Malaysian Journal of Analytical Sciences
(MJAS)
Published by Malaysian Analytical Sciences Society

ANALIS
Persatuan Sains Analisis Malaysia

THE EFFECT OF MEMBRANE THICKNESS ON THE PERFORMANCE OF PASSIVE DIRECT ETHANOL FUEL CELLS USING A POLY VINYL ALCOHOL/GRAPHENE OXIDE COMPOSITE MEMBRANE

(Kesan Ketebalan Membran Terhadap Prestasi Sel Fuel Etanol Langsung Pasif Menggunakan Membran Komposit Alkohol Polivinil/Grafin Oksida)

Zulfirdaus Zakaria*

Fuel Cell Institute,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: zulfirdaus@ukm.edu.my*

Received: 27 November 2021; Accepted: 3 February 2022; Published: 27 June 2022

Abstract

Ethanol is a renewable fuel because it can be produced from a variety of production sources that are non-toxic and environmentally friendly. Thus, the consumption of passive direct ethanol fuel cells (DEFCs) as a power supply for portable devices is intriguing and potentially marketable in the future. Unfortunately, one constraint in the application of passive DEFCs is the lack of a Nafion membrane replacement. The Nafion membrane is expensive and has high ethanol permeability. We previously synthesised a crosslinked poly vinyl alcohol/graphene oxide (PVA/GO) composite membrane for passive DEFCs using low-cost polymer materials and successfully achieved low ethanol permeability. Furthermore, the characterization and performance of a crosslinked PVA/GO composite membrane outperformed that of the Nafion membrane. In the passive DEFCs, the optimal membrane thickness is a critical parameter that influences the membrane and single-cell performance. This experimental study attempted to examine the effect of a crosslinked PVA/GO composite membrane thickness on proton conductivity, ethanol permeability, membrane selectivity, and single-cell performance. The passive DEFCs achieved a maximum performance of 7.54 mW cm^{-2} at 60 °C by using a crosslinked PVA/GO composite membrane with a membrane thickness of 0.24 mm.

Keywords: polymer electrolyte membrane, membrane thickness, passive direct ethanol fuel cells, poly (vinyl)/graphene oxide

Abstrak

Etanol merupakan bahan api yang boleh diperbaharui kerana ia boleh dihasilkan daripada pelbagai sumber pengeluaran, tidak toksik, dan mesra alam. Oleh itu, penggunaan sel fuel etanol langsung pasif (DEFCs) sebagai bekalan kuasa untuk peranti mudah alih adalah menarik dan berpotensi untuk dipasarkan pada masa hadapan. Walau bagaimanapun, satu kekangan terhadap penggunaan DEFCs pasif adalah ketiadaan penggantian membran Nafion. Membran Nafion adalah mahal dan mempunyai kebolehtelapan etanol yang tinggi. Sebelum ini, kami telah mensintesis membran komposit alkohol polivinil/grafin oksida (PVA/GO) terpaut silang untuk DEFC pasif menggunakan bahan polimer berkos rendah dan berjaya mencapai kebolehtelapan etanol yang rendah. Tambahan lagi, pencirian dan prestasi membran komposit PVA/GO silang mengatasi prestasi membran Nafion. Dalam DEFCs pasif, ketebalan membran optimum ialah parameter kritikal yang mempengaruhi prestasi membran dan sel tunggal. Kajian eksperimen ini cuba untuk mengkaji kesan ketebalan membran komposit PVA/GO terpaut silang terhadap kekonduksian proton, kebolehtelapan etanol, selektiviti membran, dan prestasi sel tunggal. DEFC pasif telah memperoleh prestasi maksimum 7.54 mW cm^{-2} pada 60 °C melalui penggunaan membran komposit PVA/GO bersilang dengan ketebalan membran 0.24 mm.

