

Experimental study on the effects of Nafion content and distribution in catalyst layer on paper-based microfluidic fuel cell

Jicheng Ma¹, Yun Chen¹, Fuqiang Bai^{1,2}, Qing Du¹, Kui Jiao¹, Zhi Liu^{1*}

1 State Key Laboratory of Engines, Tianjin University, 135 Yaguan Road, Tianjin 300350, China

2 Internal Combustion Engine Research Institute, Tianjin University, 92 Weijin Road, Tianjin, 300072, China

ABSTRACT

In recent years, the diagnostic and sensing field has put forward higher requirements for portable, sustainable and clean power sources for small electronic devices, which promoted the research and development of new micropower sources. Paper-based microfluidic fuel cell (PMFC) has gradually become the most promising micro power source because of its simple structure, low cost and zero pollution. In this paper, we have studied the effect of Nafion content in catalyst layer on the output performance of PMFC, and further explored the reaction mechanism of PMFC under different Nafion solution distribution. The results show that using the catalyst layer prepared by mixing 0.4 mL Nafion solution will produce a higher maximum current density and peak power density. Additionally, with a constant amount of Nafion solution, the prepared catalyst layer with extra 0.2 mL Nafion solution spraying on its surface can greatly reduce the starting time without affecting the performance of the fuel cell.

Keywords: PMFC, Nafion solution, Ion transport, performance

1. INTRODUCTION

Paper-based microfluidic fuel cell (PMFC) is a passive microfluidic fuel cell based on the capillary action of paper, which replaces the traditional microchannel processed by polydimethylsiloxane (PDMS) with paper material [1]. The co-layer flow of fuel and oxidizer is realized by capillary action of paper based porous medium, and the electrochemical reactions of fuel and oxidizer take place under the action of catalyst. During the reactions, an obvious diffusion zone is formed at the interface of the two liquids for ion exchange, and electrons are transferred from anode to cathode by an

external circuit. Different from Proton exchange membrane fuel cell (PEMFC) and MFC, PMFC eliminates the influence of PEM, hydrothermal management problems and the need for other auxiliary equipment. Because of its simple structure, low cost and pollution-free characteristics, PMFC has gradually become the most promising micro fuel cell. In addition, the foldable nature of paper makes PMFC suitable for integration into wearable electronics as a flexible power source [2]. In recent years, paper-based microfluidic chips based on electrochemical reactions have been widely used in diagnosis and sensing fields, such as point-of-care (POC) diagnosis [3] and blood glucose analysis [4], etc. Therefore, the development of high-performance PMFC has attracted great research interest from all around the world.

As an important part of paper-based microfluidic fuel cells, the catalyst layer structure plays important roles on the output performance of fuel cells. Lee et.al [5] prepared a catalyst electrode with a high surface area on a nanoporous foam carbon base, which enhanced the contact area between the catalyst and the fuel, they reduced the activation loss of the fuel cell. Yuan et.al[6] improved the catalytic activity and stability of fuel cells by preparing the Pd-PdO catalyst layer with ordered channels, and obtained the peak power density of 63.0 mW/cm². Yan et al [7] prepared functionalized porous carbon nanotube catalysts by laser ablation, which achieved a better catalytic performance. Nafion is an important part of the catalyst layer, and the influence of Nafion on paper-based microfluidic fuel cells has rarely been studied. In this paper, we fabricated a dual electrolyte PMFC and investigated the effects of Nafion content and distribution on the performance of PMFC through experiments.

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2. EXPERIMENT

2.1 The structure of fuel cell

The structure of dual-electrolyte paper-based microfluidic fuel cell is mainly composed of Y-shaped paper-based flow channel, cathode and anode catalytic electrode, and absorption pad (Fig.1). To make a standard size Y-shaped paper-based channel, a customized Y-shaped cutter was used to cut the filter paper, the length and width of the straight section of the liquid flow channel are 4 cm and 1 cm, and the cathode and anode catalytic electrodes (5 mm×3 mm) are arranged 1 cm away from the entrance of the straight section, the distance between the cathode and anode catalyst electrode is 4mm. The absorption pad is placed at the end of the paper-based flow channel and is used to absorb the liquid in the paper-based flow channel. The purpose is to maintain the passive transport of fuel and oxidizer through the paper-based flow channel. The cathode and anode catalytic layers were prepared by spraying catalyst mixed solution on carbon paper. Firstly, Pd/C, Nafion solution (0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml) and isopropanol solution (8 ml) were mixed to prepare the catalyst solution. In order to make the catalyst solution evenly mixed, the catalyst solution was treated by ultrasound for 1 h. Then the catalyst mixture was sprayed evenly on the hydrophilic carbon paper (TGP-H-060, 5 mm × 5 mm × 0.19 mm) by electrostatic spraying apparatus, the loading capacity of Pd/C catalyst was 0.15 mg/cm². After standing at room temperature for 30 minutes, the catalyst layer carbon paper was stored in a sealed bag for the experiment. The cathode and anode catalytic electrode (5 mm × 3 mm) were cut from the carbon paper with catalyst layer according to the experimental requirements.

