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Paper**A novel hybrid anion exchange membrane for high performance microbial fuel cells**

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A novel titanium dioxide (TiO₂) - quaternized poly(vinyl alcohol) (QAPVA) hybrid anion exchange membrane (T membrane) is prepared, and its feasibility for use in microbial fuel cells (MFCs) is investigated in this study. Compared with proton membranes, such as Nafion117 (N membrane) and an anion exchange membrane (AEM) LeHOAM-III (L membrane), the T membrane exhibits much better performance in MFCs. The oxygen mass transfer coefficient (K_o) of the T membrane ($0.05 \times 10^{-4} \text{ cm s}^{-1}$) is one order of magnitude less than that of the N membrane ($K_o = 0.3 \times 10^{-4} \text{ cm s}^{-1}$), resulting in reduced substrate loss and increased columbic efficiency (CE) for the MFC with the T membrane. The output voltage and power density of a MFC with the T membrane is higher than cells containing the other two membranes. The CE of MFC with T membrane is 1.36 times that of the N membrane and 1.4 times that of the L membrane. The maximum power density of MFCs obtained was 125.4, 65.0 and 35.6 mW m⁻² for the T, N and L membranes, respectively. The results of this study indicate that this new membrane has the potential to substitute for the Nafion membrane in MFCs.

1. Introduction

With the increasing attention to protection of the environment and the shortage of energy, clean and renewable energy sources have drawn more and more attention from around the whole world. Microbial fuel cells (MFCs) represent a prospective technology because of their capability to use microorganisms as biocatalysts to oxidize organic substances in wastewater and simultaneously generate electricity.¹⁻³ Over the past decade, MFCs have achieved exciting progress. But they still face many barriers, such as low electron recovery rate, unstable systems and high costs.⁴

The separator, which separates the anodic and cathodic chambers and simultaneously migrates protons from the anode to the cathode, is one of the key parts in an MFC. It has been widely recognized that a separator is necessary to ensure the efficient and sustainable operation of an MFC.^{5,6} Various separators have been used in MFCs, such as cation exchange membranes (CEMs) and anion exchange membranes (AEMs) and other materials.⁶⁻⁸ Until now, the Nafion membrane is the most widely used in MFCs because of its high selective permeability to protons and its mechanical stability. However, the high oxygen leakage of Nafion causes low fuel performance, and the high cost of Nafion has limited its utility for MFCs. Hence there is considerable interest in looking for a substitute for the Nafion membrane.

The hydrophilicity of membranes can affect the performance of MFCs. Membranes with superior hydrophilicity would have high ion transport and low internal resistance and have less membrane pollution from microorganisms. Many hydrophilic polymer membranes have been synthesized and utilized in MFCs, such as

sulphonated polyether ether keton (SPEEK),⁹ sulphonated polystyrene-ethylene-butylene-polystyrene (SPSEBS),¹⁰ disulfonated poly(arylene ether sulfone) (BPSH),¹¹ chitosan-functionalized multi walled carbon nano-tube membranes,¹² etc..^{13,14} The hydrophilicity of pristine polymers was increased by grafting on sulfonic acid groups through sulfonation reactions,¹⁰ and the performances of MFCs with these membranes were improved.

Poly(vinyl alcohol) (PVA) is a popular polymer material for membranes because of its good film-forming, high hydrophilicity, and good physical and chemical properties. PVA is also a low cost and environmental-friendly material. PVA has good antifouling property which can help to reduce biofilm formation and biofouling of the cathode in MFCs and enhance the performance of MFCs.¹⁵⁻¹⁶ PVA membranes, and the other membranes based on PVA, have also been synthesized and used as separators in MFCs, such as graphene oxide-impregnated PVA and silicotungstic acid composite membrane (PVA-STA-GO), PVA and polycarbonate composite membrane (PVA-PC), etc..¹⁷⁻¹⁹ MFCs with these PVA membranes showed excellent electrochemical performances; these research results reveal the potentiality of PVA in MFCs.

