

Effect of carbon fiber paper made from carbon felt with different yard weights on the performance of low temperature proton exchange membrane fuel cells

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Abstract

This study employed fuel cell gas diffusion layers (GDLs) consisting of carbon fiber paper made from carbon fiber felt with different yard weights in proton exchange membrane fuel cells (PEMFCs), and investigated the relationship between the yard weight of the carbon fiber paper and the fuel cell performance and thickness of the gasket. In this paper we discuss the relationship between carbon fiber felt with different yard weights and fuel cell performance and also explore the effect of carbon fiber paper thickness, air permeability, surface resistivity, and structural study. We focused on the material used for the gas diffusion layer in this study. Carbon fiber paper made in-house in this study contained 10 wt% (all percentages are by weight unless otherwise noted) phenolic resin. When the tested area was 25 cm², the test temperature was 40 °C, the gasket thickness was 0.06 mm, and the yard weight 70 g m⁻², fuel cell current density was 1968 mA cm⁻² at a load 0.3 V. When the gasket thickness was 0.36 mm and yard weight was 190 g m⁻², fuel current density was 1710 mA cm⁻² at a load of 0.3 V.

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1. Introduction

Because of their high efficiency, high power density, low operating temperature, and low noise, proton exchange membrane fuel cells (PEMFCs) are thought to be superior to other fuel cell systems in vehicle applications [1–4]. The focus of this study is on fuel cell gas diffusion layers (GDLs), which provide a channel for the transport of fuel and a medium for the conduction of current. PEMFCs typically use GDLs made of carbon fiber paper or carbon fabric, and GDL composition can play a major role in cell performance [5]. Carbon fiber fabric or carbon fiber paper are currently the most common materials used to make GDLs.

Because carbon possesses the advantages of high conductivity and corrosion resistance, it is very well suited to the special environment inside a fuel cell. The conductivity of carbon fiber increases and the hydrophobicity of the surface functional group

declines, with the graphitization temperature [6,7]. In this paper, we choose carbonization at a temperature of 1400 °C because carbon is created by gradual non-carbon release from fibers at a graphitization temperature from 1000 to 1400 °C [8]. Above 1400 °C, microstructure changes are mostly due to growth in the width of microcrystallites appearing as elongated ribbons at the graphitization temperature [9]. Bonding between the crystallization planes of the carbon layers is weak, and can be regarded as two-dimensional. Furthermore, the carbon atoms are bonded to one another by the π orbital composed of the sp^2 orbital and the ρ orbital [10]. The resonance vibration effect of the π bond of the carbon layer leads to the movement of π electrons in the carbon layer, which produces electrical conductivity. As carbon layer stacking increases, the π electrons contained therein will also increase, which leads to a reduction in resistivity and an improvement in conductivity.

While carbon fiber fabric is prone to warping and shrinking in fuel cells, carbon fiber paper offers excellent size stability. This study therefore selected carbon fiber paper as its subject, and investigated the effect of carbon fiber paper with different yard weights in an effort to increase the conductivity of the

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paper and boost fuel cell performance. Although there are several compelling reasons for operating at a higher temperature [11], we selected 40 °C for the temperature of the fuel cell. While Chen and Tseung [12] opted to study direct ethyl formate fuel cells at room temperature, we chose to work at 40 °C because in the future we plan to apply fuel cells in 3C products. But while 3C products operate at room temperature, they usually produce heat, which may cause the temperature of the fuel cell to rise above room temperature and reach roughly 40 °C. We focus on GDL production technology, and hope to boost fuel cell performance through improved GDLs. We also discuss the relationship between fuel cell performance and different yard weight proportions in carbon fiber paper GDLs, and investigate the effect of thickness, density, and surface resistivity.

2. Experimental parameters

This study used oxidized fiber felt (from Kuo Tung Felt Co., Ltd.) and phenolic resin (from Chang Chun Plastics Co., Ltd.) as raw materials. The oxidized fiber felt was first precarbonized at a temperature of 1000 °C to produce carbon fiber felt. The phenolic resin was mixed so as to constitute 10% of the solution. The carbon fiber felt material had yard weights of 70, 120, 190, 280, and 320 g m⁻², respectively. The carbon fiber felt was impregnated with the phenolic resin mixture, placed in an oven, and baked at a temperature of 70 °C for 15 min. Hot pressing at a temperature of 170 °C and pressure of 10 kg cm⁻² was performed to alter the composite material to the form of carbon fiber paper. Carbonization was then performed at a temperature of 1400 °C.

