Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Carbon cloth based on PAN carbon fiber practicability for PEMFC applications

Hsiharng Yang[a,b,*], *H.-C. Tu*[b], *I.-L. Chiang*[b]

[a]*Institute of Precision Engineering, National Chung Hsing University, Taichung 40227, Taiwan*
[b]*Department of Research and Development, CeTech Co., Ltd., Taichung 42745, Taiwan*

ARTICLE INFO

Article history:
Received 23 March 2009
Accepted 5 May 2009
Available online 27 June 2009

Keywords:
Gas diffusion layer (GDL)
PEMFC
Carbon cloth
PAN carbon fiber

ABSTRACT

Carbon fiber cloth based on PAN (polyacrylonitrile) material was woven and fabricated into the gas diffusion layer (GDL) for PEMFC applications. This paper describes the newly developed carbon cloth as GDL and proves its feasibility for PEMFC. Such carbon cloth based GDLs have performance equal to that of conventional carbon papers verified using the standard test instrument. The mechanical tests show that as a supporting base, carbon cloth is more practical than carbon paper because of its superior compressibility, elasticity, and flexibility performance, making it more appropriate for ongoing manufacturing and assembly processes. Furthermore, even though carbon paper is structurally flatter and smoother than carbon cloth, the discharge curves of both substrates coated with a MPL (micro-porous layer) showed similar current density (around 750 mA/cm^2) at 0.6 V. This indicates that the developed carbon cloth with MPL has achieved the required performance and provides an alternative selection from carbon paper as GDL.

1. Introduction

The membrane electrode assembly (MEA) is the fundamental working unit of PEMFC (proton exchange membrane fuel cell). Inside the MEA, the gas diffusion layer (GDL) is the bridge between the flow field and the catalyst layer [1–5]. There are two important elements in creating a qualified GDL, a supporting substrate normally composed of carbon fabric and a PTFE/carbon sub-layer called the micro-porous layer (MPL), which functions to improve the water management and balance differences resulting from varied carbon fabric selections [6–8]. The supporting materials should possess the following features: porous, conductive, hydrophobic, chemically stable and reliable [1,2,5]. MPL consisting of carbon black and water-repellent binder (such as polytetrafluoroethylene, PTFE) could modify the surface roughness, pore size distribution and mechanical strength of the supporting material. Carbon black and sintered fluoro-resin applications also give the MPL sufficient electron conductivity and hydrophobicity [6–10].

Carbon fiber fabric, including carbon paper and carbon cloth, has now become the most effective electrode substrate for PEMFC due to its excellent chemical and thermal stability and low resistance [3,5,13,14]. Carbon paper fabricated by using paper-making methods or a non-woven fabric process has well-defined size, good stability and high conductivity [5,11–13]. However, carbon paper is brittle and stiff, making it difficult to avoid damage during every process step [14].

* *Corresponding author at*: Institute of Precision Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung 40227, Taiwan. Fax: +886 4 22858362.
E-mail address: hsiharng@nchu.edu.tw (H. Yang).
0360-3199/$ – see front matter © 2009 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2009.05.019

Carbon cloth demonstrates good compressibility, elasticity and flexibility, solving the drawbacks in using carbon paper as the substrate [14].

So far, the structure and working function of GDL are complex and depend strongly on the preparative methods. A suitable manufacturing process is necessary in order to produce a reliable GDL with long life time [4,5]. In this research, a carbon cloth with a newly designed structure was prepared as the supporting substrate. The essential properties of a supporting GDL substrate, including the degree of carbonization, thickness, gas permeability, pore size distribution, mechanical strength and sheet resistance, were measured and compared with a commercial product (W0S1002 from CeTech Co., Ltd.). After the MPL coating, its practicability for PEMFC was examined using the discharge curve of a single cell.

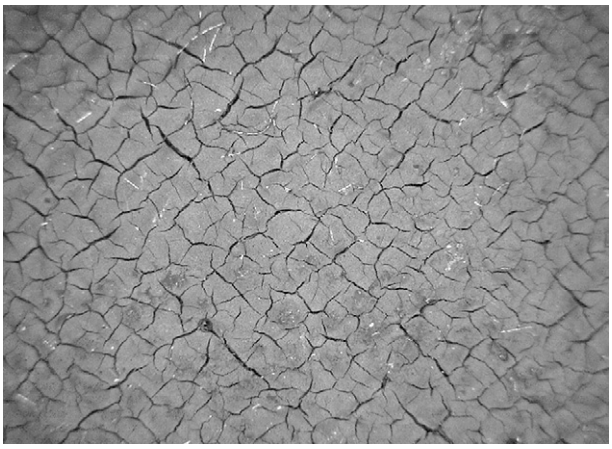

Fig. 2 – The surface morphology of the presented carbon cloth after MPL coating (using a digital microscope with the magnification, 50×).

