

Applications of Nanoscale Polypyrrole Proton Exchange Membrane in Microbial Fuel Cells

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Using simulated syrup wastewater and lake silt as substrates, a microbial fuel cell power generation system was set up, the effect of nanoscale polypyrrole proton exchange membrane on the performance of microbial fuel cells was studied. Firstly, using the Nafion membrane MFC and nanoscale TiO₂/SiO₂ proton membrane MFC as comparisons; secondly, by using the methods of surface polymerization and internal polymerization, FeCl₃ and H₂O₂ were used as initiators, polypyrrole proton exchange membrane and nanoscale polypyrrole proton exchange membrane were prepared, and the performances of several kinds of microbial fuel cells with different membrane were tested and compared. The result shows that, the performance of MFC with nanoscale polypyrrole proton exchange membrane is the best. When internal polymerized nanoscale polypyrrole proton exchange membrane prepared by using the FeCl₃ as initiator was used as the separator of MFC, the steady output voltage is 17.3 mV, COD removal is 25.24 %, and the water uptake of the membrane is 64.37 %; when surface polymerized nanoscale polypyrrole proton exchange membrane was used as the separator of MFC, the state voltage is 14.4 mV, COD removal is 36.55 %, and the water uptake of the membrane is 54.18%. And when H₂O₂ was used as initiator, the steady voltage of MFC with internal polymerized nanoscale polypyrrole proton exchange membrane is 9.2 mV, COD removal is 19.39 %, and the water uptake of the membrane is 41.59 %; the steady voltage of MFC with surface polymerized nanoscale polypyrrole proton exchange membrane is 8.4 mV, COD removal is 29.38 %, and the water uptake of the membrane is 32.39 %. The nanoscale polypyrrole proton exchange membrane improved the performance of MFC evidently.

Keywords: microbial fuel cell; proton exchange membrane; surface polymerization; internal polymerization

1. INTRODUCTION

With the rapid growth of population and the 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]. At present, the best alternative to fossil fuels is hydrogen [2]. Hydrogen has a wide range of sources, for example, hydrogen production from natural gas, hydrogen production from electrolyzed water, hydrogen production from photolysis of water, biohydrogen production and so on. Hydrogen is a clean energy to replace gasoline, diesel oil, kerosene [3].

Fuel cell is an important method for hydrogen energy, fuel cell uses hydrogen or other hydrogen containing compounds as fuel, generate water by reacting with oxygen or air, almost no emissions of environmental hazardous substances [4-5]. As a kind of fuel cell, microbial fuel cells convert chemical energy in organic matter into electric energy directly [6-7]. Because of its high energy conversion efficiency and non-pollution, it is becoming a focus and hot spot for researchers in various countries [8-9].

As a very important component of microbial fuel cell, proton exchange membrane has a great influence on its performance [10-11]. The modification of Nafion membrane is an effective way to improve the performance of microbial fuel cells [12-13]. Lately, there are a lot of studies focusing on the improvement of the proton exchange membrane using the nano particle technology [14-15].

As a kind of conducting polymer, polypyrrole has long chain conjugated chemical bonds in its molecular structure, can conduct electrons and provide proton transport channel [16], it is a good material for preparing composite membrane. In this paper, FeCl_3 and H_2O_2 were used as initiators to prepare polypyrrole proton exchange membrane and nanoscale polypyrrole proton exchange membrane by internal polymerization and surface polymerization. Explore the impact on microbial fuel cell performance.

2. EXPERIMENTAL

2.1 Structure of the experimental system

A dual-chamber microbial fuel cell was used as an experimental reaction system for this study, as shown in Fig.1. Both the volume of the cathode chamber and the anode chamber are 500 mL. The cathode and anode compartments are separated by a proton exchange membrane. During the reaction process, the aerobic state of the cathode chamber and the anaerobic state of the anode chamber need to be maintained. The electrode materials of cathode and anode are carbon cloth (Taiwan carbon energy WOS1002) with thickness of 0.36 mm, and the surface area is $6 \text{ cm} \times 7 \text{ cm}$. Microorganisms in the anode region of the fuel cell degrade the organic matter to produce electrons and protons. Electrons are transmitted to the cathode through external wires. Protons reach the cathode through the proton exchange membrane and combine with electrons to produce water, forming a complete closed loop. The real-time output voltage generated by the microbial fuel cell is collected and transmitted online through a 16-

channel multi-function USB data acquisition card (MPS-010602) in parallel with the load, and displayed, stored and processed by the computer.