A Teclock SM-114 thickness tester was used to measure the thickness of the carbon fiber paper; thicknesses were the average of measurements taken at five random points. A Gurley Model 4320 meter was used to measure air permeability. Testing and analysis of air permeability was performed in accordance with Model 4110 regulations. A Loresta GP MCP-T600 meter was used to measure surface resistivity. Testing and analysis of surface resistivity was performed in accordance with JIS K 7194 regulations. A cold field emission scanning electron microscope was used to analyze the cross-section of the carbon fiber paper.

Use the carbon fiber paper made in-house as a fuel cell gas diffusion layer entailed cutting the paper into 5 cm × 5 cm pieces and then forming a three-layer MEA with catalyst-coated membrane (CCM) from Dupont™ (type NRE-211). We focused on the material used for the gas diffusion layer in this study, and we plan to study how to spray or coat a micro-layer and PTFE on the GDL in the future. We did not use a micro-layer on the carbon fiber paper in this study. Furthermore, we did not bond the CCM and carbon fiber paper together by hot-pressing, but only used 40 kgf cm⁻¹ torsion to ensure close contact between the layers. The MEA was placed in a fuel cell testing module, which was sealed with Teflon washers before testing. The activated area was 25 cm², and the bipolar plates were gate-type grooved graphite plates made of highly compact graphite. Stainless steel plates and PTFE washers were used to seal the module and create a fuel cell. Gas flow was 500 cm³ min⁻¹ at the anode (H₂), and also 500 cm³ min⁻¹ at the cathode (O₂), and the tem-

perature at the anode and cathode was 40 °C. All single cell operations were performed without external pressurization, and using humidified pure hydrogen and pure oxygen. Gas entrance pressure was 1 kg cm⁻², and cell temperature during testing was set at 40 °C. We used gaskets with the thicknesses of 0.06 and 0.36 mm in the cells.

3. Results and discussion

Fig. 1 shows thickness curves for carbon fiber paper with different yard weights. The main factors affecting thickness include the resin content, the hot pressing pressure, and the thickness of the material. The hot pressing pressure was 10 kg cm⁻². In this process, phenolic resin content was 10 wt%. The main factor influencing thickness in this study was yard weight. The oxidized fiber felts had thicknesses of 0.55, 0.7, 1.2, 1.5, and 3 mm prior to carbonization. The oxidized fiber felts precarbonized at 1000 °C with yard weights of 70, 120, 190, 280 and 320 g m⁻² had original thicknesses of 0.55, 0.7, 1.2, 1.5 and 3 mm, respectively. The thicknesses fell by approximately 75% to 0.42, 0.53, 0.80, 1.38 and 2.54 mm, respectively after carbonization at 1000 °C. The thickness after hot pressing was approximately 55% of the original thickness. The greater the phenolic resin content of carbon fiber felt, the better the adhesion between fibers, and the more bonding between fibers in the carbon fiber felt, the lower the thickness of the carbon fiber paper. Since, however the phenolic resin content was fixed in this study, the main factor affecting the thickness of the carbon fiber paper was the carbon fiber content per unit area. When the felt is subjected to a hot pressing pressure of 10 kg cm⁻², the greater the carbon fiber content, the less space per unit volume for compression, the higher the yard weight, and the greater the thickness of the resulting paper.

Fig. 2 shows surface resistivity and thickness curves for carbon fiber paper made from carbon fiber felt with different yard weights. The ▲ curve is the surface resistivity curve of the carbon fiber paper, and the ▼ curve is the thickness curve. This graph reveals that the carbon fiber paper becomes thicker as the yard weight increases. And as the yard weight increases, the sur-

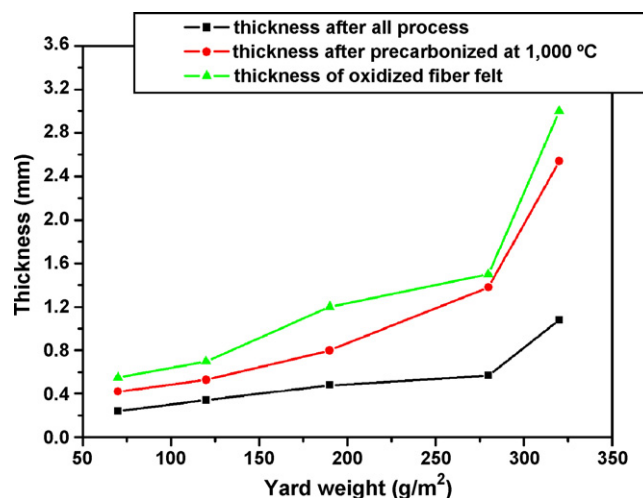


Fig. 1. Changes in the thickness of oxidized fiber felt with different yard weights after processing.

