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Effects of the Addition of Flourinated Polymers and Carbon Nanotubes in Microporous Layer on The Improvement of Performance of a Proton Exchange Membrane Fuel Cell

Widodo W. Purwanto[1,*], *Slamet*[1], *Verina J. Wargadalam*[2], *Bono Pranoto*[1,2]

[1] Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok,Indonesia
[2] Research and Development Center for Electricity, New and Renewable Energy and Energy Conservation, Ministry of Energy and Mineral Resources Republic Indonesia, Jakarta, Indonesia
[*]E-mail: widodo@che.ui.ac.id

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The purpose of this research is to improve the performance of proton exchange membrane fuel cell (PEMFC) through two approaches. The first approach is to improve water management by using hydrophobic polymers i.e. fluorinated ethylene propylene (FEP) and polytetrafluoroetilene (PTFE) in the microporous layer (MPL). The second approach is to increase the conductivity properties of membrane electrode assembly (MEA) by using carbon nanotubes in MPL.The research results show that the utilization of 20%FEP in MPL gives better cell performance and durability up to 40 h than that of 20 wt.% PTFE because there is strong bonding between FEP and support layer, and it provides high hydrophobicity property inside the pore of carbon paper. The optimum composition of 50 wt.% MWCNT in MPL gives highest cell performance. The MPL with 50 wt.% SWCNT content gives lowest resistance in MPL which corresponds to an improvement of power density about 70% and 20% relative to, respectively, pure Vulcan and 50 wt.% MWCNT.

Keywords: Proton Exchange Membrane Fuel Cell (PEMFC), Microporous Layer (MPL), Fluorinated ethylene propylene (FEP), Polytetrafluoroetilene (PTFE), Carbon Nanotube (CNT).

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) are nowadays considered a promising energy conversion devices to deals with the energy and environmental issues because of their high power density and conversion efficiency, modularity and flexibility, low operating temperatures and zero emissions. However, significant barriers are present before commercializing this fuel cell. One of the major barriers is the degradation of stack voltage due to flooding of the catalyst layer, agglomeration of Pt/C particles, mass transport limitation, and corrosion of the carbon supports [1,2].

Water management has become one of the key engineering challenges to achieve maximum performance and durability for PEMFCs [2-4]. Some minimum level of hydration is required to maintain good proton conductivity of the membrane. However, the pores of the catalyst layer (CL) and the gas diffusion layer (GDL) as well as gas flow channels may be flooded by excessive liquid water, resulting in a higher mass transport resistance. Therefore, understanding of the water transport is critical to achieve both effective membrane hydration and fast reactant delivery, which ultimately the improves fuel cell performance .

Several studies have demonstrated that a hydrophobic microporous layers (MPL) coated on the GDL has been successfully used for improvement of the water management by reducing the electrode flooding under high humidity conditions and by preventing dryout of the MEA under low humidity conditions [5-11]. The excellent properties of carbon nanotubes such as mechanical, electrical and structural have attracted interest in many potential applications ranging from catalytic supports, electrochemical sensors, and fuel cells [12-17]. However, few works have been done towards understanding the synergetic roles of the addition of flourinated polymers and CNT in microporous layer.

The aim of this work is to investigate the roles of hydrophobic polymers type and the effects of the addition of MWCNT in MPL to improve the performance of proton exchange membrane fuel cell. The comparison of MWCNT and SWCNT on the cell performance is also studied.

2. EXPERIMENTAL

2.1. Preparation of Nafion membrane

Nafion 115 membrane (DuPont) that has been cut was soaked into first-deionized water, hydrogen peroxide, second-deionized water, hydrogen sulfide, third-deionized water, and fourth-deionized water, each step for 1 h. Lift the membrane of the final rinse and put it onto the base glass. Save a membrane in a place protected from dust, but allow the membrane to dry then let membrane dry by itself for one night.

2.2. Preparation of cathode

The experiment consist of two investigations, first, effect of polymers types in MPL, PTFE (Teplon PTFE 30, DuPont) and FEP (Teplon FEP 121, DuPont) .

The carbon slurry for the MPL was prepared using the following procedure: The carbon black powder (Vulcan XC-72) was ultrasonically mixed with PTFE (20 wt.% of MPL) and ethylene glycol.

