heteropolyacid salt nano membrane is used as the exchange membrane for MFC, the power generation performance of microbial fuel cells is improved significantly. For the MFC with heteropolyacid salt nano membrane, when the lake water is used as anode substrate, the output voltage of MFC is 0.0272V, and when the molasses wastewater is used as anode substrate, the output voltage is 0.0356V, which was increased by 403.7% and 406.9% respectively than that of Nafion membrane. In addition, the power generating capacity of molasses wastewater is much higher than that of lake water.

From the perspective of water purification effect, because of the low concentration of pollutants in the lake water itself, the purifying effect of MFC feeding lake water is not obvious. But the purifying effect of MFC feeding molasses wastewater is evident. Especially for MFC with heteropolyacid salt nano membrane, the COD removal rate can reach 53.1%.

In this experiment, the water purification effect and power generating capacity of the MFCs with heteropolyacid salt is still just passable. Further studies will focus on reducing the migration of heteropolyacid salt from the membrane, and also exploring a more effective method of membrane modification, so as to further improve the sewage treatment effect and power generating capacity of the microbial fuel cell.

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