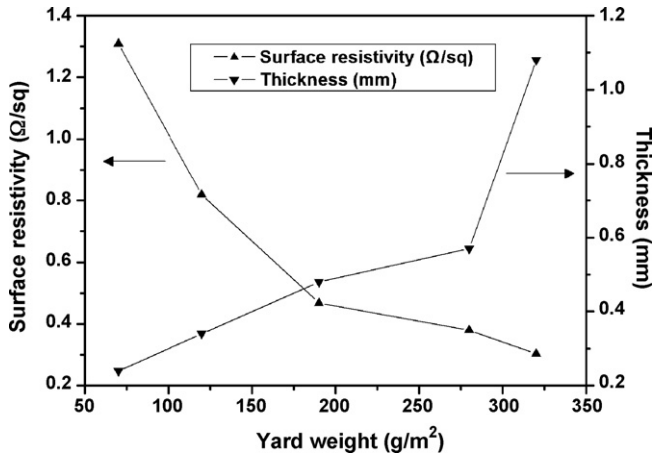


Fig. 2. Surface resistivity versus thickness for carbon fiber paper made from felt with different yard weights: (▲) surface resistivity; (▼) thickness.

face resistivity of the carbon fiber paper displays a significant decreasing trend, which implies that its conductivity increases. Carbon fiber paper prepared from felt with a yard weight of 70 g m^{-2} had a surface resistivity of $1.2 \text{ } \Omega \text{ sq}^{-1}$, while paper prepared from felt with a yard weight of 320 g m^{-2} had a surface resistivity of $0.3 \text{ } \Omega \text{ sq}^{-1}$, which is a 75% decrease in resistance. This is explained by the fact that carbon fiber paper made from carbon fiber felt with a higher yard weight contains more carbon fibers per unit volume, and has a more compact internal structure and more electron conduction pathways, than carbon fiber paper made from felt with a lower yard weight. In contrast, the looser structure of carbon fiber paper made from low yard weight carbon fiber felt results in fewer electron conduction pathways, which hampers the conduction of electrons and causes surface resistivity to increase. The figure shows that producing carbon fiber paper from carbon fiber felt with a higher yard weight can yield a higher conductivity, and the thickness of the carbon fiber paper will be relatively high.

Fig. 3 shows gas permeability and thickness curves for carbon fiber paper made from carbon fiber felt with different yard weights. The ▲ curve is the gas permeability of the carbon fiber paper, and the ▼ curve is the thickness curve. This graph reveals

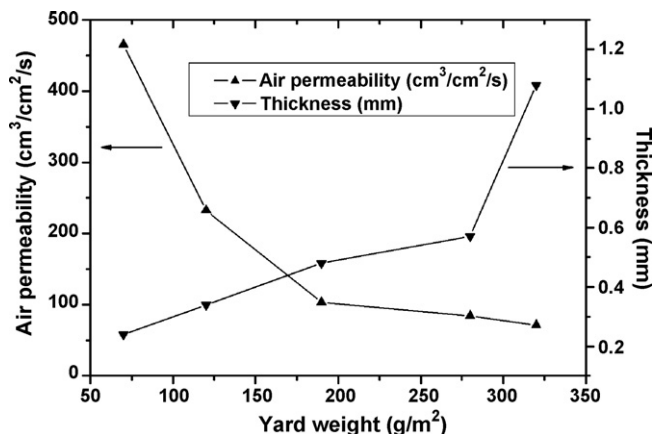


Fig. 3. Air permeability versus thickness for carbon fiber paper made from felt with different yard weights: (▲) air permeability; (▼) thickness.