2. Experimental

2.1. *Manufacture of carbon cloth*

A newly developed cloth formed by oxidized PAN-based fiber was used as the carbon cloth precursor. The structural changes in this plane-woven fabric were produced by controlling the fabric count and yarn plies. At 1000 °C, under an inert atmosphere (N_2 as the inert gas), the oxidized fiber cloth is first carbonized and turned into a carbon cloth after 8 h. To make the carbon cloth more conductive and anticorrosive, the carbon cloth is further graphitized for 2 h at 1700 °C under an inert atmosphere (Argon as the inert gas). The material structure was characterized using scanning electron microscope (SEM) as shown in Fig. 1.

2.2. *Characteristic measurement*

2.2.1. *Degree of carbonization*

After the graphitization process, the oxidized fiber transforms into carbon fiber. The element inside the fabric is nearly pure carbon. However, this process may be incomplete due to the sealing problem. Therefore, an elemental analyzer (Elementar vario EL III, Elementar, Germany) was used to examine the carbon content inside the carbon cloth.

2.2.2. *Degree of graphitization*

Laser Raman spectroscopy has been widely used to analyze the degree of graphitization [14]. The Raman spectra of the carbon cloth treated at 1000 °C and 1700 °C were measured using a JY-T6400 spectrometer, using the 325 nm line of a He–Cd laser.

2.2.3. *Thickness measurement*

The carbon cloth thickness was measured using an electric micrometer (HT- 8189A, Hung Ta Instrument), following the ASTM D645 testing standard. During testing, the sample (5 cm × 5 cm) would be pressed under 6.9 kPa pressure. The tested specimen would be virtually separated into four quadrants. The thickness shown in this paper is the average thickness of these four quadrants.

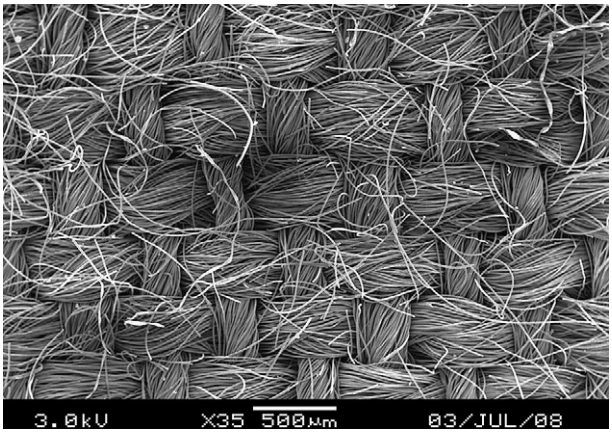

Fig. 1 – The SEM image of the new carbon cloth after graphitization (the magnification is 35×).

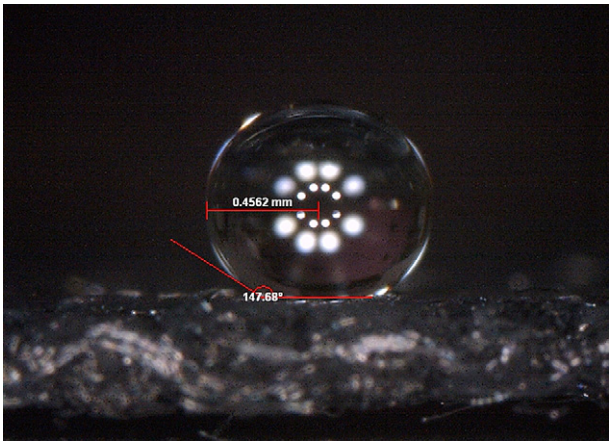

Fig. 3 – The contact angle measurement upon the MPL coated carbon cloth (using a digital microscope with the magnification, 200×).

Table 1 – The element content inside the new carbon cloth.

Element	N	C	Others (H, S, O)
Content (%)	0	98.24	1.76

2.2.4. *Gas permeability and mean pore size distribution*

A capillary flow porometer (Porous Materials, Inc.) was applied to measure both gas permeability and pore size distribution. The gas source used here was nitrogen and the size of every sample was 25 cm^2. For gas permeability, the capillary flow porometer working theory based on Darcy's law was used to automatically calculate the Darcy's coefficient. The Darcy's coefficient unit in this paper is m^2.