In our previous research, quaternized PVA membranes were synthesized and used as an anion exchange membrane in alkaline methanol fuel cells because of their good conductivities and perfect resistance to methanol.²⁰⁻²³ In these membranes, the QAPVA and SiO₂ hybrid membrane had the most conductivity ($1.4 \times 10^{-2} \text{ S cm}^{-1}$) attributed to the network between the organic and inorganic materials and the

hydrophilicity of the two materials.²² The addition of inorganic material could increase the mechanic strength, the thermal stability, the conductivity and the working life of the membrane.²⁴

In this paper, a new organic-inorganic hybrid anion exchange membrane was synthesized with QAPVA and inorganic TiO_2 . We have researched the characterization of three QAPVA/ TiO_2 membranes for alkaline fuel cell.²⁵ The addition of TiO_2 not only enhances the thermal stability, but also increases the hydrophilicity of the hybrid membranes because of the hydrophilicity of TiO_2 particles. The QAPVA/ TiO_2 membrane with TiO_2 content 5% has good ion conductivity and excellent alcohol resistance. In order to investigate the possibility utilization in MFCs, the electrochemical performance of MFC with QAPVA/ TiO_2 membrane with TiO_2 content 5% was measured and compared with MFCs with Nafion 117 membrane and a commercial anion exchange membrane - LeHoAM-III membrane, respectively.

2. Experimental

2.1. Materials and preparation of QAPVA / TiO_2 membrane

Poly(vinyl alcohol) (PVA, polymerization degree of 2400, hydrolysis degree of 98–99%, Sinopharm Chemical Reagent Co., Ltd), (2,3-epoxypropyl) trimethylammonium chloride (EPTMAC, purity $\geq 95\%$, Shandong Guofeng Fine Chemistry Factory), Glutaraldehyde (GA, 25 wt% content in distilled water, Sinopharm Chemical Reagent Co., Ltd) and titanium dioxide (TiO_2 , Sinopharm Chemical Reagent Co., Ltd) were used directly after purchase. The preparation of QAPVA was given previously.²⁰ TiO_2 particles and 10 wt% GA solution were added

into the QAPVA solution in deionized water at pH 5, and then stirred 1 h and statically deaerated. The mixed membrane solution was cast onto a glass plate and dried at 45 °C for 6 h. After the membrane was removed from the glass plate, it was further dried at 80 °C for 3 h and at 130 °C for 2 h. The produced membrane was a QAPVA/TiO₂ hybrid anion exchange membrane and is henceforth designated as ‘T membrane’. **Fig. 1** shows the photo of The QAPVA/TiO₂ membranes with TiO₂ content 5%. The Nafion 117 membrane was from Dupont Company USA and is henceforth designated as ‘N membrane’. The LeHoAM-III membrane (Hangzhou Lvhe Environmental technology Co., Ltd, China) is a kind of anion exchange membrane, and is henceforth designated as ‘L membrane’. The membrane thickness was measured by SEM (JSM-6701F, JEOL).

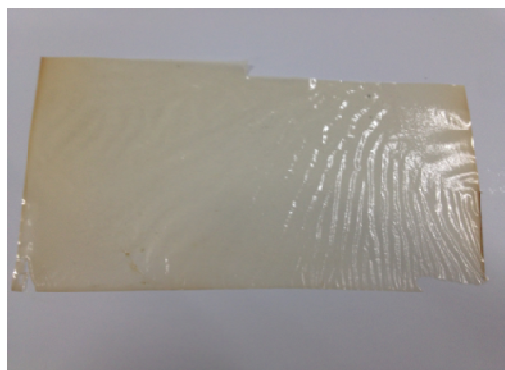


Fig. 1 The QAPVA/TiO₂ membranes with TiO₂ content 5%

2.2. MFC construction and operation

The MFC employed was a dual-chamber reactor according to the literature.²⁶⁻²⁸ The volume of anode chamber is 120 mL and the volume of cathode chamber is 60 mL. The N, L and T membranes were assembled respectively to separate the two chambers in the MFCs. The membrane area is 27.5 cm². The anode (carbon felts,