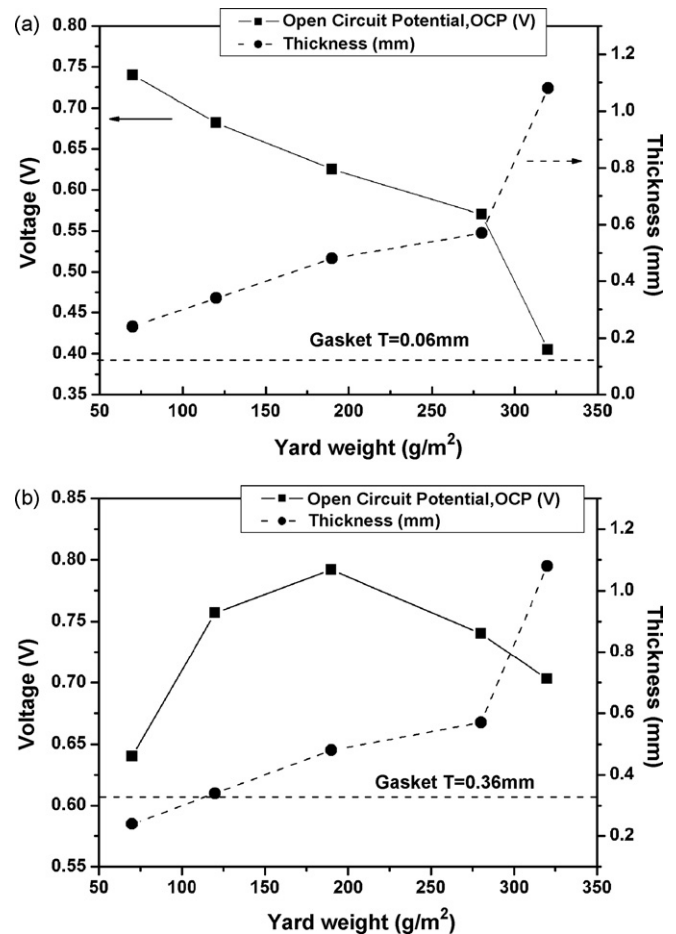


Fig. 4. (a) OCP versus thickness for GDLs made from oxidized fiber felt with different yard weights (gasket thickness of 0.06 mm). (b) OCP versus thickness for GDLs made from oxidized fiber felt with different yard weights (gasket thickness of 0.36 mm).

that the carbon fiber paper becomes thicker as the yard weight increases. And as the yard weight increases, the gas permeability of the carbon fiber paper displays a significant decreasing trend. Carbon fiber paper prepared from felt with a yard weight of 70 g m^{-2} had a gas permeability of $465 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$, while paper prepared from felt with a yard weight of 320 g m^{-2} had a gas permeability of $72 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$, which is a decrease in permeability of approximately 85%. Since carbon fiber paper made from carbon fiber felt with a higher yard weight contains more carbon fibers per unit volume, it has a more compact internal structure than carbon fiber paper made from felt with a lower yard weight. This compact structure tends to block the transmission of gas molecules, which reduces the gas permeability within the carbon fiber paper. This figure reveals that producing carbon fiber paper from carbon fiber felt with a lower yard weight can yield a higher gas permeability, and the thickness of the resulting carbon fiber paper will be relatively low.

A 0.06 mm gasket was used to test the fuel cell, and the relationship between open circuit potential (OCP) and thickness plotted. Fig. 4(a) shows that a GDL made from oxidized carbon fiber felt with a yard weight of 70 g m^{-2} yielded an OCP of 0.74 V, and a GDL made from felt with a yard weight of

320 g m⁻² yielded an OCP of 0.406 V. It can be seen that a GDL with a thickness slightly greater than that of the gasket yields the best performance and the thicker the GDL, the worse the OCP. When a gasket applies a fixed pressure and compresses the GDL to a certain thickness, the greater the yard weight, the more fibers there will be in a unit volume, and the worse the diffusion of the gaseous fuel. As a result, the greater the GDL thickness beyond the thickness of the gasket, the worse the fuel cell performance.

A 0.36 mm gasket was used to test the fuel cell, and the relationship between open circuit potential (OCP) and thickness plotted. It can be seen from Fig. 4(b) that a GDL made from felt with a yard weight of 70 g m⁻² yielded an OCP of 0.64 V, a GDL made from felt with a yard weight of 190 g m⁻² yielded an OCP of 0.792 V and a GDL made from felt with a yard weight of 320 g m⁻² yielded an OCP of 0.703 V. It can be seen that fuel cell performance is best when the GDL thickness is slightly greater than that of the gasket. As can be seen from the left-hand side of the graph, the greater the thickness of the GDL, the lower the OCP. And when the GDL thickness is less than that of the gasket, the OCP also decreases. This is because the GDL cannot effectively contact the bipolar plate when the GDL is too thin,

which impedes the effective transmission of gaseous fuel and electrons and thereby harms fuel cell performance.

