

Wire rod coating process of gas diffusion layers fabrication for proton exchange membrane fuel cells

A.M. Kannan^{a,*}, S. Sadananda^a, D. Parker^a, L. Munukutla^a, J. Wertz^b, M. Thommes^c

^a *Electronic Systems Department, Arizona State University, 7001 E Williams Field Road, Mesa, AZ 85212, United States*

^b *Hollingsworth & Vose Co., A.K. Nicholson Research Lab, 219 Townsend Road West Groton, MA 01472, United States*

^c *Quantachrome Instruments, 1900 Corporate Drive, Boynton Beach, FL 33426, United States*

Received 26 October 2007; received in revised form 1 December 2007; accepted 3 December 2007

Available online 15 December 2007

Abstract

Gas diffusion layers (GDLs) were fabricated using non-woven carbon paper as a macro-porous layer substrate developed by Hollingsworth & Vose Company. A commercially viable coating process was developed using wire rod for coating micro-porous layer by a single pass. The thickness as well as carbon loading in the micro-porous layer was controlled by selecting appropriate wire thickness of the wire rod. Slurry compositions with solid loading as high as 10 wt.% using nano-chain and nano-fiber type carbons were developed using dispersion agents to provide cohesive and homogenous micro-porous layer without any mud-cracking. The surface morphology, wetting characteristics and pore size distribution of the wire rod coated GDLs were examined using FESEM, Goniometer and Hg porosimetry, respectively. The GDLs were evaluated in single cell PEMFC under various operating conditions (temperature and RH) using hydrogen and air as reactants. It was observed that the wire rod coated micro-porous layer with 10 wt.% nano-fibrous carbon based GDLs showed the highest fuel cell performance at 85 °C using H₂ and air at 50% RH, compared to all other compositions.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Non-woven carbon paper; Gas diffusion layers; Wire rod coating process; Surface morphology; Pore size distribution

1. Introduction

Fuel cells, which can offer the possibility of zero emission at the point of use, have been widely advocated to be the best candidate capable of replacing the internal combustion engines (ICEs). Among various fuel cell types, the proton exchange membrane fuel cell (PEMFC) has the greatest potential as an alternative power source for transportation application due to its relatively low temperature (<100 °C) of operation. A critical component in controlling the performance, durability and cost of the PEMFCs is the membrane electrode assembly (MEA). The MEA consists of a pair of catalyst layers (anode and cathode) adjacent to both sides of a proton exchange polymer electrolyte membrane with a pair of gas diffusion layers (GDLs) just on the outside surfaces of the catalyst layers.

The power density values of PEMFCs are normally controlled by the mass transport characteristics (high current density region) at the cathode, when air is used as oxidant instead of oxygen. Balanced hydrophilicity/hydrophobicity properties of the GDLs can play a significant role in controlling the fuel cell performance over a wide range of operating conditions of relative humidity (RH) of the feed gases and cell temperatures [1]. This was specifically carried out by continuous variation of pore diameters from the macro-porous layer towards the catalyst layer, by changing the polytetrafluoroethylene (PTFE) and the composition of carbon. In addition, the PTFE content in the GDL changes the electrode microstructure and the total porosity decreases by increasing PTFE content. Furthermore, a minimum quantity of PTFE in the GDL is necessary to bond together the carbon particles [2]. A well balanced amount of hydrophobic amount is very critical to facilitate liquid water removal, and excessive amounts of hydrophobic agents could lead to blocking the GDL surface pores. Effects of fluorinated ethylene propylene (FEP) hydrophobic polymer content in carbon paper GDL on the power density of H₂/air PEM fuel cells have been studied and

* Corresponding author. Tel.: +1 480 727 1102; fax: +1 480 727 1723.
E-mail address: amk@asu.edu (A.M. Kannan).

characterized comprehensively. The single cell tests under various cathode humidification and flow rate conditions, however, reveal that the MEA with 10 wt.% FEP-impregnated cathode GDL provided much higher power densities than the one with 30 wt.% FEP-impregnated carbon paper. It appears that 10 wt.% FEP loading is sufficient to result in a hydrophobic surface to facilitate liquid water removal, and that higher FEP content in excess of 10 wt.% can only block GDL surface pores, thus imposing significant mass transport limitations due to both oxygen transport and water removal through a highly restricted GDL surface [3]. The effect of PTFE amount, which influences the gas permeability, pore diameter, hydrophobicity, total porosity, surface area, limiting current density, etc. has also been studied in the literature [4,5].