Kata kunci: membran elektrolit polimer, ketebalan membrane, sel bahan api etanol langsung pasif, alkohol polivinil/grafin oksida

Introduction

High reliance on fossil fuel consumption tends to increase greenhouse gas emissions, resulting in impending climate change. Furthermore, as fossil fuel sources deplete, researchers and industry are attempting to boost the use of renewable fuels such as fuel cells. Fuel cells of many forms have been investigated, including proton exchange membrane fuel cells (PEMFCs), direct alcohol fuel cells (DAFCs), and solid oxide fuel cells (SOFCs). According to the fuel cell design, each type of fuel cell has a specific application based on the physical fuel condition and type of electrolyte used [1]. For example, direct ethanol fuel cells (DEFCs) are commonly utilised for portable device applications such as electrical and electronic devices due to the fact that these fuel cell systems can be manufactured on a small micrometre scale. Although methanol is more commonly used in the systems of DAFCs for portable device applications, there are numerous advantages to using ethanol in fuel cell systems over methanol. Ethanol is a low-cost, less-toxic, naturally existing, green, and renewable fuel that can be easily manufactured through the fermentation process [2]. Besides, the energy density of ethanol (i.e., 8.00 kW h kg^{-1}) is higher than that of methanol (i.e., 6.09 kW h kg^{-1}). Furthermore, ethanol is safe for human consumption (i.e., used in medicine). Thus, ethanol is easier to handle for the processes of storage, transfer, and management [3].

Passive DEFCs are appropriate for small portable device applications due to the unavailability of an external component required. For example, this fuel cell system does not require an external fuel pump or air blower to supply the fuel and oxidant needed for energy generation [4]. Passive DEFCs can be operated in the single-cell mode with a polymer electrolyte membrane (PEM) located in the centre cell and a pair of electrodes, as presented in Figure 1. PEM is a critical component that influences the overall performance of passive DEFCs. To achieve excellent long-term operating conditions for fuel cells, PEM should exhibit high chemical and mechanical stability, high proton conductivity, and low ethanol permeability to obtain high membrane selectivity [5]. Unfortunately, the conventional membrane that is widely used in fuel cell systems, which is a perfluorinated sulfonic acid electrolyte membrane (Nafion membrane, manufactured by DuPont), has significant ethanol permeability and leads to rapid ethanol crossover. As a result, the performance of the cell is degraded and damaged on the cathode side [6].

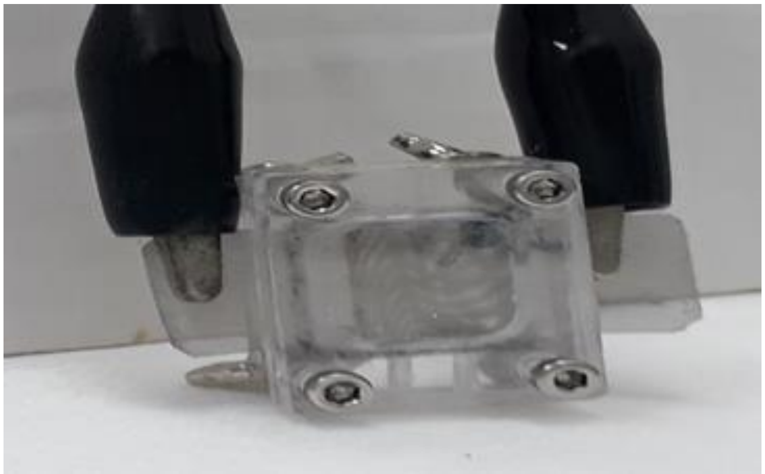

Figure 1. DIY single-cell passive DEFCs

The thickness of the membrane has a considerable effect on the membrane properties and performance of the fuel cell. Numerous studies have examined the influence of membrane thickness on fuel cell performance [7, 8]. For example, Sudaroli et al. [9] tested two distinct types of Nafion membranes with varying membrane thicknesses for fuel cell applications, Nafion 117 and Nafion 1110. According to Sudaroli et al. [9], that thicker membranes substantially decrease fuel crossover and improve single-cell efficiency. While raising the membrane thickness is efficient at decreasing fuel crossover, it has a detrimental effect on the polymeric membrane's conductivity qualities. Thus, the optimal membrane thickness is necessary to achieve the appropriate conductivity-fuel crossover balance [10].