The literature [13] states that a fuel cell's open circuit potential, E^{OCP} , can be expressed as:

$$E^{OCP} = E_c^r - E_a^r \tag{1}$$

where E_c^r and E_a^r can be expressed in the Nernst form as follows:

$$E_c^r = E_c^0 + \frac{RT}{4F} \ln(P_{O_2}[H^+]^4) \text{ (cathodic reaction : } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O) \tag{2}$$

$$E_a^r = E_a^0 + \frac{RT}{2F} \ln\left(\frac{[H^+]^2}{P_{H_2}}\right) \text{ (anodic reaction : } H_2 \leftrightarrow 2H^+ + 2e^-) \tag{3}$$

In Eqs. (2) and (3), E_c^0 and E_a^0 are the standard cathode and anode potentials, respectively. E_c^0 is a temperature dependent constant ($=1.229 - 0.000846X(T - 298.15)$) [14], E_a^0 is zero at

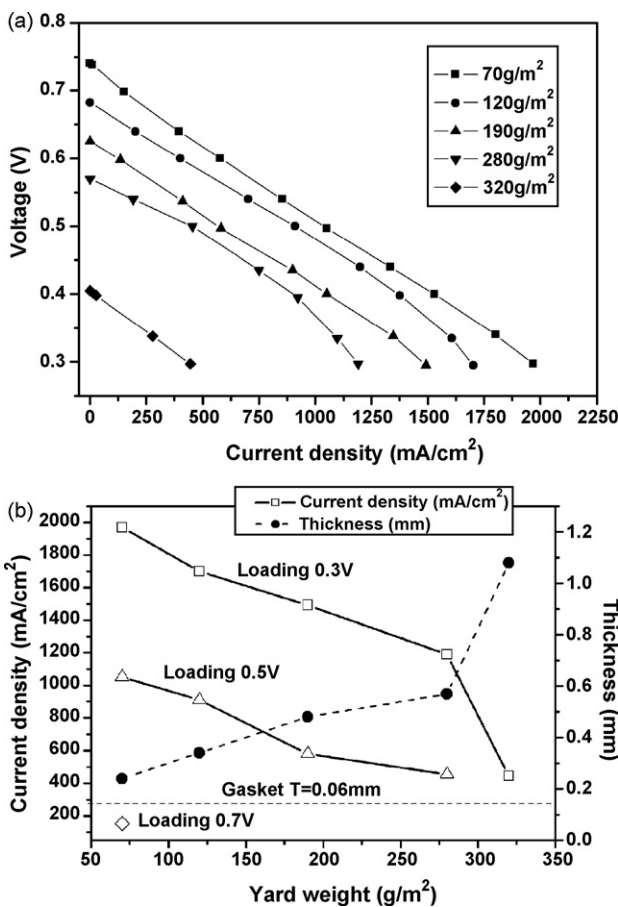


Fig. 5. (a) Current density versus operating voltage at 40 °C for GDLs made from oxidized fiber felt with different yard weights (gasket thickness of 0.06 mm). (b) Current density at loads of 0.3, 0.5, and 0.7 V versus thickness for GDLs made from oxidized fiber felt with different yard weights (gasket thickness of 0.06 mm).