Effects of fabrication processes and influence of GDL's material parameters on cell performance of a PEM fuel cell have been very well documented by Yan et al. [6] by using various amounts of fluorinated ethylene propylene (FEP) based hydrophobic agent. Furthermore, it is also important to have GDLs with optimized pore size to attain the best performance of the fuel cell [7,8]. The influence of micro-porous layer with optimum convection characteristics on the limiting current density when air is used as oxidant was studied extensively by Williams et al. [9]. This study clearly demonstrated that the GDL with higher gas permeability in the micro-porous layer is one of the key requirements to obtain higher limiting current due to more enhanced convection. The structure of the GDLs can also influence the fuel cell performance at various operating conditions. For example, the GDLs were shown to support the fuel cell operation with no external humidification at 80 °C [10].

Hence, the fuel cell performance at the mass transport region can be improved by designing and developing the GDLs with unique characteristics [11,12]. In this context, Wang et al. have examined the strategy of developing a micro-porous layer with composites using Black Pearl and Acetylene Black type carbons for improving gas and water transport properties. It has also been reported that the pore diameters of the micro-porous layers could be manipulated by varying the composition of the carbon types and peak power density of about 0.9 W cm^{-2} with H_2 and air reported with back pressure for 10% Black Pearl and 90% Acetylene Black carbons based micro-porous layer [13,14]. Several GDL fabrication techniques have been investigated in the past, which include low-shear coating, rod coating, screen printing, doctor blade, impregnation [15–20], etc. It is worth mentioning about the dry deposition technique for GDL fabrication, reported by Yu et al. [21]. The fabrication involves dry deposition of a mixture of carbon black and polytetrafluoroethylene powders onto water-proofed carbon paper in combination with a subsequent rolling process. Three types of carbon materials, including Ketjenblack EC-600JD, Vulcan XC-72 and Denka, were investigated in the dry method. However, most of these studies including the dry powder method of GDL fabrication appears to be slow and is difficult to adopt for mass production. The objective of the present study is to demonstrate a coating process of micro-porous layer using wire wound rod, on the non-woven carbon paper as an efficient way to manufacture GDLs. In addition, GDLs were also fabricated by using various composi-

tions of carbon nano-fibers and carbon nano-chains for creating pores with different pore diameter in the micro-porous layers. The wire rod coated GDLs were characterized by several techniques including Scanning Electron Microscope, Goniometer and Hg porosimetry. The MEAs with the wire rod coated GDLs and catalyst-coated Nafion-212 membranes were evaluated in single cell fuel cell at various temperatures using H_2 and air.

2. Experimental

2.1. Gas diffusion layer

Gas diffusion layers were fabricated with a teflonized non-woven carbon paper developed by Hollingsworth & Vose Company, West Groton, MA. Teflon content in the macro-porous carbon paper substrate is about 15 wt.% to avoid flooding by the product water. Hydrophobic characteristic of the micro-porous layers was provided by TE5839 Teflon suspension (Dupont, Wilmington, DE). Vapor grown carbon fiber (VGCF-H) manufactured by Showa Denko America Inc., NY was mixed with nano-chain Pureblack[®] 205-110 Carbon (Superior Graphite Co., Chicago, IL) to provide improved mechanical strength and adhesion between the micro-porous and macro-porous layers. A slurry of carbons (75 wt.% Pureblack carbon and 25 wt.% nano-fibrous carbon (VGCF)) with PTFE dispersion (25 wt.%) in isopropanol was prepared by ultrasonication followed by magnetic stirring, along with Novec 7200 dispersion agent (3M Electronics, MN) for the fabrication of micro-porous layers used in this study.

The slurry was coated on to the non-woven carbon paper using wire wound rods, obtained from RD Specialties, NY (<http://www.rdspecialties.com>) and a motorized set-up for the wire wound rod is developed in-house. Wire wound rods are stainless steel rods (0.5 in. diameter) wrapped very tightly with stainless steel wire of various thicknesses (RDS50 has a 50 mil wire). The carbon loading of the micro-porous layer was controlled by the slurry composition (10 wt.% carbon in isopropyl alcohol) and the wire thickness on the wire rod. The gap between the wires on the wire rod determined the amount of carbon material during the coating process. A schematic representation in Fig. 1 shows the semi-automatic set-up used for the GDL fabrication. The carbon substrate was fixed in place and the wire rod was driven at a speed of about an in. s^{-1} . The coating speed in the semi-automated process set-up was qualitatively optimized to obtain continuous and uniform coating. It was observed that the wire rod speed $>1 \text{ in. s}^{-1}$ led to less coherent slurry coating in the set-up developed in this study. Subsequently, carbon paper with the micro-porous layer was dried at 150 °C for 2 h and then sintered at 350 °C in air for about an hour. The carbon loading for the micro-porous layer was between 2.5 and 3 mg cm^{-2} with RDS50 wire rods. It was observed that the wire rods with finer wires (RDS30, RDS20, RDS10) had smaller gaps between the wires leading lower amounts of carbon loading.