Previously, the performance of a crosslinked poly vinyl alcohol/graphene oxide (PVA/GO) composite membrane in the use of passive DEFCs has been described. Compared to the Nafion membrane, the crosslinked PVA/GO composite membrane has a 15 wt.% loading of GO and demonstrated low ethanol permeability and good membrane selectivity [11]. In this study, the effect of the membrane thickness of a crosslinked PVA/GO composite membrane was studied to enhance the cell performance of passive DEFCs. In order to achieve the optimal membrane thickness for the crosslinked PVA/GO composite membrane, several evaluations were performed, including membrane composite self-performance and performance on single-cell passive DEFCs.

Materials and Methods

All chemicals and procedures for fabricating the membranes used in this study were previously described in our prior study utilising the simple casting solution method [11]. The GO loading was maintained at 15% by weight throughout this research. Additionally, the membrane thickness was modified according to the volume of the solution created, resulting in four distinct membrane thicknesses (i.e., 0.16 mm, 0.20 mm, 0.24 mm, and 0.28 mm). The membrane self-performance was evaluated for proton conductivity, ethanol permeability, and membrane selectivity with various membrane thicknesses. Next, the performance of single-cell passive DEFCs was measured with different membrane thicknesses of crosslinked QPVA/GO composite membranes. The cell condition was constant with 4 mg cm^{-2} of Pt/Ru catalyst (i.e., anode), 2 mg cm^{-2} of Pt catalyst (i.e., cathode), and 2 cm^{2} of active cell area at 30 °C. The technical and calculation information followed the details of the experiment from our previous work [11].

Results and Discussion

The self-performance of a crosslinked QPVA/GO composite membrane, comprising proton conductivity, ethanol permeability, and membrane selectivity, is shown in Table 1. According to the self-performance results, lowering the membrane thickness substantially boosted proton conductivity. This indicated that decreasing the membrane thickness reduced the ohmic resistance slightly and shortened the proton pathway. As a result, proton transfer within the PEM was rapid. The mechanism of proton conductivity inside the crosslinked PVA/GO composite membranes is depicted in Figure 2. The proton is mostly diffused via the vehicle and hopping mechanisms. Thus, the thin membrane thickness is generated during the proton transfer process, which is accelerated due to the resistance effect, resulting in lower resistance and a shorter diffusion pathway [12].

Table 1. Self–performance of a crosslinked PVA/GO composite membrane with varying membrane thicknesses

Membrane thickness (mm)	**σ, × 10^{-3} S cm^{-1}**	**ρ, × 10^{-7} cm^{2} s^{-1}**	**Membrane selectivity, × 10^{4} S s cm^{-3}**
0.16	11.3	2.34	4.829
0.20	9.5	1.78	5.337
0.24	8.4	1.51	5.562
0.28	7.6	1.46	5.241

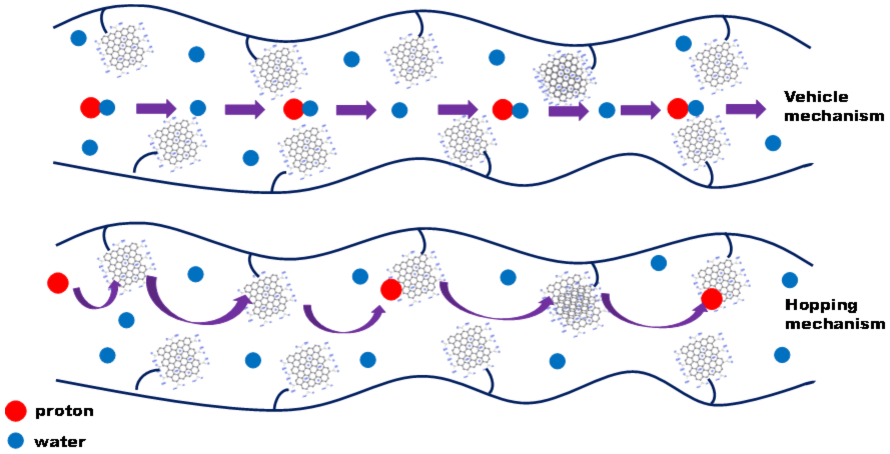

Figure 2. The mechanism of proton conductivity within the crosslinked PVA/GO composite membranes