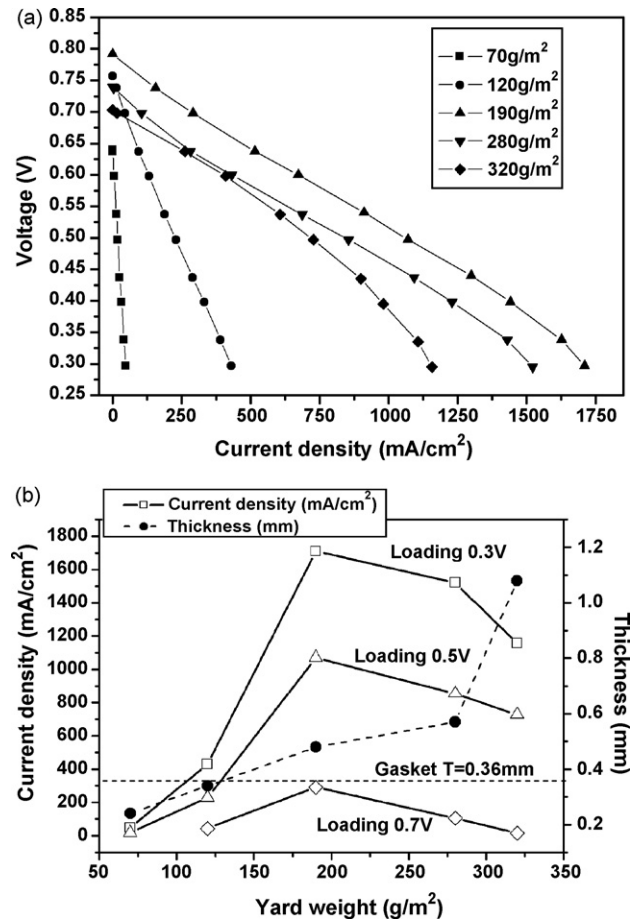


Fig. 6. (a) Current density versus operating voltage at 40 °C for GDLs made from oxidized fiber felt with different yard weights (gasket thickness of 0.36 mm). (b) Current density at loads of 0.3, 0.5, and 0.7 V versus thickness for GDLs made from oxidized fiber felt with different yard weights (gasket thickness of 0.36 mm).

all temperatures, P_{O_2} and P_{H_2} are the partial pressures (atm) of O_2 and H_2 , respectively, and $[H]^+$ is the molar concentration of protons (molL^{-1}). A theoretical OCP can be calculated by deriving Eqs. (2) and (3) to yield Eq. (4)

$$E_{\text{theor}}^{\text{OCP}} = 1.229 - 0.000846(T - 298.15) + \frac{RT}{4F} \ln[P_{O_2}(P_{H_2})^2] \quad (4)$$

This formula indicates that the chief factors affecting OCP are the operating temperature and the partial pressures of oxygen and hydrogen. When the GDL thickness is greater than the gasket

thickness, the GDL will be subject to pressure, its porosity will decrease, and the fuel gases cannot readily react. The OCP will consequently decrease. When the GDL thickness is less than that of the gasket, the GDL cannot effectively discharge the product water, and cannot effectively transmit electrons and the reactant fuel, which also causes OCP to decrease.

A 0.06 mm gasket was used to test the fuel cell, and samples of carbon fiber paper produced from oxidized carbon fiber felt with different yard weights were assembled as single fuel cells for testing. The fuel cells' polarization curves at a reaction temperature of 40 °C are shown in Fig. 5(a). The carbon