Since the GDL could become the transporting channel for gas and liquid water only through holes in the fabric, a capillary flow porometer that detected only through holes was chosen to analyze the pore size distribution. In this kind of porometer, the bubble point, which means the maximum pore size, and the mean pore size are two critical indices.

2.2.5. *Mechanical strength*

The tensile strength was measured using a material testing machine (HT-2328, Hung Ta Instrument) based on the ASTM D828 test standard, a constant-rate-to-elongation test standard. The test specimen size was 2.54 cm × 6.5 cm. The initial distance between the grip clamping zones was 4.5 cm, which increases with a grip separation rate of 6.35 mm min^{-1} during testing. The tensile strength of both the machine direction (MD) and cross machine direction (XD) was tested. The MD and XD tensile strength shown is this paper is the average of five tests. The tensile strength unit used in this paper is kPa cm.

2.2.6. *Sheet resistance*

According to ASTM C611, the carbon cloth sheet resistance was measured using a four point probe ohmmeter [11]. The sample was separated into nine parts and the sheet resistance shown here is the sheet resistance average measured from these nine parts. The sheet resistance unit based on ASTM C611 is expressed as mΩ/□.

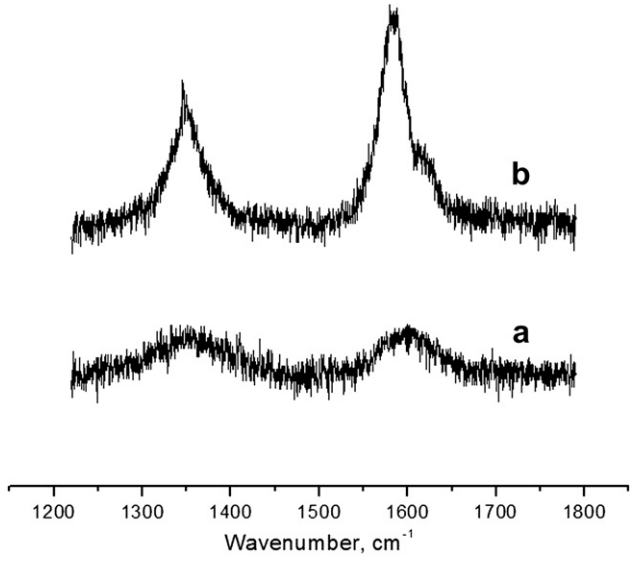

Fig. 4 – The Raman spectra of the carbon cloth after (a) 1000 °C carbonization and (b) 1700 °C graphitization.

Table 2 – The ratios of integral intensities of characteristic peaks after 1000 °C (carbonization) and 1700 °C (graphitization) treatments.

Process	I_{1360}	I_{1580}	I_{1360}/I_{1580}
1000 °C	406.0	358.9	1.13
1700 °C	691.8	1260.9	0.55

2.2.7. *The single cell discharge performance*

Before the discharge experiment, the MPL must be coated onto the carbon cloth. The MEA and MPL fabrication processes are not shown in detail here because this is not the point of this research. The surface morphology of the presented carbon cloth after MPL coating is shown in Fig. 2. Like other commercial GDLs, some cracks, which help create the necessary size pores exist on the MPL surface. The hydrophobicity of the hand-made MPL was examined by the contact angle experiment. As shown in Fig. 3, the hand-made MPL was hydrophobic because the contact angle was near 150 °C for a water drop with a 0.456 mm radius.

A fuel cell test station (PCFD PD50, APFCT) was employed to obtain the MEA polarization curve using the Tafel method. The operating conditions are shown as follows.

(1) Stoichiometry: H_2/Air = 1.5/2.5
(2) Cell temperature: 55 °C
(3) Humidification temperature: 65 °C for both anode and cathode
(4) Scanning range and rate: 0.95 V ~ 0.3 V, 50 mV/min

3. Results and discussion

As shown in Table 1, the carbon content inside the graphitized carbon cloth was over 98%. Since any carbon fiber oxidation reaction may induce a fragile structure, poor hydrophobicity and high resistance, this result indicated that the carbonization and graphitization process for the carbon cloth were complete with no oxidation reaction occurring to damage the carbon cloth. The other important feature of the carbon cloth

Table 3 – The properties of different carbon cloth.