To emphasize the requirement of nano-sized pores in the micro-porous layers, four GDL samples were also fabricated by wire rod coating with different amounts of VFCF fibers and Pureblack carbons and evaluated at various operating conditions.

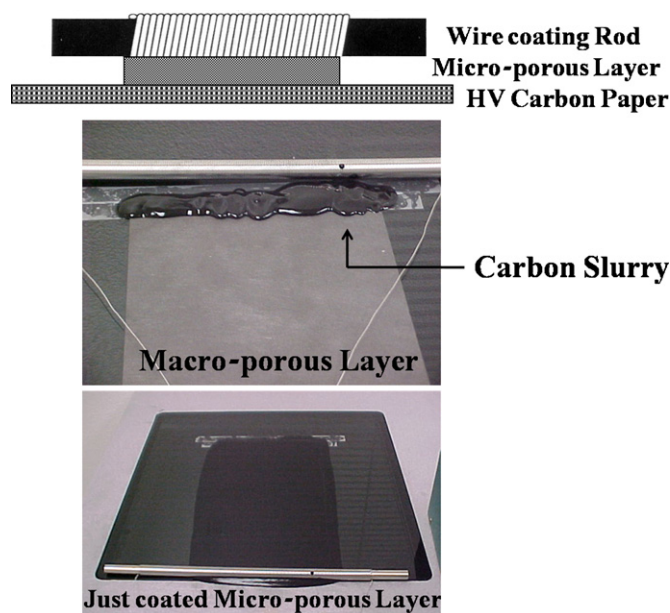


Fig. 1. Schematic representation of coating the non-woven carbon paper (Hollingsworth & Vose) with a micro-porous layer using a wire rod (RDS 50) by a semi-automatic process.

Table 1
Composition of micro-porous layers of the GDL samples and their respective pore diameter

Sample	Carbon composition (%)		Pore diameter (μm)
	VGCF	Pureblack	
1	75	25	1
2	50	50	0.2 and 0.5
3	25	75	0.12
4	10	90	0.08

As given in Table 1, the GDL samples had the compositions of 75:25, 50:50, 25:75 and 10:90 wt.%, respectively, with a uniform PTFE composition of 25 wt.%.

The surface morphology of the GDL samples was examined by JEOL JSM-5900LV Scanning Electron Microscope. The robustness of the micro-porous layer and the adhesion of the micro-porous layer to the macro-porous substrate were evaluated by subjecting the GDLs to ultrasonic vibration [22]. In brief, the disintegration time required for the GDLs containing Pureblack and VGCF composite was almost three times (say 30 min against 10 min) compared to that without nano-fibrous carbon. NRL CA Goniometer (Ramehart 100) was used to study the wetting characteristics of the micro-porous layer of the GDL samples. The contact angle of a droplet of water and ethanol mixture (1:1 ratio) on the micro-porous layer was measured after 5 min. The wetting angle measurement was made in at least three locations on the micro-porous layer side in each sample. The data provided in the present study is a representative point. The pore diameter and pore size distribution of the wire rod coated GDL samples were measured by using PoreMaster-60 GT in both low and high pressure modes by Hg intrusion method in fixed speed mode.

2.2. Catalyst-coated membrane

Catalyst-coated membranes (CCM) with 5 cm^2 active area were fabricated using Pt/C catalyst slurry in isopropanol (20 ml for 1 g of electrocatalyst) using the micro-spray method for anode and cathode sides on Nafion[®] membrane (NRE 212, Ion Power Inc., New Castle, DE, USA). The isopropanol was added after purging the catalyst powder in flowing nitrogen gas for about 30 min to avoid any flame/ignition. In order to extend the reaction zone of the catalyst layer, 5% Nafion[®] solution from (30 wt.% to Pt catalyst; 10 ml Nafion solution for 1 g of electrocatalyst) was added to the catalyst slurry. The membrane was fixed in a home-made fixture to ensure anode and cathode catalyst layers are exactly on the same area of the membrane. The catalyst loadings on the anode and cathode sides were about 0.5 and 1 mg Pt cm^{-2} , respectively. The catalyst coated Nafion-212 membrane was vacuum dried at about 70°C for an hour before assembling it in the fuel cell test cell.