The resulting carbon slurry was coated onto one side of the GDL using a doctor blade technique. The GDL used was a carbon-fiber paper (TGP-H-060, Toray) pre-treated with 20 wt.% PTFE. The GDL sample was then heat-treated at 350 ^{o}C for 30 min to evaporate all remaining ethylene glycol.

At the same procedure is applied when using FEP, instead of PTFE but at temperature of 260 ^{o}C. The carbon loading was maintained at 2.0 mg cm^{-2}.

The second experiment is to invesigate the effect of CNT loading and type in MPL.

The carbon slurry for the MPL was prepared using the following procedure: The carbon black powder (Vulcan XC72R) was ultrasonically mixed with CNTs (MWCNT and SWCNT, Chengdu Organic Chemical Co.Ltd) and coated onto one side of the macroporous carbon substrate.

The macroporous substrate used was pre-treated with 20 wt.% FEP. The GDL sample was heat-treated at 260 ^{o}C for 30 min to allow to uniform distribution of FEP throughout the MPL. In the MPL, the carbon loading was maintained at 2.0 mg cm^{-2} and the MWCNT was varied from 30, 50, 70, and 100 wt.%.

The cathode catalyst ink was prepared by ultrasonically blending Pt/C powder (Electrochem Inc. 20 wt.% Pt) with Nafion solution (5 wt.% Nafion, DuPont), deionized water, ethylene glycol, and methyl alcohol. The catalyst ink was sprayed onto MPL side in GDL, followed by drying at 80 ^{o}C for 15 min. The platinum loading was maintained at 0.4 mg cm^{-2}.

2.3. Preparation of anode

In anode, there is no MPL attached on GDL. The anode catalyst ink was prepared by ultrasonically mixing Pt/C powder with Nafion solution, deionized water, ethylene glycol, and methyl alcohol.

The catalyst ink was sprayed onto GDL, followed by drying at 80 ^{o}C for 15 min. The platinum loading was maintained at 0.4 mg cm^{-2}.

2.4. Preparation of membrane electrode assembly (MEA)

MEA was prepared by making sandwich position of electrode i.e. anode-membrane-cathode layers, then simultaneously pressing and heating MEA at temperature of 140 ºC for 4 min. After this pressing, MEA is ready for use.

2.5. Single cell test

The electrochemical experiments were carried out in a single cell with parallel flow channels (ECL 150 Electrochem Inc.).

Pure hydrogen and oxygen gas at room temperature without humidification were supplied to the anode and cathode compartments, respectively. All measurements were performed at ambient temperature and 10 psi pressure for each inlet gas. The active area of the MEA used in this study was 50 cm^2. Single cell test is done by measuring the voltage and current generated PEMFC in certain loading conditions.

3. RESULTS AND DISCUSSION

3.1. Effects of polymers type

Based on SEM image analysis as shown in Fig.1, the polymers is seen attached to the carbon fibers, partially cover pores between the carbons so that the porosity of sample become smaller.