Properties		New developed carbon cloth	CeTech W0S1002
Thickness (μm)@6.9 kPa		320	350
Gas permeability (1×10^{-12} m^2)		12.36	13.71
Bubble point (μm)		220.0	93.1
Mean pore size (μm)		62.4	52.5
Tensile strength (kPa)	MD strength	30.0	21.43
	XD strength	11.5	19.1
Sheet resistance (mΩ/□)		820	710

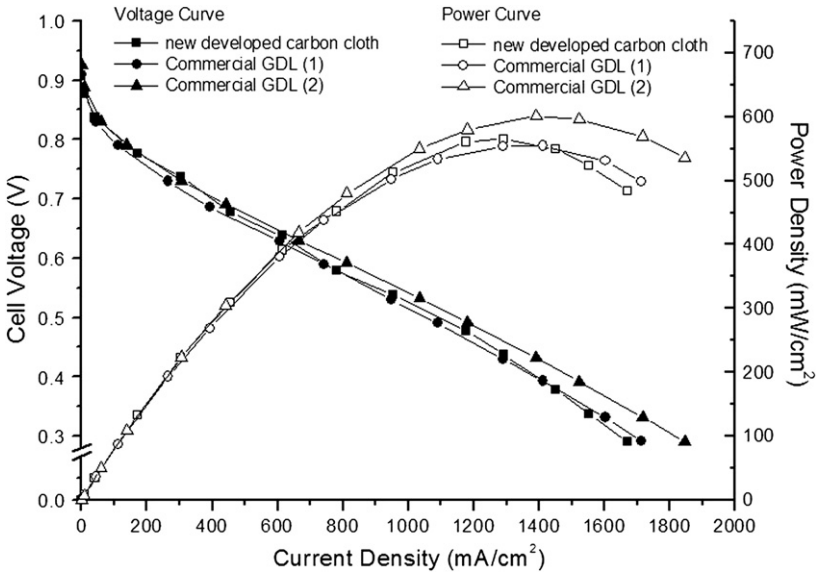

Fig. 5 – Polarization curves of PEMFC cells with different MPL coated GDLs.

was the degree of graphitization. The Raman spectra for the carbon cloth before and after the thermal treatment at 1700 °C are shown in Fig. 4. There are two Raman spectra characteristic peaks, 1580 cm^{-1} and 1360 cm^{-1}, that correlate directly to the carbon–graphite structure. The peak at 1580 cm^{-1} represents the graphite crystalline structure, which is oriented and symmetrical. The other peak, 1360 cm^{-1}, is related to the amorphous graphitized carbon [14]. The Raman spectra, shown in Fig. 4, did not have other peaks induced by the unexpected functional groups, except 1580 cm^{-1} and 1360 cm^{-1}. This indicated that the carbon cloth was totally carbonized after the thermal treatment at 1000 °C. The following graphitized process still maintained the same characteristics. The ratio of the integrated intensities of the two peaks, I_{1360}/I_{1580} was further applied to elucidate the degree of graphitization [14]. The higher ratio of I_{1360}/I_{1580} means a lesser degree of graphitization. The integrated intensities of each peak and the ratio of I_{1360}/I_{1580} after different thermal treatments are listed in Table 2. The ratio of I_{1360}/I_{1580} is clearly shown to decrease after the graphitization process. The graphitized step enhanced the graphite structure ratio and made the carbon cloth more conductive and chemical stable.

The physical properties of the newly developed carbon cloth are demonstrated in Table 3. The W0S1002 specifications made by CeTech are listed for comparison because the performance of a 240 W PEMFC stack with W0S1002 was demonstrated at HANNOVER MESSE 2008. In order to minimize the fuel cell stack volume, the GDL thickness should be as thin as possible. As shown in Table 3, a carbon cloth thinner than W0S1002 was successfully obtained. Furthermore, it should be noticed that two critical indexes for GDL, gas permeability and sheet resistance, still maintained similar values using this method. Considering the pore size distribution, this newly developed carbon cloth had similar mean pore size, but a larger bubble point compared with W0S1002. In other words, most of the pores inside this carbon cloth were still within an acceptable size range even though this weaving design may bring some huge pores into the carbon cloth. The following Tafel test further proved that the fuel cell performance was not influenced by these few huge pores.

The mechanical strength, including MD and XD strength strongly influences the practicability for mass production [5,15]. Because the new carbon cloth already demonstrated superior MD strength, the weaker XD strength (11.5 kPa for the presented carbon cloth) was the only concern for its mass production. However, the commercial carbon cloth, W0S1001, made by CeTech is available in a roll with a lower XD strength (6.53 kPa). Therefore, the weaker XD strength should not restrict mass production of the presented carbon cloth.