2.3. Membrane electrode assembly and fuel cell performance

The GDLs and the CCM were not hot-pressed but assembled by just sandwiching inside the single cell test cell (Fuel Cell Technologies Inc, Albuquerque, NM, USA). Gas sealing was carried out using silicone coated fabric materials (Product #CF1007, Saint-Gobain Performance Plastics, USA) and with a uniform torque of 40 lb in. The single cell performance of a fuel cell for various GDLs was evaluated at various temperatures ($65, 70$ and 85°C) and relative humidity conditions (50, 75, 100% RH) with H_2/air under ambient pressure by galvanostatic polarization using Greenlight Test Station (G50 Fuel cell system, Hydrogenics, Vancouver, Canada). The gas flow rates were fixed at 200 and 400 SCCM for hydrogen and air, respectively. The steady state voltage values were collected by holding the cell at each current density values for 60 s. The relative humidity of the reactant gases were maintained at various values (50, 75 and 100% RH) by controlling the humidity bottle temperature.

3. Results and discussion

Fig. 2a–c show the SEM images of the micro-porous layer at three different magnifications ($250\times$, $15,000\times$ and $40,000\times$), respectively, fabricated with the semi-automatic process using 75 wt.% Pureblack carbon and 25 wt.% nano-fibrous carbon. The low magnification SEM image shows homogeneous carbon distribution and crack free surface morphology leading to uniform gas distribution. The surface morphology explains clearly the mechanical characteristics of the micro-porous layer's reinforcement by the presence of carbon nano-fibers (Fig. 2b and c). The nano-fibers are not ordered and they are entangled both in and through the plane to provide structural integrity of the micro-porous layer to the GDL substrate. The bubble point pressure (0.23 psi) of the coated GDLs was slightly lower than that fabricated by spray method using Vulcan XC-72R (0.45 psi). As expected, the pore size was also found to be larger than that of the commercially available GDLs. Fuel cell performance of

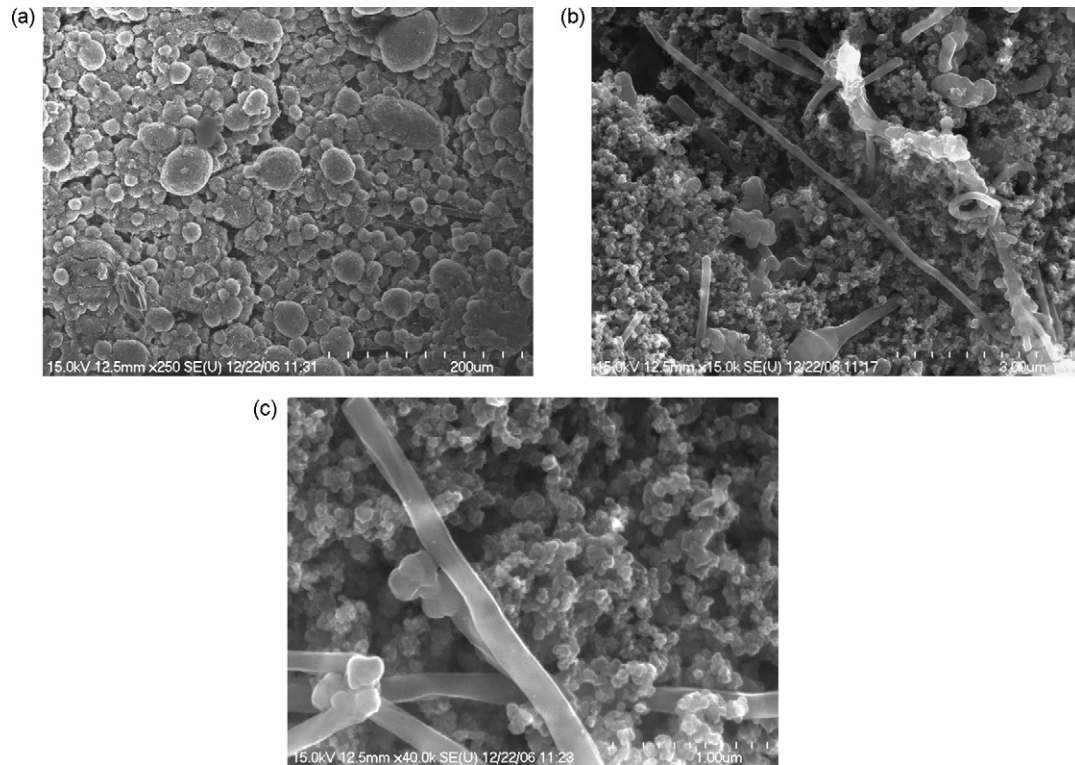


Fig. 2. Scanning electron micrographs of a gas diffusion layer fabricated with Pureblack and VGCF (75:25 wt.%) by using wire wound rod (RDS 50) on HV carbon paper.

the GDLs was evaluated using Nafion-212 with hydrogen/air at ambient pressure at various temperatures and RH condition.