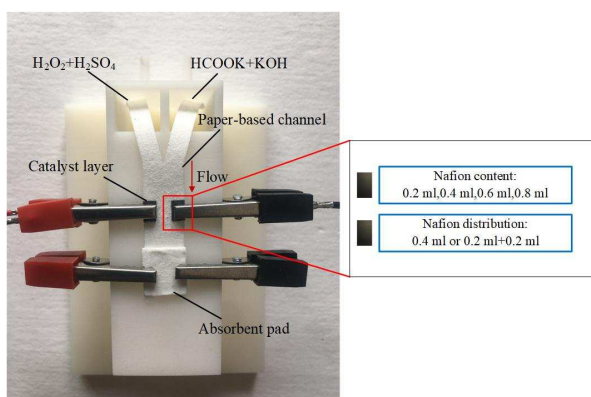
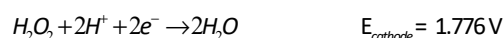
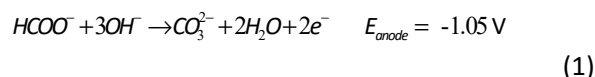


Fig.1 Schematic diagram of dual-electrolyte paper-based microfluidic fuel cell structure

According to the previous literature [8], when the distance between cathode and anode catalytic electrode along the liquid flow direction is zero, the PMFC has the best output performance. Therefore, the anode and cathode electrodes are arranged in parallel on the Y-shaped paper-based flow channel in this experiment. Based on previous research [9], Dual electrolytes not only enhance the electrochemical reaction kinetics of the electrode, but also increase the open circuit voltage (OCV) of PMFC. Therefore, 2 mol/L KOH was used as the anode electrolyte and 2 mol/L H₂SO₄ as the cathode electrolyte, and the electrochemical reaction equation occurred was :



2.2 Testing technique

At the beginning of the experiment, the fuel for the anode and the oxidizer for the cathode enter the PMFC inlet simultaneously. The fuel and oxidant flow in parallel in the paper-based channel under the capillary action of the paper. The electrochemical workstation controlled by SmartManager software was used to record the open circuit voltage of the fuel cell, when the OCV of the fuel cell reached a stable state, linear scanning was carried out from OCV to 0 mV at a voltage interval of 10 mV by potentiometric step timing current method of the electrochemical workstation to complete the V-I measurement of the fuel cell. We use the cathode of the fuel cell as the working electrode and anode as the opposite electrode, a constant voltage of 0.6V was applied to the PMFC using a DC load, and then the Electrochemical impedance spectroscopy (EIS) test was carried out by an electrochemical workstation, the frequency range of the electrochemical workstation is set to 50 kHz-50 mHz, and the amplitude is 10 mV to obtain the EIS curve of the fuel cell. The ohmic impedance and activation impedance of the fuel cell can be obtained from the real intercept of the EIS curve, which can help us understand the reaction process inside the fuel cell deeply. In order to ensure the accuracy of experimental results, each group of experiments was repeated at least 3 times.

3. RESULTS AND DISCUSSION

The catalyst layer is a key part of PMFC and plays a vital role in the electrochemical reaction of PMFC. Therefore, this research built a PMFC test platform to

explore the influence of Nafion content and distribution on PMFC performance.

3.1 Effect of Nafion content

As an ionomer, Nafion can promote the dispersion of catalysts and improve the conductivity of ions (protons) in the catalyst layer, so that the catalyst has a high catalytic activity. In order to study the influence of Nafion content on the output performance of paper-based microfluidic fuel cells, the catalyst mixture solution was prepared by adding different doses of Nafion solution (0.2ml, 0.4ml, 0.6ml, 0.8ml) into 0.8mL isopropanol solution. As shown in Fig.2, when Nafion content is 0.2 mL, the fuel cell needs a long time to reach the highest OCV and has an extremely low peak power density. When Nafion solution content is increased to 0.4 mL, PMFC only needs 500s to reach the highest output voltage and peak power density of 11.4mw/cm², as the increase of Nafion content accelerates the rate of ion exchange in the reaction process of the fuel cell, PMFC has a shorter time to reach the highest OCV and a better output performance. However, as Nafion solution content increased to 0.6 mL and 0.8 mL, PMFC needed more than 10 minutes to reach the highest output voltage, and the peak power density also showed a trend of decline. We think that the root cause of this result is that excessive Nafion increases the movement resistance of electrons in the catalyst layer, which leads to low utilization efficiency of the catalyst.