According to the semi-empirical model concept [16,17], the cell resistance and mass transfer efficiency strongly affects PEMFC performance when the current density increases. Previous researches [3,4,6] also exhibited that the contact resistance and the degree of flooding inside the MEA were highly related to the quality of the GDL. For this purpose, the GDL needs a smooth and hydrophobic surface to minimize the contact resistance and liquid water flooding [6–8,15]. Since carbon cloth is more uneven than carbon paper, carbon cloth must have an MPL coating to overcome this problem [15]. The cell performances of different MPL coated GDLs are shown in Fig. 5, where the commercial GDL (1) and (2) were cloth and paper-type GDLs, respectively. Although the carbon paper surface was originally more level than that of carbon cloth, the carbon cloth function was still comparable to that of carbon paper when coated with MPL. In other words, this result verified that the presented carbon cloth had the applicability for use as GDL after the MPL coating. Carbon cloth does not have the drawbacks of carbon paper, for example it is non-brittle, incompressible, unbending etc. Therefore, carbon cloth should be considered as a supporting substrate for GDL.

4. Conclusion

A thinner PAN-based carbon cloth was newly developed for PEMFC applications. After graphitization, this carbon cloth exhibits high gas permeability and low sheet resistance, suitable for use as a GDL substrate. Its mechanical strength was also sufficient for mass production. The Tafel experiment result clearly showed that the carbon cloth was a competent GDL after the MPL treatment.

Acknowledgement

Support from the Small Business Innovation Research (SBIR) program of the Ministry of Economic Affairs (MOEA) and the National Science Council (series no. NSC96-2221-E-005-068-MY3) of Taiwan is appreciated.

REFERENCES

[1] Carrette L, Friedrich KA, Stimming U. Fuel cells principles, types, fuels, and applications. ChemPhysChem 2000;1:162–93.
[2] Carrette L, Friedrich KA, Stimming U. Fuel cells – fundamentals and applications. Fuel Cells 2001;1(1):5–39.
[3] Litster S, McLean G. PEM fuel cell electrodes. J Power Sources 2004;130:61–76.
[4] Middelman E. Improved PEM fuel cell electrodes by controlled self-assembly. Fuel Cell Bull 2002;11:9–12.
[5] Wild PM, Mändle M, Murata M, Berg N. Structural and physical properties of GDL and GDL/BPP combinations and their influence on PEMFC performance. Fuel Cells 2004;4(3):180–4.
[6] Kong CS, Kim D-Y, Lee H-K, Shul Y-G, Lee T-H. Influence of pore-size distribution of diffusion layer on mass-transport problems of proton exchange membrane fuel cells. J Power Sources 2002;108:185–91.
[7] Lee H-K, Park J-H, Kim D-Y, lee T-H. A study on the characteristics of the diffusion layer thickness and porosity of the PEMFC. J Power Sources 2004;131:200–6.
[8] Qi Z, Kaufman A. Improvement of water management by a microporous sublayer for PEM fuel cells. J Power Sources 2002;109:38–46.
[9] Park G-G, Sohn Y-J, Yang T-H, Yoon Y-G, Lee W-Y, Kim C-S. Effect of PTFE contents in the gas diffusion media on the performance of PEMFC. J Power Sources 2004;131:182–7.
[10] Antolini E, Passos RR, Ticianelli EA. Effects of the carbon powder characteristics in the cathode gas diffusion layer on the performance of polymer electrolyte fuel cells. J Power Sources 2002;109:477–82.
[11] Zhang X, Shen Z. Carbon fiber paper for fuel cell electrode. Fuel 2002;81:2199–201.
[12] Walker NJ. Carbon fibers: technology, uses and prospects. The Plastics and Rubber Institute; 1986.
[13] Gaffney John J, Loszewski Raymond C. Carbon-matrix composites, compositions and methods related thereto. U.S. patent 6,127,059.
[14] Zou L, Huang B, Huang Y, Huang Q, Wang C. An investigation of heterogeneity of the degree of graphitization in carbon–carbon composites. Mater Chem Phys 2003;82:654–62.
[15] Kato Hiroshi. Gas diffusion layer for solid polymer electrolyte fuel cell. U.S patent 6,127,059.
[16] Kim J, Lee SM, Srinivasan S, Chamberlin CE. Modeling of proton exchange membrane fuel cell performance with an empirical equation. J Electrochem Soc 1995;142:2670–4.
[17] Tu HC, Wang YY, Wan CC, Hsueh KL. Semi-empirical model to elucidate the effect of methanol crossover on direct methanol fuel cell. J Power Sources 2006;159:1105–14.