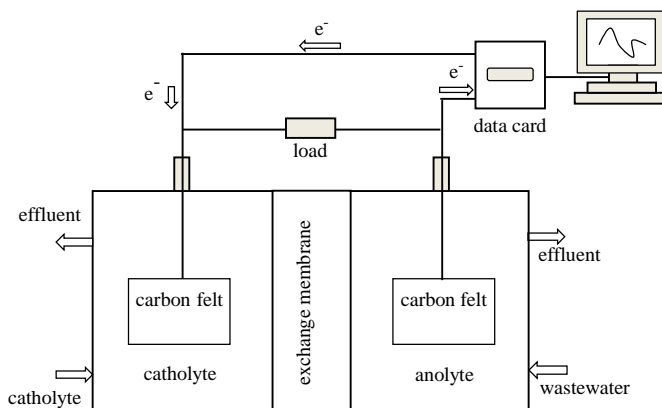


Figure 1. Experimental system of microbial fuel cell

2.2 Domestication of sludge

The sludge used in the experiment was taken from the bottom of the campus lake. 10 g sludge gathered from the bottom of a campus lake and an appropriate amount of molasses wastewater were placed in a culture flask, and cultured in a constant temperature incubator at 20 °C for 5 days. Then the cultured sludge and molasses wastewater were taken out and used for experimental studies.

2.3 Pretreatment of proton exchange membrane

Proton exchange membrane used in this experiment is Nafion117 series of membrane made by DuPont, United States. Since proton exchange membrane absorb organic small molecules in the air when placed in air, the proton exchange membrane becomes brown, so the proton exchange membrane needs to be pretreated before use.

First, the proton exchange membrane was placed in a 3% hydrogen peroxide solution and treated at 80°C for 1 h to remove organic impurities on the membrane surface. The membrane was taken out and placed in deionized water at 80 °C for 1 h to remove residual hydrogen peroxide on the surface of the membrane. Later, the membrane was placed in a 1 mol/L sulfuric acid solution and treated at 80 °C for 1 h to remove metal impurities on the surface of the membrane. Then, the membrane was taken out and placed in deionized water at 80 °C for 1 h to remove residual sulfuric acid on the surface of the membrane. Finally, the membrane was placed in deionized water for use.

2.4 Preparation of anolyte

The study used molasses wastewater as a reaction substrate for microbial fuel cells. The configuration of the molasses wastewater is as follows: 3.13 g/L NaHCO₃, 0.31 g/L NH₄Cl, 6.338 g/L NaH₂PO₄·H₂O, 6.8556 g/L Na₂HPO₄·12H₂O, 0.13 g/L KCl, 0.2 g/L MgSO₄·7H₂O, 0.015 g/L CaCl₂, 0.01 g/L MnSO₄·H₂O, and 3 g/L brown sugar. The mixture of molasses wastewater and domesticated sludge was used as anode feed for microbial fuel cell.

2.5 Preparation of catholyte

In this experiment, the catholyte of the microbial fuel cell was a mixture of $K_3[Fe(CN)_6]$ and NaCl. Dissolve 32.9 g 0.2 mol/L ferricyanide with PBS solution, hold it in a 500 mL volumetric flask by PBS solution; prepare a 11.7g 0.4 mol/L NaCl solution and hold it in another 500 mL volumetric flask; finally, put the ferricyanide solution and NaCl solution to the cathode chamber of the microbial fuel cell at the ratio of 1:1 to use as the catholyte.

2.6 Preparation of nano TiO_2 and SiO_2 composite membrane

The nano TiO_2 and SiO_2 composite membrane was prepared by following steps: First, place a Nafion membrane with the size of 10 cm \times 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; Next, 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°C 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. The membrane was protonated and placed in deionized water for storage.

2.7 Preparation of surface Polymerized Nanoscale Polypyrrole composite membrane

Surface polymerization is to control the pyrrole solution to polymerize only on one side of the proton exchange membrane. The reaction device is shown in Figure 2.

Polymerization must be carried out in a solution in which the monomers are uniformly dispersed. Pyrrole is insoluble in water but soluble in ethanol, so ethanol was chosen as the solvent [17]. First, 0.02 mol/L pyrrole aqueous ethanol solution was placed on one side of the reaction device, and then a certain concentration of ethanol and an aqueous initiator solution was placed on the other side of the reaction device. Sealed the inlet with a rubber stopper and reacted for about 2.5 hours at room temperature under anaerobic conditions, until the nano- TiO_2/SiO_2 proton exchange membrane became black, then the nanoscale polypyrrole TiO_2/SiO_2 modified membrane was obtained. The membrane was placed in deionized water for storage.