Fig. 3 shows the scanning electron micrograph of the cross-section of a GDL fabricated with 75 wt.% Pureblack carbon and 25 wt.% nano-fibrous carbon based micro-porous layer. As seen from Fig. 3, the wire rod coated micro-porous layer shows a thickness of above 100 μm . The GDL cross-section is also free from any carbon bleed-through from the micro-porous layer to the uncoated side of the macro-porous carbon paper substrate, keeping the pores in the macro-porous layer unblocked. The

structural characteristics of the porous features in the cross-section highlight the combination of mechanical robustness of the nano-chain and nano-fibrous type carbons.

The wetting angle profiles using water–ethanol (1:1 ratio) are given in Fig. 4 for a GDL fabricated with a micro-porous layer containing Pureblack and VGCF (75:25 wt.%) by using a wire wound rod (RDS50). Ethanol was mixed with water to improve the wetting characteristics, as pure water alone could not be used for wetting angle measurements. As indicated in Fig. 4, the wetting angle is the angle that the tangent makes with the point of contact of the drop with the micro-porous layer, the surface

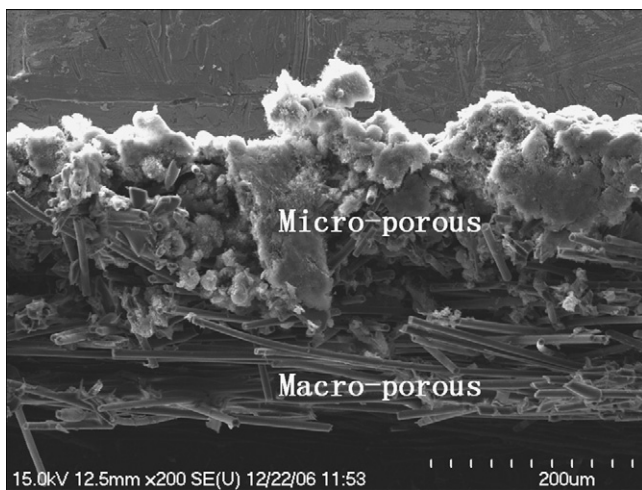


Fig. 3. Scanning electron micrograph (cross-sectional view) of a gas diffusion layer fabricated with Pureblack and VGCF (75:25 wt.%) by using wire wound rod (RDS 50) on HV carbon paper.

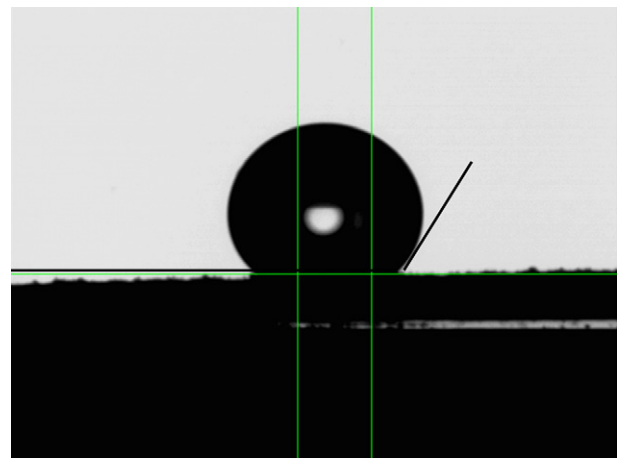


Fig. 4. Contact angle image for a micro-porous layer fabricated with Pureblack and VGCF (75:25 wt.%) containing 25 wt.% PTFE by using wire wound rod (RDS 50) on HV carbon paper.