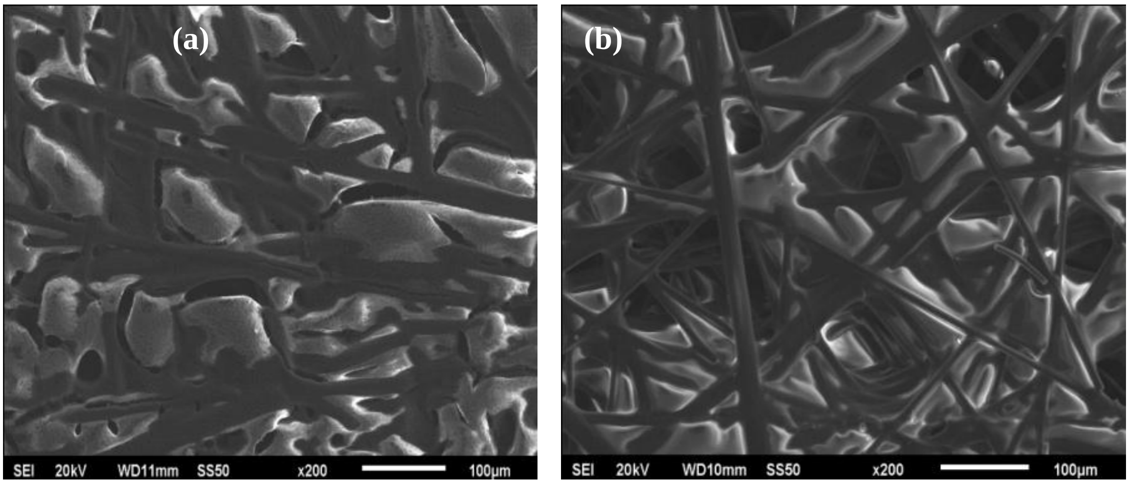


Figure 1. Surface morphologies of GDL: (a) carbon paper with PTFE; (b) carbon paper with FEP

The results of cross-sectional SEM (Figure 2) show that the PTFE coating is only able to coat top surface of the carbon paper, while the FEP is able to penetrate down to the center layer of carbon paper.

The same image on GDL are also shown in Figure 3. This occurs because the FEP is a dispersive solution, if high loading of hydrophobic polymers prevailed, then the polymers occupied gas channels in the GDL layer and cause the decrease in porosity of GDL [10], but this is no the case for PTFE.

The porosity of GDL with MPL-FEP became smaller than GDL with MPL-PTFE, but the DGL with MPL-FEP has a strong bonding.

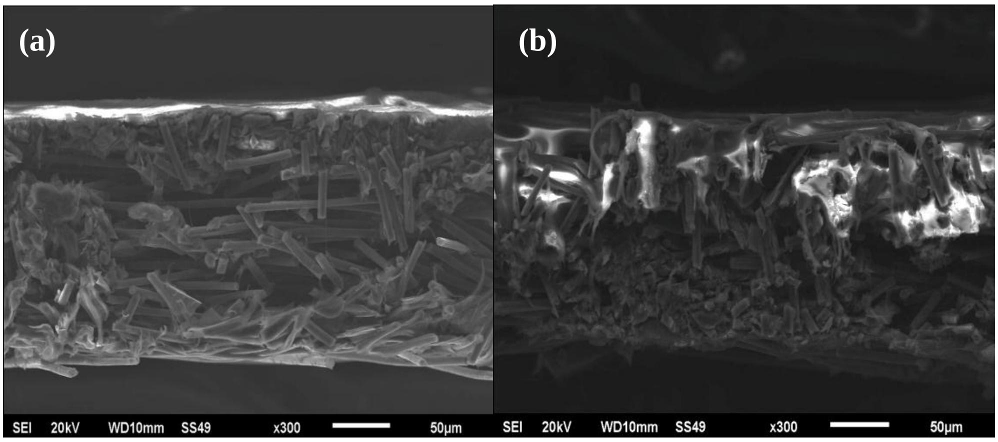


Figure 2. Cross Section morphologies of GDLs:(a) carbon paper with PTFE; (b) carbon paper with FEP

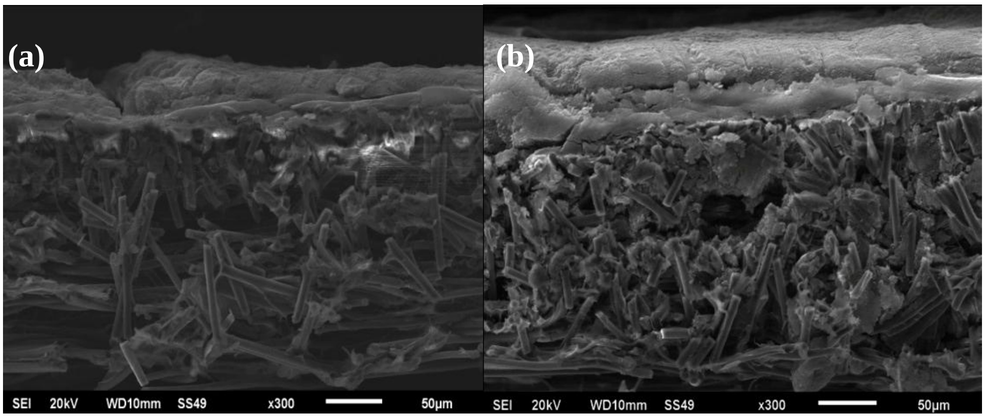


Figure 3. Cross Section morphologies of MPL+GDL :(a) MPL+GDL with PTFE; (b) MPL+GDL with FEP