Unfortunately, the thin membrane thickness allowed for high ethanol permeability to occur quickly due to the reduction of obstacle regions within the matrix polymer. Based on Table 1, the increasing membrane thickness is beneficial for the ethanol barrier because the fuel movement becomes more difficult to penetrate the three-dimensional matrix polymer structure between PVA, GO, and crosslinking interaction [13]. However, the proton conductivity is sacrificed due to the large membrane thickness. As a result, determining the optimal membrane thickness is critical for balancing both the membrane's self-performance and the membrane's performance. Thus, membrane selectivity is a precise metric that demonstrates the optimal membrane thickness, which balances proton conductivity and ethanol permeability [14]. According to Table 1, the maximum membrane selectivity is 5.562×10^4 S s cm^{-3} for a crosslinked QPVA/GO composite membrane with a membrane thickness of 0.24 mm. This indicated that the optimum membrane thickness is 0.24 mm and that the higher power density should be shown during the single-cell performance.

Overall, all membrane thicknesses have good results in terms of proton conductivity in the range of $\sim 10^{-3}$ S cm^{-1} and ethanol permeability in the range of $\sim 10^{-7}$ cm^2 s^{-1}. As illustrated in Figure 3, the characterization of a crosslinked PVA/GO composite membrane demonstrated suitable morphologies and structures for usage as a PEM in applying passive DEFCs. Figure 1 presents our previous characterization results, which include the analyses of FTIR, XRD, and FESEM [11]. As illustrated in Figure 3(a), the modification of PVA with GO and a crosslinked agent resulted in the presence of numerous oxygenic functional groups necessary for the hopping mechanism and the retention of water in the vehicle mechanism for proton transfer within the PEM. The crystalline and amorphous structures of a crosslinked PVA/GO composite membrane are then balanced to enhance the self-performance of the membrane, particularly in terms of proton conductivity and ethanol permeability, as shown in Figure 3(b). Besides, the dense morphology of a crosslinked PVA/GO composite membrane that was successfully synthesised as presented in Figures 3(c) and 3(d) has contributed to the critical function of managing the issue of ethanol crossover [15, 16].

All the different membrane thicknesses of a crosslinked PVA/GO composite membrane were evaluated in single-cell passive DEFCs with 2 M ethanol. Figure 4 shows the cell voltage and power density performance for all samples. The result has proven that the highest membrane selectivity with 0.24 mm membrane thickness obtained the highest power density with 5.71 mW cm^{-2}. Besides, the open cell voltage of 0.24 mm membrane thickness produced a maximum voltage of 0.85 V. This indicates that the minimum ethanol crossover was obtained with the optimal membrane thickness [17]. Furthermore, the high proton conductivity of a crosslinked PVA/GO composite membrane enhanced the electrochemical properties that rapidly transferred the proton within the matrix polymer. As a result, the redox reaction occurred smoothly and produced high cell voltage and power density [18]. Hence, the optimal membrane thickness of a crosslinked PVA/GO composite membrane for this study was 0.24 mm.