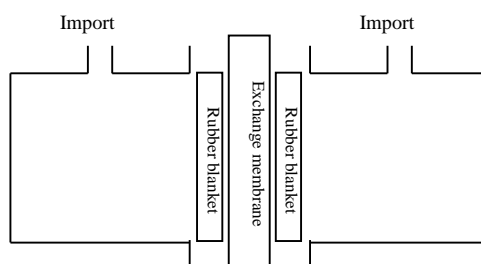


Figure 2. Surface Polymerization Reaction Chart

2.8 Preparation of inside Polymerized Nanoscale Polypyrrole composite membrane

The pyrrole ethanol solution of 0.02mol/L is arranged in the 500mL beaker. The nanoscale polypyrrole TiO₂/SiO₂ modified membrane is immersed in a sealed beaker for 24 h; then took out the soaked membrane, immersed it in the new ethanol solution and added a certain amount of initiator, sealed for polymerization reaction for 48 h. When the membrane became dark brown, took it out and placed it in deionized water for storage.

3. RESULTS AND DISCUSSION

3.1 Effect of H₂O₂ Nanoscale Polypyrrole membrane on MFC Power Generation Performance

When the initiator is H₂O₂, the voltage changes of MFCs with the nanoscale polypyrrole proton exchange membrane obtained by internal polymerization and surface polymerization are compared with those of MFCs with common Nafion membrane and TiO₂/SiO₂ modified proton exchange membrane, as shown in Figure 3.

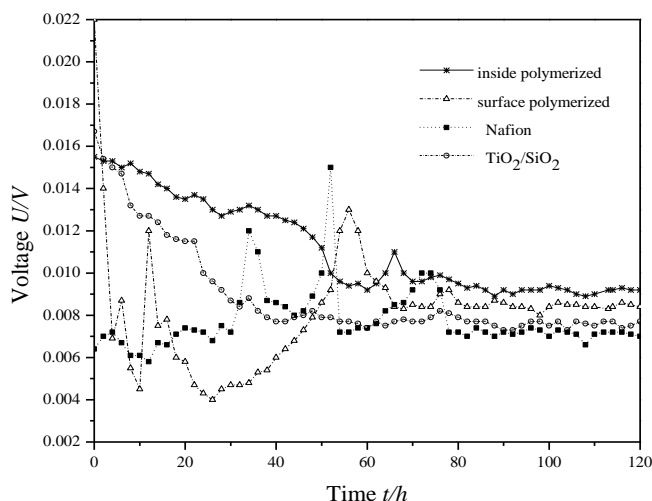


Figure 3. Voltage curves of MFCs with four different membranes when using H₂O₂ as initiator

Some results can be seen from Figure 3. When using H₂O₂ as initiator, the voltage of MFC with nanoscale polypyrrole proton exchange membrane obtained by internal polymerization was significantly higher than those of the other three MFC. The steady-state voltage was 0.0092V, which was 9.52% higher than that of MFC with the surface-polymerized nanoscale polypyrrole membrane, 27.78% higher than that of MFC with the common Nafion membrane, and 19.48% higher than that of MFC with the nano-TiO₂/SiO₂ membrane. The experimental results show that proton conductivity of the membrane has been significantly improved by adding polypyrrole conductive polymer, and the modified membranes obtained by internal polymerization are more conductive than those obtained by surface

polymerization, which is because internal polymerization can increase the adhesion of polypyrrole on the membrane, and the adhesion is more uniform.

3.2 Effect of $FeCl_3$ Nanoscale polypyrrole membrane on MFC Power Generation Performance

When the initiator is $FeCl_3$, the voltage changes of MFCs with the nanoscale polypyrrole proton exchange membrane obtained by internal polymerization and surface polymerization are compared with those of MFCs with common Nafion membrane and TiO_2/SiO_2 modified proton exchange membrane, as shown in Figure 4.