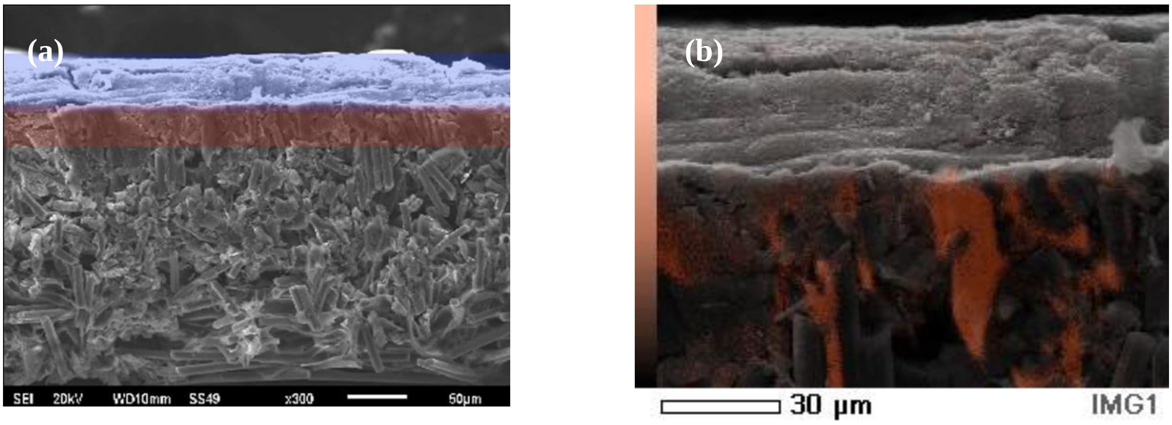


Figure 4. Cross Section morphologies of CL+MPL+GDL:(a) Electrode with FEP(blue:CL, orange: MPL); (b) SEM EDX of fluor of FEP(orange color) in electrode

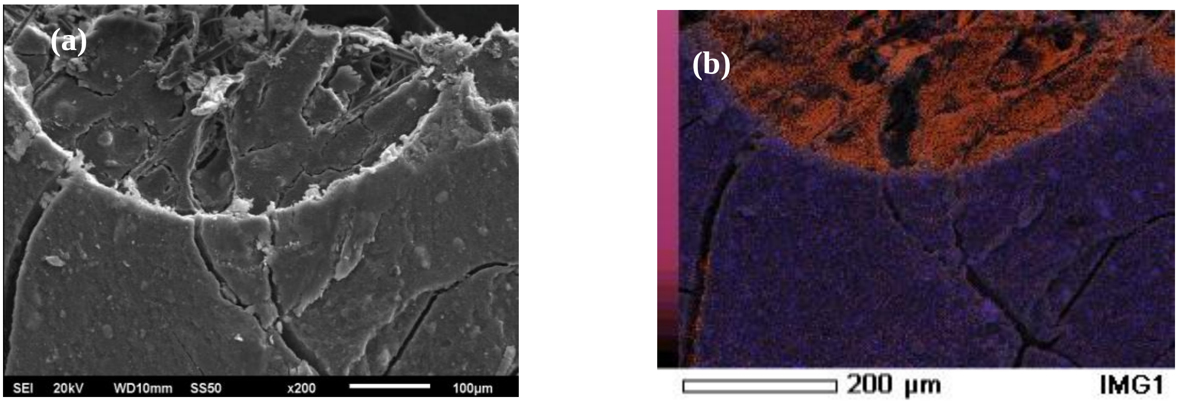
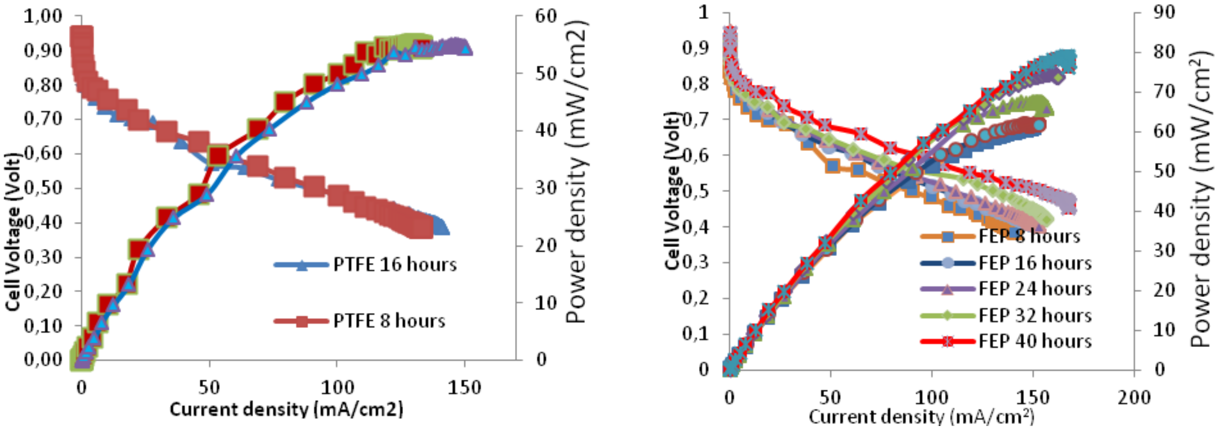