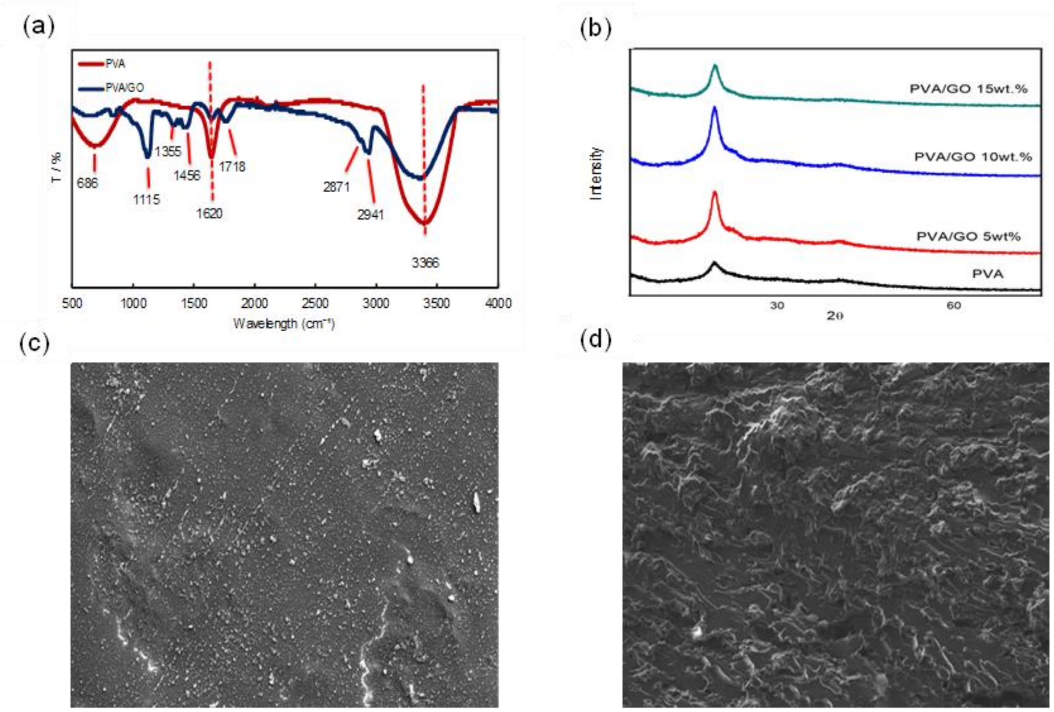

Figure 3. (a) FTIR analysis of a crosslinked PVA/GO composite membrane; (b) XRD analysis of membranes; FESEM analysis of membrane; (c) surface; (d) cross-section [11]

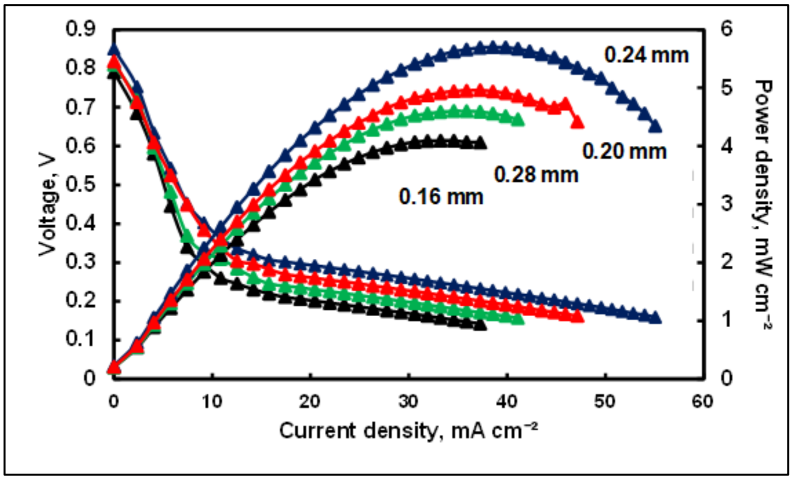

Figure 4. Cell voltage and power density of a crosslinked PVA/GO composite membrane in the passive DEFCs by varying the membrane thickness.