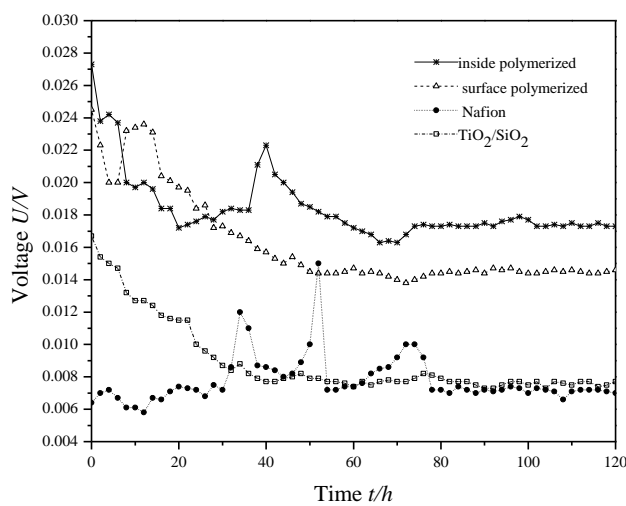


Figure 4. Voltage curves of MFCs with four different membranes when using $FeCl_3$ as an initiator

Aslo, some results can be seen from Figure 4. When the initiator is $FeCl_3$, the voltage of MFC with nanoscale polypyrrole proton exchange membrane obtained by internal polymerization was significantly higher than those of the other three MFC. The steady-state output voltage of MFC with internal polymerized polypyrrole nano membrane was 0.0173 V, which was 20.14% higher than that of MFC with surface polymerized polypyrrole nano membrane, 140.28% higher than that of MFC with common Nafion membrane, and 124.68% higher than that of MFC with nano TiO_2/SiO_2 membrane. Further, the conductivity of these membranes were tested, and the test results showed that the conductivity of the internally polymerized nanoscale polypyrrole membrane was 0.0208 s/cm, and the conductivity of the surface polymerized nanoscale polypyrrole membrane was 0.0206 s/cm. According to the literature, the conductivity of the common Nafion membrane is 0.0185 s/cm, and the conductivity of the nano TiO_2/SiO_2 membrane is 0.0166 s/cm [18]. Therefore the conductivity of the nanoscale polypyrrole membrane is more excellent. By comparing Fig. 3 and Fig. 4, it can be seen that when the initiator is $FeCl_3$, the power generation voltage of the nanoscale polypyrrole membrane MFC is higher than that of the nanoscale polypyrrole membrane MFC using H_2O_2 as an initiator, which is because the metal ions were introduced when $FeCl_3$ is used as an initiator, and the introduction of metal ions further enhances the conductivity of the membrane.

3.3 Analysis of water absorbability of the membrane

The water absorbability of the membrane is judged by measuring the water content of the membrane. The water content of the membrane is the mass ratio of the water saturated membrane to the dry membrane. The higher the water content of the membrane, the better the protons transfer effect of the membrane and the better the electrical conductivity. In order to compare the Water Uptake (WU) properties of the nanoscale polypyrrole membrane with H₂O₂ as an initiator with that of FeCl₃ as an initiator, the Water Uptake of the membranes were calculated. First, the treated membrane was placed in an oven to dry at 80 °C for 24 h, then weighed the dried membrane and recorded its quality as W₀. The membrane was then placed in deionized water until the membrane was saturated with water, then removed the membrane from the deionized water and weighed. The wet quality of the water saturated membrane was W₁. Then the Water Uptake of the membrane is

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

Table 1 shows the Water Uptake test data of the several different membranes. It can be seen from the table that when FeCl₃ was used as the initiator, the water absorption rate of the internal polymerization nanoscale polypyrrole membrane was 64.37 %, which was 1.19 times as large as that of the surface polymerization nanoscale polypyrrole membrane, 1.55 times as large as that of the internal polymerization nanoscale polypyrrole membrane with H₂O₂ as initiator, and 1.99 times as large as that of the surface polymerization nanoscale polypyrrole membrane with H₂O₂ as initiator. This further indicates that polypyrrole does improve the proton conductivity of the membrane, and the introduction of metal ions also improves the proton conductivity of the membrane.

Table 1. Water Uptake corresponding to the several conditions

	wet weight W ₁ (g)	dry weight W ₀ (g)	Water Uptake ΔW (%)
H ₂ O ₂ surface polymerization	4.21	3.18	32.39
H ₂ O ₂ internal polymerization	4.63	3.27	41.59
FeCl ₃ surface polymerization	4.98	3.23	54.18
FeCl ₃ internal polymerization	5.49	3.34	64.37

When FeCl₃ is used as an initiator, the Water Uptake of the internal polymerized nanoscale polypyrrole membrane is 64.37%, which is higher than that of most other proton exchange membranes. Test data at room temperature (25°C) showed that the Water Uptake of Nafion 117 was 16% [19]; of heteropolyacid salt nano membrane was 23.26% [20]; and of sulfonated polytriazole (SPTA) membranes were 9.6%~41.7% [21]. The comparison results show that internal polymerized nanoscale polypyrrole membrane prepared by using FeCl₃ as initiator has significant effect on improving the Water Uptake of the proton exchange membrane.