Beijing Sanye Carbon Co. Ltd., China) was connected to the cathode (carbon plate) by titanium wires. Fig.2 shows the photograph of the assembled MFC. The carbon felt was soaked in 1 M HCl for 24 h and in 1 M NaOH for 3 h, and was then washed with deionized water to neutral pH to remove any possible contaminants attached onto the surface. The data of cell voltages across an external resistance of 300 Ω was collected on a PC by a data acquisition recorder (ADAM-4017 Analog Input Model, Advantech Co. Ltd., PRC). All experiments were operated at 35 $^{\circ}\text{C}$ in a temperature-controlled chamber (SPX-150, Shanghai Yuejin Medical Instruments Factory, PRC).

The anode chamber was inoculated with mixed culture (anaerobic sludge: anodic medium = 1:1). A sterilized nutrient medium in the anodic chamber contained 1.00 g L^{-1} CH_3COONa , 0.31 g L^{-1} NH_4Cl , 6.82 g L^{-1} $\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 3.67 g L^{-1} $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and 0.13 g L^{-1} KCl . The cathode chamber was filled with tap water purged with air.

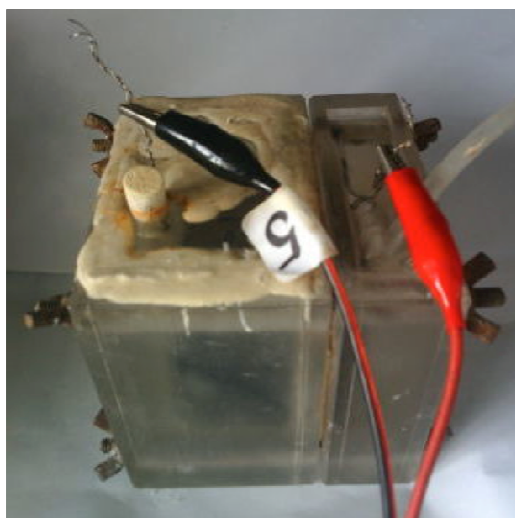


Fig. 2 The assembled MFC

2.3 Oxygen transfer coefficients

The oxygen mass transfer coefficients for the three membranes were measured with the same MFC, and the anode chamber was uninoculated. A dissolved oxygen (DO) meter (YSI 52CE, US) was used to detect the DO in the anode and cathode chambers. The anolyte was sparged with nitrogen gas to remove dissolved O₂ until the DO was below 0.25 mg L⁻¹. Then the anode was sealed with the oxygen probe immersed in the anolyte. The catholyte was tap water and pumped with air to maintain the DO at 7.0 mg L⁻¹. The air flow was maintained 100 mL min⁻¹. The change of DO in the anode chamber was measured by the oxygen probe over a period of 6 h with continuous aeration in the cathode chamber.

The oxygen mass transfer coefficient (K_o , cm s⁻¹) in the membrane was calculated using the following Equation 1.⁸

$$K_o = -\frac{V_{An}}{At} \ln\left(\frac{C_{Cat} - C_{An}}{C_{Cat}}\right) \quad (1)$$

where V is the liquid volume of the anode chamber, A is the cross-section of the membrane, C_{Cat} is the saturated oxygen concentration in the cathode chamber, and C_{An} is the dissolved oxygen concentration in the anode chamber at time t .

The diffusion coefficient (D_o , cm² s⁻¹) was calculated as the Equation 2:

$$D_o = K_o L_t \quad (2)$$

where L_t is the membrane thickness (cm).