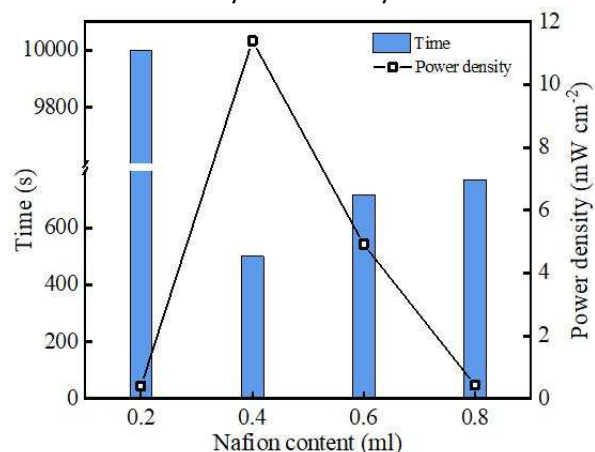


Fig.2 Optimization of Nafion solution content in preparing catalyst layer

As shown in Fig. 3, in order to further understand the cause of time to reach the highest OCV delay, EIS method was used to characterize the performance of fuel cell. The results show that 0.4 mL Nafion solution has a lower activation resistance, while high concentration Nafion solution has a higher activation resistance, and the ohmic resistance does not change. This result indicates that

excessive Nafion content will lead to a decrease in the amount of charge transfer in the catalyst layer, which is also the root cause of the excessively long time to reach the highest OCV and the degradation of fuel cell performance. In conclusion, when Nafion solution content is 0.4 mL, the time to reach the highest OCV is the shortest and output performance is the highest. Therefore, Nafion solution is used in subsequent experiments.

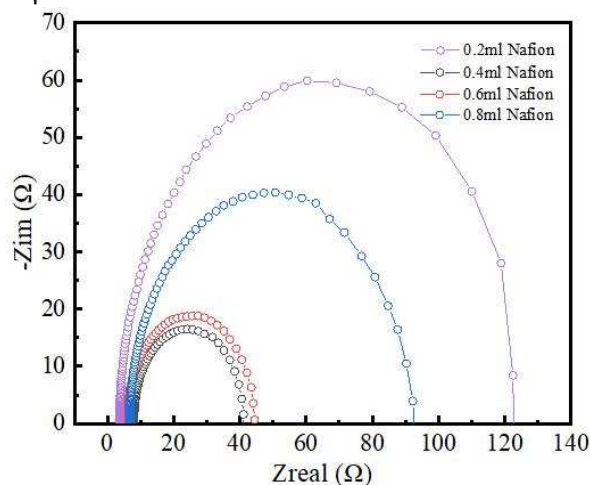


Fig.3 The EIS analysis for different Nafion content in preparing catalyst layer

3.2 Effect of Nafion distribution

At present, the optimization of output performance of PMFC focuses on the improvement of limiting current density and peak power density. Few researchers mention time of the fuel cell, which means the time from the initial reaction to the highest output voltage. Therefore, this study tries to optimize the reaction time of PMFCs by changing the distribution of Nafion.

Under the condition that the total amount of Nafion remains unchanged at 0.4 ml, 0.2 ml Nafion solution is added into 0.8 ml isopropanol solution to prepare catalyst mixed solution, and the prepared catalyst mixed solution is sprayed onto hydrophilic carbon paper to prepare the first catalyst layer electrode. Then, another 0.2ml Nafion solution mixed with 0.8 mL isopropyl alcohol solution was sprayed onto the first catalyst layer electrode to prepare catalyst layer electrode, which was used in the experiment testing. As shown in Fig.4, compared with previous fuel cells, the time to reach the highest OCV of PMFC with changed Nafion distribution (0.2ml+0.2ml) is almost doubled. As the Nafion solution on the electrode surface of the catalyst layer rapidly contacts the oxidizer of the cathode and the fuel of the anode, the ion movement rate in the fuel cell is increased, and the rate of ion participation in the

reaction of the cell is accelerated, thus the time to reach the highest OCV of PMFC is optimized.