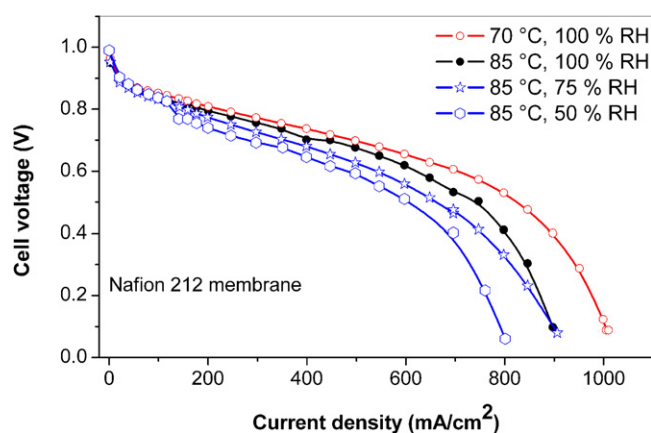


Fig. 5. Fuel cell performance of MEAs with GDLs fabricated with Pureblack and VGCF (75:25 wt.%) by using wire wound rod (RDS 50) on HV carbon paper and Nafion-212 membrane, at various RH conditions at 70 and 85 °C using hydrogen and air at ambient pressure.

characteristics and its constituents influence this property. The angle measured by the tangent line is about 120 degrees, which is a typical value for all the GDLs fabricated with various other carbons using PTFE as a binder and hydrophobic agent, depending on the pore diameter and hydrophobic characteristics. Wang et al. have reported wetting angle values between 53° and 153° for Black Pearl, Acetylene Black and their composite materials based micro-porous layers [14].

The fuel cell performance for a GDL fabricated with VGCF and Pureblack (75:25 wt.%) is shown in Fig. 5. As seen from Fig. 5, the FC performance of the wire rod coated GDL is low especially at low RH conditions. This is mainly due to the manifestation of larger pores during the wire rod coating process. In order to reduce the pore diameter, the reduction in VGCF and densification methods of the micro-porous layer are being explored. However, the performance at 70 °C, 100% RH is slightly higher due to favorable mass transport characteristics at higher current density values. This is explained by the gas diffusion during the fuel cell operation. Reactant gases move from the flow field to the catalyst layer is mainly by diffusion and partly by convection through the GDL for both anode and cathode. Diffusional gas transport in the GDL occurs primarily bulk diffusion in the pores dominates when the pore diameter is larger in the micro-porous layer fabricated by using 75 wt.% Pureblack carbon and 25 wt.% nano-fibrous carbon.

The pore size distribution data measured by Hg porosimetry in low and high pressure modes for wire-rod coated micro-porous layer based GDLs fabricated using various compositions of VGCF and Pureblack (75:25, 50:50, 25:75 and 10:90 wt.%) are shown in Fig. 6. In our earlier publication, it was observed that the presence of carbon nano-fibers or carbon nano-tubes in the micro-porous layer leads to larger pores [22]. As seen from Fig. 6, there is a systematic increase in pore diameters as the VGCF content is increased from 10 to 75 wt.% in the micro-porous layer. For example, a GDL with VGCF and Pureblack (10:90 wt.%) shows pores with pore diameter as low as 80 nm, whereas another GDL containing VGCF and Pureblack (75:25 wt.%) shows pores only with pore diameter of 1 μm (see

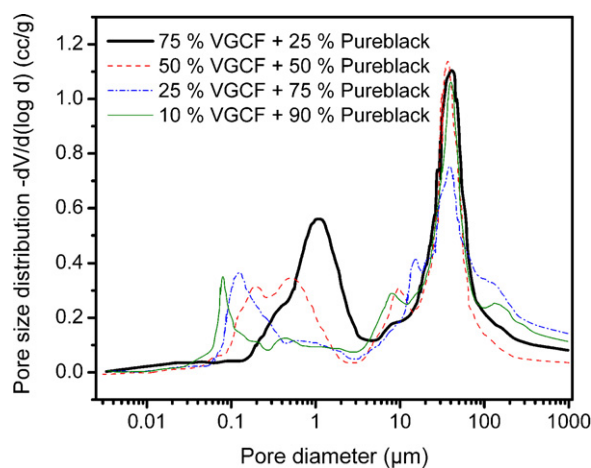


Fig. 6. Pore size distribution data as measured using Hg porosimetry for four GDLs with various compositions of micro-porous layers with VGCF and Pureblack with low and high pressure modes.

Table 1). GDLs with other compositions show pores with pore diameters between these two values. Hg porosimetry data for composite micro-porous layers using Black Pearls 2000 and Acetylene Black were reported to have different pore diameters, in the literature. If the fuel cell operates at 100% RH of the reactant gases, the GDLs with smaller micro-pores are reported to be flooding and larger micro-pores are favored for water and gas transportation [14]. Based on this observation, it is expected that the GDLs with various compositions of VGCF and Pureblack based micro-porous layers would exhibit unique characteristics under specific fuel cell operating conditions (temperature and RH) at higher current density regions. In general, the pore diameter values of the micro-porous layers with various compositions of VGCF and Pureblack based GDLs fabricated by wire wound rods are smaller than that by spray methods. In order to reduce the pore diameter in the micro-porous layer fabricated by using wire wound rods, increase of solid loading in the carbon slurry as well as densification methods of the micro-porous layer are being explored. Porosity values are 70–75% for all the GDLs with Pureblack and VGCF composite based micro-porous layers. The variation in the composition of Pureblack and VGCF in the micro-porous layers did not lead to any significant change in the porosity, as the major contribution comes from the macro-porous layer.