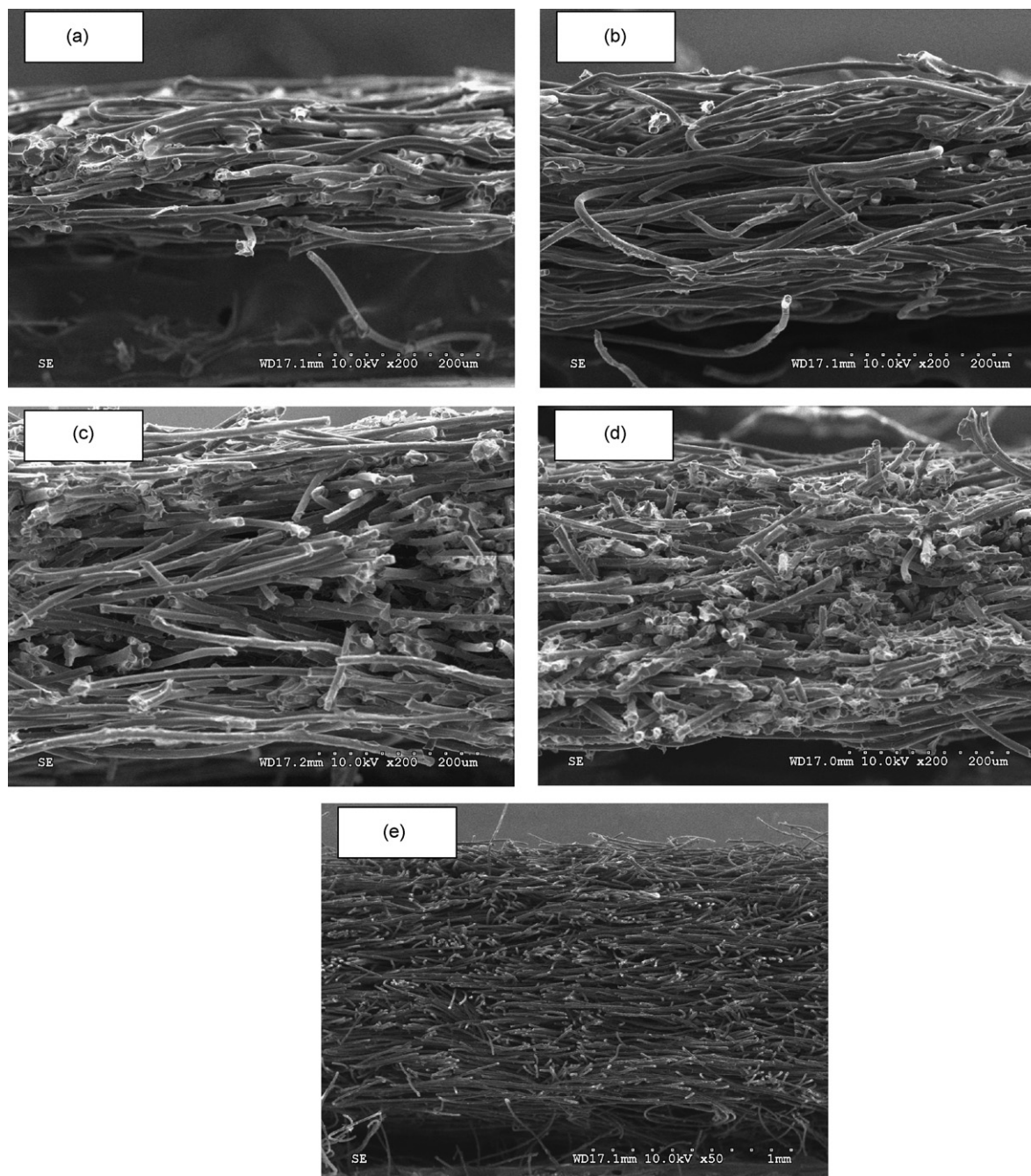


Fig. 7. SEM micrographs of the cross-section of carbon fiber paper containing different yard weight, cross-section of (a) 70 g m^{-2} ; (b) 120 g m^{-2} ; (c) 190 g m^{-2} ; (d) 280 g m^{-2} ; (e) 320 g m^{-2} .

fiber paper used as the GDL was not subjected to hydrophobic treatment and no electrode micro-layer was applied. Fig. 5(a) shows that a GDL made from oxidized carbon fiber felt with a yard weight of 70 g m^{-2} yielded relatively ideal fuel cell performance, and the current was 1968 mA cm^{-2} when the load was 0.3 V. A GDL made from oxidized carbon fiber felt with a yard weight of 320 g m^{-2} yielded a current density of 445 mA cm^{-2} when the load was 0.3 V. When carbon fiber paper samples made from oxidized carbon fiber felt with different yard weights were subjected to loads of 0.3, 0.5, and 0.7 V, the chart of current density against thickness was plotted, and the gasket thickness indicated, as shown in Fig. 5(b). It can be seen that fuel cell performance is maximal when the GDL thickness is slightly greater than that of the gasket. The thicker the GDL, the lower the current density. When a gasket applies a fixed pressure and compresses the GDL to a certain thickness, the greater the yard weight, the more fibers there will be in a unit volume, and the worse the diffusion of the gaseous fuel. As a result, the greater the GDL thickness beyond the thickness of the gasket, the worse the fuel cell performance.

GDL performance is chiefly governed by two laws: Darcy's Law, which describes the flow of fuel through the pores of the GDL, and Fick's Law, which describes the diffusion of fuel within the GDL. According to Ref. [15], applying pressure to the GDL will reduce its porosity, and will cause the flow of reactant to the catalyst layer to decrease. This will cause fuel cell performance to deteriorate. In particular there is a concentration overpotential when the load is 0.3 V, and the chemical reaction tends to be limited by the rate at which reactants can be supplied.