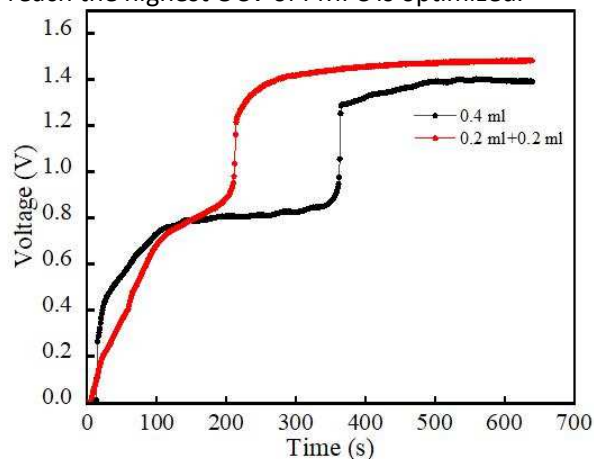


Fig.4 The comparison of reaction time of PMFC for different Nafion distribution

In order to explore the influence of changing Nafion distribution on the maximum current density and peak power density of paper-based microfluidic fuel cells, we use electrochemical testing platform to tested I-V curve and EIS curve of PMFC with changing Nafion distribution. As shown in Fig. 5, the paper-based microfluidic fuel cell with changed Nafion distribution has almost the same maximum current density and peak power density as the previous fuel cell. According to the EIS curve shown in Fig. 6, the two types of Paper-based microfluidic fuel cells with Nafion distribution have the same activation resistance. The results showed that the change of Nafion distribution only changed the ion transport rate, The catalytic efficiency of the catalyst is not affected during the reaction process, that is, the presence of 0.2 mL Nafion solution on the surface further improved the conduction velocity of the reaction solution and the ions in the catalyst layer without affecting the catalytic effect of the catalyst.

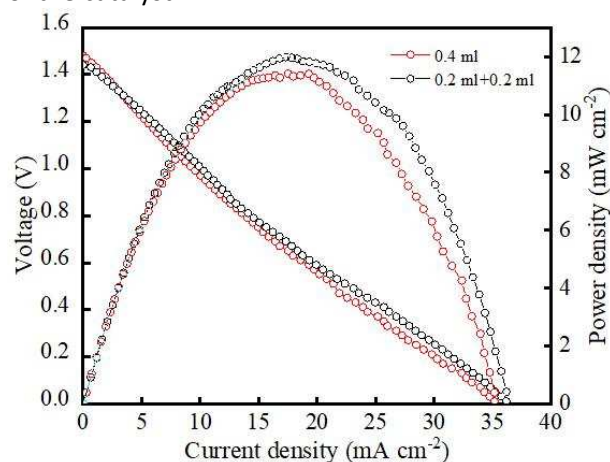


Fig.5 The comparison of PMFC performances for different Nafion distribution

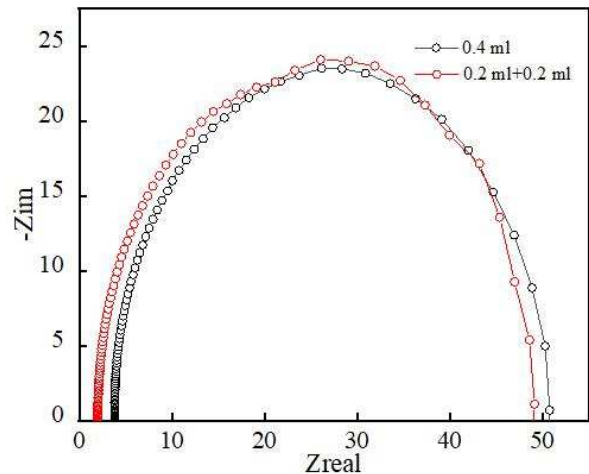


Fig.6 The EIS of PMFC for different Nafion distribution

4. CONCLUSION

In this work, we performed an experimental study on the content and distribution of Nafion in the catalyst layer. Through the analysis of V-T curve, I-V curve and EIS curve, the catalyst layer prepared by 0.4 mL Nafion solution has the shortest time to reach the maximum output voltage and has the maximum peak power density. Under the condition that the total amount of Nafion is kept constant, PMFC sprayed with 0.2 mL Nafion solution on the surface of the catalyst layer has a shorter time to reach the highest OCV. Nafion solution on the surface accelerates the ion conduction rate without affecting the action of the catalyst, so that PMFC has the same peak power density and stable output performance.

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