GDLs with various compositions of VGCF fibers and Pureblack in the micro-porous layers were evaluated at various operating conditions. Fig. 7 compares the fuel cell performance at 65 °C, 100% RH. As expected, the presence of various amounts of VGCF in the slurries leads to performance variation at 100% RH of the anode (H₂) and cathode (air) feed gases due to difference in pore diameter as well as porosity. As seen from Fig. 7, the presence of higher amount of VGCF is more beneficial due to larger pores at higher relative humidity (100% RH). For example, the GDL with 75% VGCF and 25% Pureblack shows better performance at 65 °C, 100% RH, whereas the GDL with lowest amount of VGCF (say, VGCF and Pureblack, 10:90 wt.%) composition shows the lowest performance (smaller limiting current). This could be due to larger pores con-

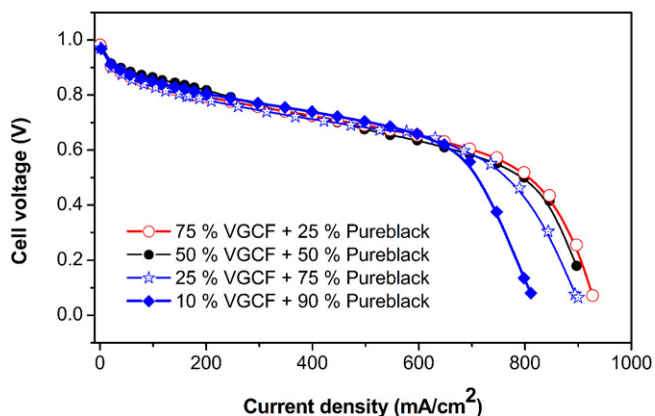


Fig. 7. Comparison of fuel cell performance of GDLs fabricated with various composition of Pureblack and VGCF by wire wound rod (RDS50), at 65 °C, 100% RH using H₂ and air at ambient pressure.

tributing to quick removal of water at higher relative humidity of the feed gases, at higher operating current density values.

Fig. 8 compares the fuel cell performance at 85 °C, 50% RH. Similar to what is observed at 100% RH conditions, the presence of various amounts of VGCF in the slurries leads to performance variation at 50% RH of the anode (H₂) and cathode (air) feed gases at 85 °C, due to difference in pore diameter as well as porosity. As evident from Fig. 8, the presence of higher amount of Pureblack is more beneficial due to the formation of narrow pores (as low as 80 nm diameter) at lower relative humidity (50% RH). For example, the GDL with 10% VGCF and 90% Pureblack shows the best performance at 85 °C, 50% RH, where as the GDL with highest amount of VGCF (say, VGCF and Pureblack, 75:25 wt.%) composition shows the lowest performance (smaller limiting current). The higher performance with lower amount of VGCF could be due to smaller pores contributing to retaining the product water for maintaining the required proton conductivity of the Nafion-212 electrolyte with the feed gases at 50% RH conditions, at higher operating current density values. At lower relative humidity, the presence of higher amount of Pureblack carbon is more beneficial due to smaller pores. While at higher relative humidity conditions, the presence of higher

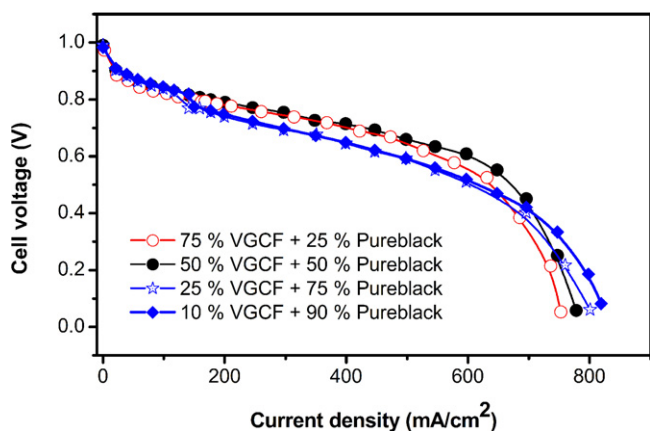


Fig. 8. Comparison of fuel cell performance of GDLs fabricated with various composition of Pureblack and VGCF by wire wound rod (RDS50), at 85 °C, 50% RH using H₂ and air at ambient pressure.

amount of VGCF proved to be more beneficial in terms of the FC performance.