3. Results and discussion

3.1. Oxygen transfer through membranes

Fig. 3 indicates the DO concentration in the anode chamber assembled with the three membranes, respectively, over a 6 h period. During this time, the DO concentration of chamber increased from 0.10 to 0.98 mg L⁻¹ with the N membrane as the separator. On the other hand, when the two anion exchange T and L membranes were used as the separators, the DO concentration changed little after 6 h. The details of oxygen mass transfer coefficient (K_o) and diffusion coefficient (D_o) for the three membranes are provided in **Table 1**. Compared with the N membrane, the K_o values for the T and L membranes were an order of magnitude lower, which indicated that these two anion exchange membranes could effectively prevent O₂ leaking from the cathode to the anode chambers. D_o for the L membrane was higher than that for the T membrane, which arose from the thinner T membrane thickness. The network was formed by the crosslinking reaction between QAPVA and GA, which made the membrane structure compact. Meanwhile, the addition of TiO₂ particles filled the pores in the membrane matrix. These two factors reduced the oxygen crossover through the membrane from the cathode to anode chambers. It is also well-known that electrochemically-active bacteria are facultative anaerobes that will switch from anaerobic to aerobic respiration in the presence of oxygen, which would reduce the MFC performances.¹ Hence the MFC with the T membrane had the highest power generation which is discussed in the following sections.

Table 1 Oxygen transfer coefficient K_o and diffusion coefficient D_o for various

membranes			
Membrane	T	N	L
Thickness (mm)	0.043	0.18	0.24
$K_o (\times 10^{-4} \text{ cm s}^{-1})$	0.05	0.3	0.05
$D_o (\times 10^{-6} \text{ cm}^2 \text{ s}^{-1})$	0.02	0.55	0.11

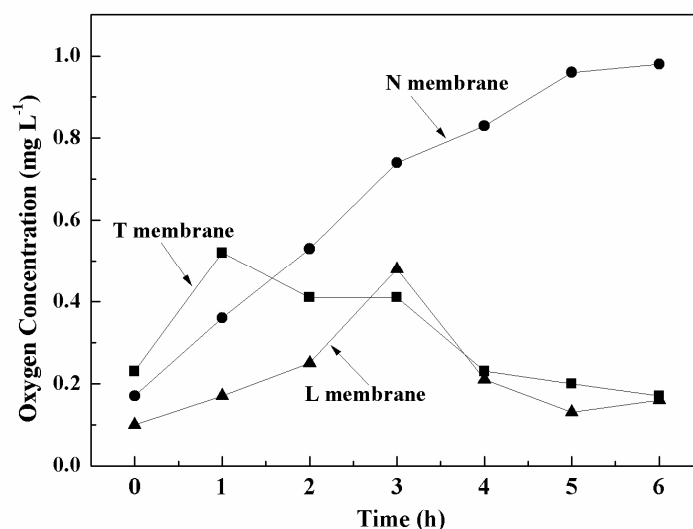


Fig.3 Oxygen diffusion from cathode through QAPVA/ TiO₂, Nafion 117 and LeHoAM-III membranes in an uninoculated MFC

3.2 Performance evaluation of three membranes in MFCs

The three membranes were used as separators primarily to examine their performances in the inoculated MFCs. **Fig. 4** shows the open circuit voltage of three batches of MFCs with T, N and L membranes, respectively, after 60 days operation. The chamber was refilled each time with fresh nutrient medium when the voltage decreased. The MFC systems regained their potential after the addition of fresh medium. Then the cell voltage of three MFCs slowly declined over the next 40 h. The

operating cycles indicated that the performances of MFCs with the three membranes were stable. The MFCs with T, N and L membranes showed maximum voltages of 434, 195 and 165 mV, respectively. The output voltage of MFC with the T membrane was about twice those with N and L membranes. Stable power generation using the MFC with T membrane indicated the feasibility of the substitution of the novel QAPVA/TiO₂ hybrid anion exchange membrane for commercial membranes.