Figure 5. Surface morphologies of Catalyst Layer:(a) SEM 200x; (b) SEM EDX (orange: fluor of MPL, blue: Pt of CL)

In Fig.4a, the cross sectional SEM images of various layers such as CL, MPL and GDL are clearly shown. For the MPL, SEM EDX result showed that the fluorine content of FEP could be detected up to the center layer (Fig.4b). Surface morphologies are also displayed by Figure 5 in which the orange color in Fig.5b represents the flourine element of FEP and presence of platinum in catalyst layer is shown in blue color. The existence of a strong bonding between the polymer with its support layer is expected solve the problems of residual water. The hydrophobic agent content inside the MPL will provide water droplets because the water is not able to adhere to the layer of MPL [6].

Figure 6 compares the cell polarization of MPL-PTFE coated GDL and MPL-FEP coated GDL. It was found that the cell with MPL-FEP gives better performance than that with PTFE for all operation times. Table 1 indicates that the cell with MPL-PTFE achieves the short durability performance up 16 h and lower cell performances, while the MPL-FEP shows the highest durability performance up to 40 h and better power density than that with PTFE.



(a) **(b)**

Figure 6. Polarization curves; (a) MPL-PTFE, (b) MPL-FEP

Table 1. MEA resistance values and power densities

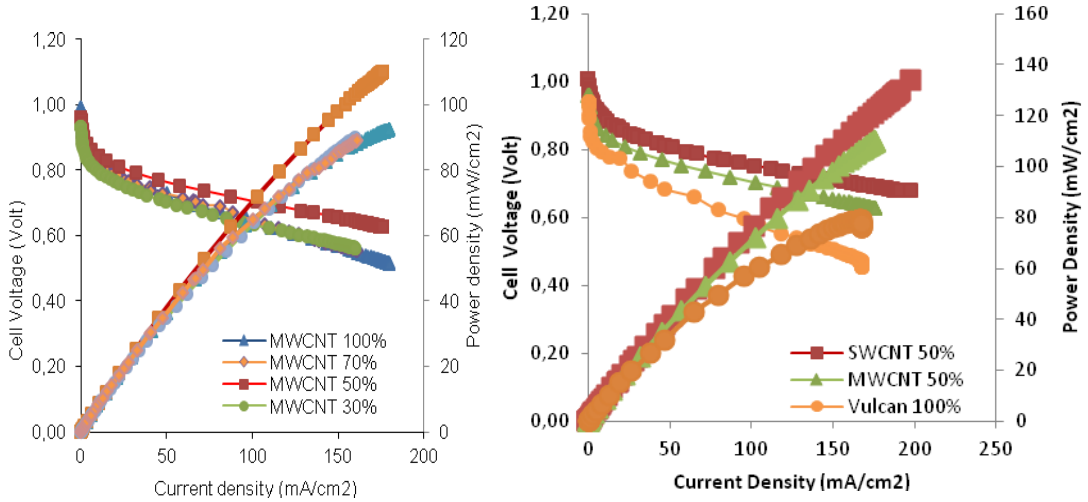
MEA tested	r (Ω.cm^2)	P (mW/cm^2)
PTFE 8 h	2.68	55
PTFE 16 h	2.93	55
FEP 8 h	2.44	60
FEP 16 h	2.32	62
FEP 24 h	2.12	67
FEP 32 h	1.98	74
FEP 40 h	1.93	79