Finally, the optimal membrane thickness was determined using various ethanol concentrations in order to improve the cell performance of single-cell passive DEFCs using a crosslinked PVA/GO composite membrane. Three ethanol concentration values were used with the constant parameters of catalyst loading and cell operating temperature. Figure 3 presents the effect of varying ethanol concentrations, ranging from 2 M ethanol to 6 M ethanol. Obviously, the maximum power density of passive DEFCs utilising a crosslinked PVA/GO composite membrane increased from 5.71 mW cm^{-2} to 7.04 mW cm^{-2} when the ethanol concentration was changed from 2 M to 4 M. This indicates that a fuel concentration of 4 M of ethanol is a good fuel concentration to consume that can significantly improve the electrochemical activity for this investigation and boost the attainment of current density. In fact, the increment in ethanol concentration will result in a high density of ethanol molecules that can be converted to energy during the oxidation reaction at the anode [19, 20]. Unfortunately, the increment level of ethanol concentration has a limited level. Thus, this study provided a significant discovery for fuel limitation concentration. As shown in Figure 5, when 6 M ethanol was applied in passive DEFCs, the power density of a crosslinked PVA/GO composite membrane significantly decreased, going from 7.04 mW cm^{-2} to 4.45 mW cm^{-2}. This indicates that the high ethanol concentration caused the ethanol crossover to occur quickly due to the high density of ethanol molecules present at the anode. As a result, the ethanol osmotic state within the cell and ethanol transfer significantly occurred due to the different ethanol concentration conditions between the anode side and cathode side. Thus, ethanol transfers to the cathode side from the anode side through a crosslinked PVA/GO composite membrane without being affected by the oxidation process. Furthermore, this circumstance may result in both a potential problem on the cathode side and a reduction in cell performance [21, 22]. As a result, the ideal ethanol concentration was set at 4 M for this study in order to boost the performance of a crosslinked PVA/GO composite membrane in passive DEFCs.

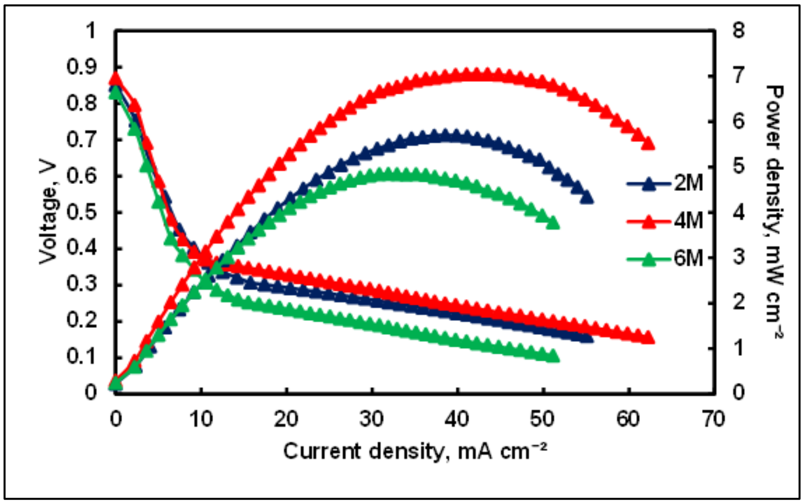

Figure 5. Cell voltage and power density of a crosslinked PVA/GO composite membrane in the passive DEFCs with optimum membrane thickness by varying the ethanol concentration

Conclusion

A simple casting solution method managed to synthesise a crosslinked PVA/GO composite membrane with good morphology and characterization. Furthermore, the thermal, mechanical, and chemical stability of this membrane has been demonstrated in our previous study, as has the excellent performance of single-cell passive DEFCs. In this study, the membrane thickness of a crosslinked PVA/GO composite membrane was manipulated to improve the cell performance of this membrane in passive DEFCs. The 0.24 mm membrane thickness demonstrated good membrane selectivity with 5.562 104 S s cm^{-3}. Thus, 0.24 mm was obtained as an optimal membrane thickness that effectively balanced the crucial parameters of a PEM (i.e., proton conductivity and ethanol permeability). At 30 °C, the power density of single-cell passive DEFCs using a crosslinked PVA/GO composite membrane was 7.04 mW cm^{-2} at an optimal ethanol concentration of 4 M. In conclusion, the membrane thickness of a PEM significantly influences the performance of passive DEFCs.

Acknowledgement

The authors gladly acknowledge their gratitude to the University of Kebangsaan Malaysia for providing this research with financial support under the Dana Modal Insan grant.

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