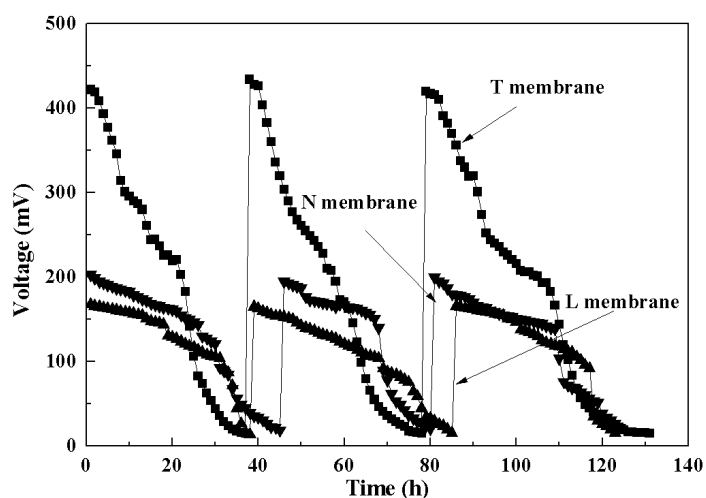


Fig. 4 Cell voltage of MFCs with three membranes

After the MFCs with three membranes achieved the highest power generation over a period of 100 days, the experiments were conducted in duplicate using the same MFCs with an external resistance. Polarization curves were obtained by varying the external resistance (range from 5 Ω to 5 k Ω) in discrete steps and measuring the corresponding voltage drop.

Fig. 5 shows the polarization curves and power density curves for MFCs with T, N and L membranes. The maximum power density obtained was 125.4, 65.0 and 35.6 mW m⁻², for the T, N and L membranes, respectively. It is known that the maximum power is produced when the internal resistance is equal to the external resistance.¹ The

internal resistance (100Ω) of the MFC with the T membrane was the smallest compared to those containing the N membrane (250Ω) and the L membrane (300Ω). The membrane area in MFCs is 27.5 cm^2 , so the area resistances are 3.64, 9.09 and $10.91 \Omega \text{ cm}^{-2}$ of T, N, L membranes, respectively. The low internal resistance for T membrane was attributed to the hydrophilicity of QAPVA and TiO_2 , which promoted ion transport, and the quaternary ammonium groups in QAPVA reduced the production of biofilm on the surface of the separators.