3.4 Analysis of the water quality

Microbial fuel cells have become a research hotspot, not only because of its power generation capacity, but also because it is an alternative process for sewage treatment. Molasses wastewater belongs to a kind of high-concentration organic wastewater. The main treatment methods for molasses wastewater are some terminal degradation methods, which usually gives low COD removal rate. For example, the photodegradation method has a COD removal rate of only 2% for molasses wastewater, The COD removal rate of the $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$ zeolite/mixture system is approximately 15% [22]. Table.2 shows the influent and effluent COD of MFCs using molasses wastewater as anode substrate. It can be seen that all the effluent COD values of the microbial fuel cells with four different proton exchange membrane were lower than those of the influent water. This indicates that MFC has good sewage treatment effect. Further analysis shows that the COD removal efficiency of MFC with the surface polymerized nanoscale polypyrrole proton exchange membrane is the best when the initiator is FeCl_3 . Because the content of pyrrole in the internal polymerized polypyrrole nanomembrane was more than that in the surface polymerized polypyrrole nanomembrane, after a long time running of MFC, pyrroles were migrated from the membrane more or less, leading to a decrease in COD removal rate.

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

	Influent (mg/L)	Effluent (mg/L)	COD removal rate (%)
H_2O_2 surface polymerization	13300	10280	29.38
H_2O_2 internal polymerization	13300	11140	19.39
FeCl_3 surface polymerization	13300	9740	36.55
FeCl_3 internal polymerization	13300	10620	25.24

3.5 Analysis of SEM

Polypyrrole is a kind of high quality conductive polymer. Adding polypyrrole into the proton exchange membrane can effectively improve the conductivity of the proton exchange membrane. The conductive property of the internally polymerized nanoscale polypyrrole membrane is better than that of the surface-polymerized nanoscale polypyrrole membrane because internal polymerization can attach more polypyrrole particles to the membrane. The SEM images of the surface polymerized nanoscale polypyrrole membrane and the internal polymerized nanoscale polypyrrole membrane are shown in Fig. 5 and Fig. 6 separately.

It can be seen from the SEM images that the polypyrrole content on the internal polymerized nanoscale proton exchange membrane is larger than that of the surface polymerized nanoscale proton exchange membrane, and this structural difference results in better conductivity of the internal polymerized nanoscale proton exchange membrane than the surface polymerized nanoscale proton exchange membrane.