The possible explanation of durability is based on Fig 2 and Fig. 3, in which the MPL with FEP has a strong bonding and high hydrophobicity property than MPL with PTFE. This implies that cell resistance declines during the test because of increasing water removal ability from catalyst layer and therefore avoiding water flooding. However, some minimum level of hydration is required to maintain good ionic conductivity of the membrane. The short durability performance of the cell with MPL-PTFE is due to poor bonding quality between CL and GDL and low hydrophobicity because of the PTFE is only able to coat the top surface of carbon paper.

3.2 Effect of CNT loading

Figure 7(a) and Table 2 show that the addition of MWCNT from 30 wt.% to 50 wt.% in the MPL increases the cell power density because of increasing electrical conductivity and porosity, thus better electrical and mass transfers. It is also noted that the CNT are intrinsically hydrophobic, which gives better water removal ability. The addition of more than 70 wt.% MWCNT presents mass transport limitation due to high gas void fraction and liquid saturation which affects mass transfer resistance. There is a trade off between water balance and limitation of electrical conductivity due to variation of layer thickness of MPL. The similar results have also been confirmed by Li et al [7] and Garabhi et al [16]. Our results indicate that MWCNT content of 50 wt.% in MPL yields the best cell performance (110 mW/cm^2) and consequently the lowest resistance (1.09 Ωcm^2).

Figure 7 (b) and Table 3 reveal that the addition of 50 wt.% SWCNT in MPL achieves a better cell performance than those 50 wt.% MWCNT. However, 50 wt.% MWCNT remains better performance than pure carbon black Vulcan. Based on Tapel plot, three types of MEA can be identified the losses activation area representing by charge transfer coefficient as shown in Tabel 3. It was found that MPL with SWCNT has the best coefficient of charge transfer than that with 50 wt.% MWCNT and pure Vulcan. The similar conclusion is obtained based on resistances. The MPL with 50 wt.% SWCNT gives lowest resistance (1.07 Ωcm^2) corresponding to an improvement power densities about 70% and 20% relative to pure Vulcan and 50 wt.% MWCNT, respectively.



(a) **(b)**

Figure 7. Polarization and power density MEA; (a) MWCNT varied composition; (b) comparison MWCNT, SWCNT and Vulcan

Table 2. MEA resistance and power density

MEA tested	r (Ω.cm^2)	P (mW/cm^2)
MEA MWCNT 100 wt.%	1.65	92
MEA MWCNT 70 wt.%	1.60	90
MEA MWCNT 50 wt.%	1.09	110
MEA MWCNT 30 wt.%	1.36	90

Table 3. Comparison MEA: charge transfer coeficient (α), resistance and power density

MEA	α	r (Ω.cm^2)	P (mW/cm^2)
MEA Vulcan 100 wt.%	0.377	1.93	78
MEA MWCNT 50 wt.%	0.399	1.09	110
MEA SWCNT 50 wt.%	0.419	1.07	134

4. CONCLUSIONS

Synergetic effect of the addition of flourinated polymer 20 wt.% FEP and 50 wt.% SWCNT in microporous layer gives significant improvement of PEMFC performance with the maximum power density of 134 mW/cm^2. It was found that the utilization of 20 wt.% FEP in MPL gives better cell performance and durability than that of PTFE because of strong bonding between FEP and support layer, and high hydrophobicity property inside the pore of carbon paper. The use of SWCNT in microporous layer provides a significant improvement of 70% and 20% of PEMFC performance than carbon black Vulcan and MWCNT, respectively, due to excellent properties of electrical conductivity, porosity and hydrophobicity.

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