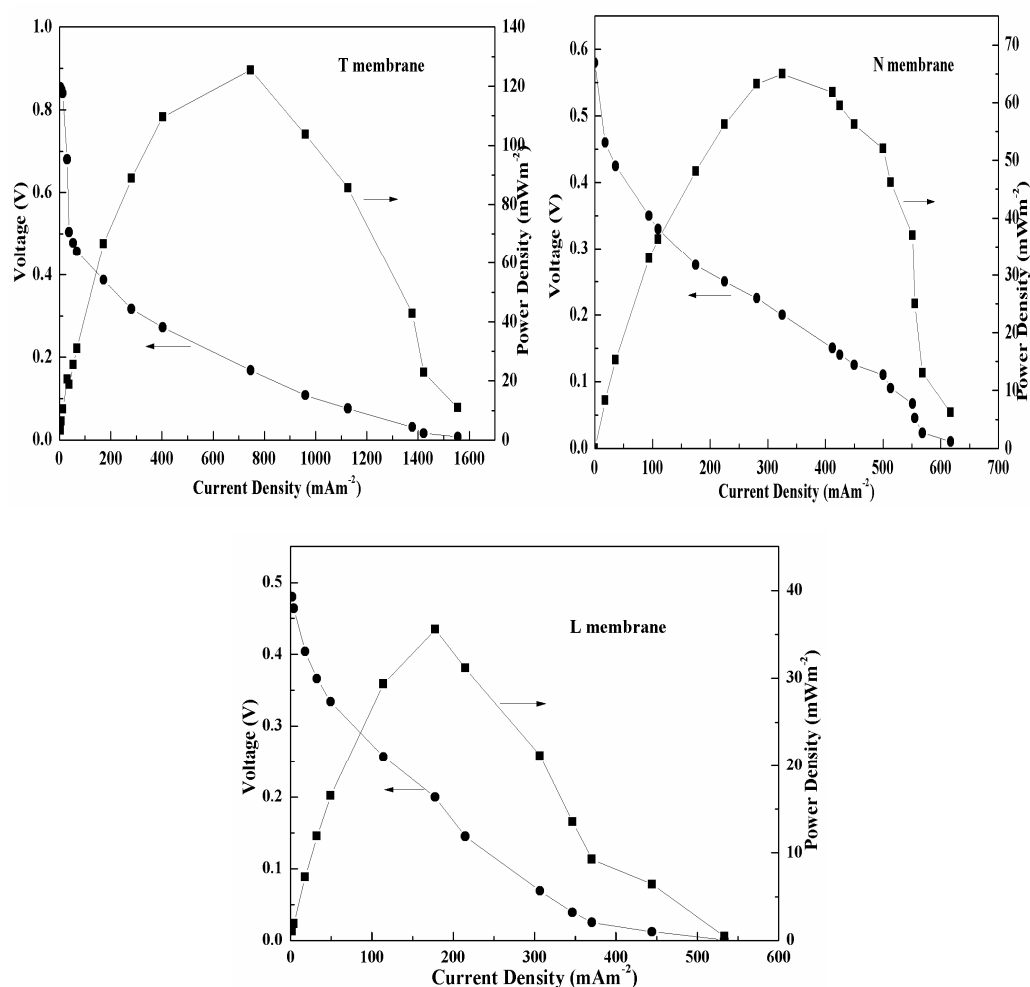


Fig. 5 Polarization curves of QAPVA/ TiO_2 (T), Nafion 117 (N) and LeHoAM-III (L) membranes

The chemical oxygen demand (COD) removal rates were 89%, 80%, 75%, and the columbic efficiencies (CEs) were $13.6\% \pm 1.06\%$, $10\% \pm 0.42\%$ and $9.7\% \pm 0.28\%$ for the MFCs with T, N, L membranes, respectively, when the external resistance was 300 Ω . These results revealed the excellent performance of the T membranes, which was attributed to three factors. (1) A lower oxygen crossover which maintained the anaerobic environment of the anode chamber; (2) the hydrophilicity of the QAPVA/TiO₂ membrane which reduced the internal resistance; (3) the quarternary ammonium groups grafted onto QAPVA had antibacterial properties, preventing the formation of biofilms on the surface of the membrane which would reduce the ion transport and increase the internal resistance of MFC. Therefore, the QAPVA/TiO₂ membrane is an excellent substitute for Nafion and other commercial membranes used as a separator in MFCs.

The cost of a separator is another factor when a membrane is chosen and used in MFCs. PVA is a common polymer material, and the materials that were used to synthesize the QAPVA/TiO₂ membrane are cheap and easily obtained. It was estimated that the cost of the QAPVA/TiO₂ membrane would be about \$0.30 per 100 cm². Commercial Nafion membranes are about \$55 per 100 cm², which is almost 200 times of the cost of the QAPVA/TiO₂ membrane. Meanwhile, the preparation method of the QAPVA/TiO₂ membrane was simple. Considering the low cost and the good performance of MFCs with QAPVA/TiO₂ membrane, the QAPVA/TiO₂ membrane is a promising separator for the future use in MFCs.

4. Conclusions

An organic-inorganic hybrid anion exchange membrane composed of quarternized poly(vinyl alcohol) (QAPVA) and titanium dioxide (TiO_2) was prepared and evaluated as a separator in double-chambered microbial fuel cells (MFCs). The QAPVA/ TiO_2 membrane showed excellent oxygen resistance compared to the two commercial membranes, namely Nafion 117 and LeHOAM-III. The power density obtained for the QAPVA/ TiO_2 membrane (125.4 mW m^{-2}) was the highest compared to those of Nafion (63.2 mW m^{-2}) and LeHOAM-III (35.6 mW m^{-2}), which was attributed to the good oxygen resistance and the antibacterial activity of the QAPVA/ TiO_2 membrane. The results indicated that the QAPVA/ TiO_2 membrane has the potential to substitute for Nafion membranes in MFCs.

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