A relatively thick 0.36 mm gasket was also used to test the fuel cell, and samples of carbon fiber paper produced from oxidized carbon fiber felt with different yard weights were assembled as single fuel cells for testing. The fuel cells' polarization curves at a reaction temperature of 40°C are shown in Fig. 6(a). The carbon fiber paper used as the GDL was not subjected to hydrophobic treatment and no electrode micro-layer was applied. It can be seen from Fig. 6(a) that a GDL made from oxidized carbon fiber felt with a yard weight of 190 g m^{-2} yielded relatively ideal fuel cell performance, and the current was 1710 mA cm^{-2} when the load was 0.3 V. In contrast, a GDL made from felt with a yard weight of 70 g m^{-2} yielded a current density of 48 mA cm^{-2} when the load was 0.3 V, and a GDL made from felt with a yard weight of 320 g m^{-2} yielded a current density of 1157 mA cm^{-2} . When carbon fiber paper samples made from oxidized carbon fiber felt with different yard weights were subjected to load of 0.3, 0.5, and 0.7 V, the chart of current density against thickness was plotted, and the gasket thickness indicated, as shown in Fig. 6(b). It can be seen that fuel cell performance falls when the GDL is much thicker than the gasket, and fuel cell performance is worst when the GDL is much thinner than the gasket. This is because the GDL cannot effectively contact the bipolar plate when the GDL is too thin, which impedes the effective transmission of gaseous fuel and electrons and thereby harms fuel cell performance. According to Ref. [16], a thinner GDL is less able to prevent water evaporation from the MEA, resulting in membrane dehydration and hence reduced ionic conductivity.

SEM observation of carbon fiber paper showed that the methods used in this study caused phenolic resin to enter the carbon felt which yard weight is 70, 120, 190, and 280 g m^{-2} . Following hot pressing, the phenolic resin induced the fibers to bind together, creating the desired carbon fiber paper. Fig. 7 shows the carbon fiber paper produced using oxidized fiber felt pre-carbonized at 1000°C and various yard weight carbon felts. In Fig. 7(a), when the yard weight is 70 g m^{-2} , the fibers of the carbon fiber paper are bound together in bunches to any noticeable degree. In Fig. 7(b), when the yard weight is 120 g m^{-2} , fibers are clearly bound together as bunches like Fig. 7(a), but not so together because the phenolic resin content is still 10% but the carbon fibers add 50 g m^{-2} . In Fig. 7(c) and (d), when the yard weight is getting larger, it can also be seen that, as the yard weight increases, excess carbon fiber is more difficult to bind by phenolic resin. When the yard weight is 320 g m^{-2} , this kind of situation is more obvious like Fig. 7(e).

4. Conclusions

Samples of oxidized carbon felt with yard weights of 70, 120, 190, 280, and 320 g m^{-2} , respectively were pre-carbonized at 1000°C to produce carbon fiber felt. The carbon fiber felt samples were impregnated with 10% phenolic resin and carbonized at 1400°C to produce carbon fiber paper, which was used to make carbon fuel cell electrodes. This study chiefly assumed the yard weight of the oxidized fiber felt to be the main factor affecting the thickness of the carbon fiber paper. It was found that when the thickness of the carbon fiber paper was 0.24 mm when the yard weight was 70 g m^{-2} , and the thickness of the paper was 1.08 mm when the yard weight was 320 g m^{-2} . In other words, an increasing yard weight of oxidized fiber felt increased the thickness of the carbon fiber paper. Moreover, surface resistivity decreased as yard weight increased: Carbon fiber paper prepared from felt with a yard weight of 70 g m^{-2} had a surface resistivity of $1.2 \Omega \text{ sq}^{-1}$, while paper prepared from felt with a yard weight of 320 g m^{-2} had a surface resistivity of $0.3 \Omega \text{ sq}^{-1}$. Furthermore, gas permeability decreases as yard weight increases: Carbon fiber paper prepared from felt with a yard weight of 70 g m^{-2} had a gas permeability of $465 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$, while paper prepared from felt with a yard weight of 320 g m^{-2} had a gas permeability of $72 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$. Fuel cell performance was tested using gaskets with thickness of 0.06 and 0.36 mm, respectively, and it was found that fuel cell performance is best when the GDL thickness is slightly greater than that of the gasket. When the gasket thickness was 0.06 mm and the GDL was made from felt with a yard weight of 70 g m^{-2} , the current density was 1052 mA cm^{-2} at a load of 0.5 V. And when the gasket thickness was 0.36 mm and the GDL was made from felt with a yard weight of 190 g m^{-2} , the current density was 1070 mA cm^{-2} at a load of 0.5 V.

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