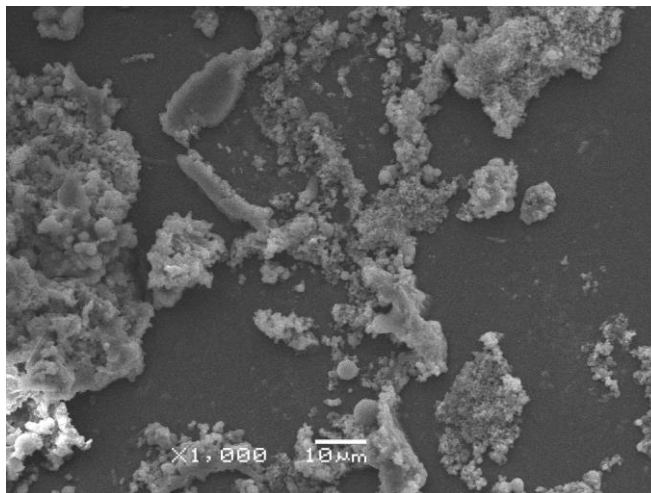


Figure 5. SEM of surface polymerized nanoscale polypyrrole membrane

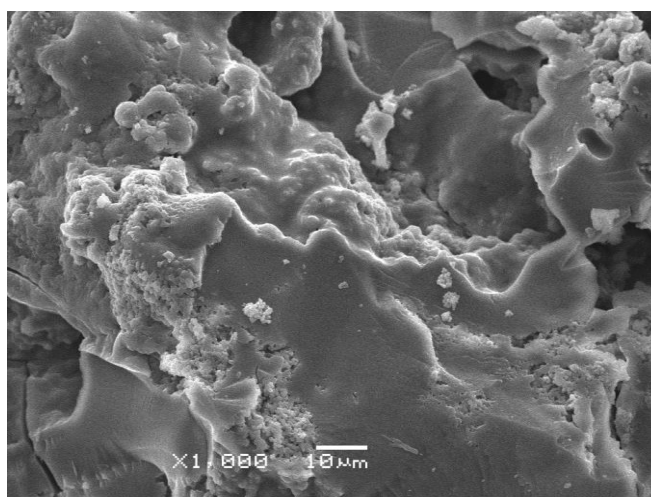


Figure 6. SEM of internal polymerized nanoscale polypyrrole membrane

3.6 Test and analysis of CV curve

In order to further analyze the influence of internal polymerization and surface polymerization on the performance of proton exchange membrane, the cyclic voltammetry (CV) curves of internal polymerized and surface polymerized nanoscale polypyrrole proton exchange membrane were tested by the electrochemical workstation (Shanghai, CHI660E). The CV test was performed using the three-electrode system of the electrochemical workstation, using 50 mmol/L PBS as the buffer, the pH of this buffer was 7.2, the potential range was (-1.0 V)~1.0 V, and the scan rate was 10 mV/s. The whole test process was performed at room temperature. The CV curves are shown in Fig. 7.

It can be seen from Fig. 7 that the symmetry of the oxidation and reduction waves of the internal polymerized nanoscale polypyrrole proton exchange membrane has improved, which shows that the internal polymerized nanoscale polypyrrole proton exchange membrane improves the reversibility of the electroactive substances. On the other hand, the oxidation peak and reduction peak currents of the

internal polymerized nanoscale polypyrrole proton exchange membrane were higher than those of the surface polymerized nanoscale polypyrrole proton exchange membrane, and the larger the peak current, the better the electron transfer effect. Therefore, the internal polymerized nanoscale polypyrrole proton exchange membrane increases the reaction rate of molecules or ions on the surface of the electrode, and also enhance the ability to move directionally in solution.

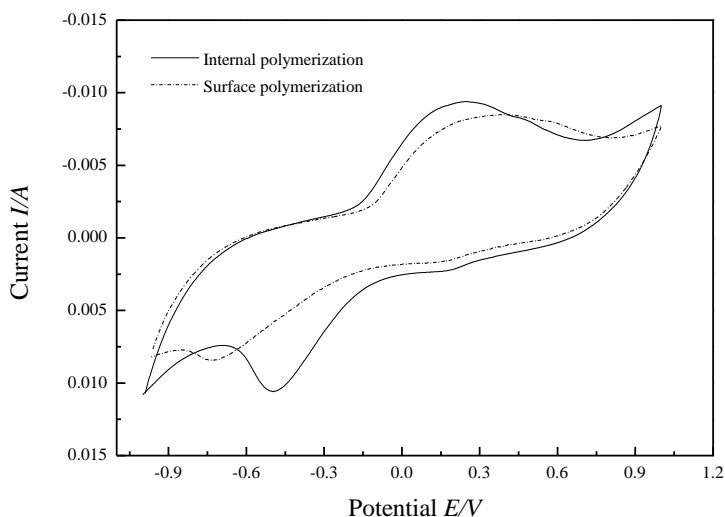


Figure 7. CV characteristics of internal polymerized and surface polymerized nanoscale polypyrrole proton exchange membrane

4. CONCLUSION

Microbial fuel cells are not only sewage purification devices, but also have good electricity production performance. The treatment of the proton exchange membrane with polypyrrole can effectively improve the conductivity of the proton exchange membrane. The MFC with internal polymerized nanoscale polypyrrole proton exchange membrane have better performance than others. This is due to the fact that the internal polymerization method allows more conductive polymer azoles to adhere to the proton exchange membrane, enhancing the conductivity of the membrane. The steady state output voltage of MFC with internal polymerized nanoscale polypyrrole proton exchange membrane is 0.0173 V, which was 20.14 % higher than that of MFC with surface polymerized nanoscale polypyrrole membrane, 140.28 % higher than that of MFC with common Nafion membrane, and 124.68 % higher than that of MFC with the nano $\text{TiO}_2/\text{SiO}_2$ membrane. From the aspect of purifying sewage, the nanoscale polypyrrole membrane MFC using the surface polymerization method has better purification effect than internal polymerization. Nanoscale polypyrrole can be used in proton exchange membranes for innovation. Nanoscale polypyrrole proton exchange membrane improved the overall performance of MFC effectively.

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