4. Conclusion

A proprietary coating process with wire wound rod was developed for mass fabrication of micro-porous layer on a non-woven macro-porous carbon paper substrate developed by Hollingsworth & Vose, using a semi-automated process with single pass. The GDLs were characterized for surface morphology, wetting characteristics, pore size distribution and also by single cell PEM fuel cells. Fuel cell performance evaluation of the GDLs was conducted using Nafion-212 at various operating conditions with H₂/air under ambient pressure. The micro-porous layer exhibited homogeneous carbon distribution and crack free surface morphology. The FC performance of the wire rod coated GDLs was found to be low especially at low RH conditions due to the manifestation of larger pores in the micro-porous layer during the wire rod coating process. In general, the carbon loading on the micro-porous layer varies between 2.5 and 3 mg cm⁻² in the GDLs fabricated by wire wound rod coating. Near term work will address optimization of carbon loading in the micro-porous layer. Further, the pore diameter of the wire rod coated GDLs are larger compared to that with micro-sprayed GDLs. In order to improve low RH performance of the GDLs the pore diameter has to be lowered to retain the product water which would keep the electrolyte moist for required proton conduction. This will be done by increasing the solid loading of the carbon slurry and also by compressing the micro-porous layer after drying the GDLs.

Acknowledgements

The authors would like to acknowledge financial support from Hollingsworth & Vose Company and Arizona State University.

References

- [1] A.M. Kannan, L. Cindrella, L. Munukutla, *Electrochim. Acta* 53 (2008) 2416–2422.
- [2] L. Giorgi, E. Antolini, A. Pozio, E. Passalacqua, *Electrochim. Acta* 43 (1998) 3675–3680.
- [3] C. Lim, C.Y. Wang, *Electrochim. Acta* 49 (2004) 4149–4156.
- [4] G. Park, Y. Sohn, T. Yang, Y. Yoon, W. Lee, C. Kim, *J. Power Sources* 131 (2004) 182–187.
- [5] D. Bevers, R. Rogers, M. von Bradke, *J. Power Sources* 63 (1996) 193–201.
- [6] W.M. Yan, C.Y. Hsueh, C.Y. Soong, F. Chen, C.H. Cheng, S.C. Mei, *Int. J. Hydrogen Energy* 32 (2007) 4452–4458.
- [7] V. Gurau, M.J. Bluemle, E.S. De Castro, Y.M. Tsou, T.A. Zawodzinski, J.A. Mann, *J. Power Sources* 165 (2007) 793–802.
- [8] L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle, M. Forsyth, *J. Power Sources* 86 (2000) 250–254.
- [9] M.V. Williams, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* 151 (2004) A1617–A1627.
- [10] M.V. Williams, H.R. Kunz, J.M. Fenton, *J. Power Sources* 135 (2004) 122–134.
- [11] H. Tang, S. Wang, M. Pan, R. Yuan, H. Tang, *J. Power Sources* 166 (2007) 41–46.

- [12] Z. Zhan, J. Xiao, Y. Zhang, M. Pan, R. Yuan, *Int. J. Hydrogen Energy* 32 (2007) 4443–4451.
- [13] X. Wang, H. Zhang, J. Zhang, H. Xu, X. Zhu, J. Chen, B. Yi, *J. Power Sources* 162 (2006) 474–479.
- [14] X. Wang, H. Zhang, J. Zhang, H. Xu, Z. Tian, J. Chen, H. Zhong, M. Liang, B. Yi, *Electrochim. Acta* 51 (2006) 4909–4915.
- [15] E. Antolini, R.R. Passos, E.A. Ticianelli, *J. Power Sources* 109 (2002) 477–482.
- [16] J.W. Frisk, W.M. Boand, J.M. Larson, US Patent 6,465,041, October 15 (2002).
- [17] C. Ji, J.E. O'Hara, M.F. Mathias, US Patent 7,063,913, June 20(2005).
- [18] M. Han, S.H. Chan, S.P. Jiang, *J. Power Sources* 159 (2006) 1005–1014.
- [19] Y.H. Pai, J.H. Ke, H.F. Huang, C.M. Lee, J.M. Zen, F.S. Shieu, *J. Power Sources* 161 (2006) 275–281.
- [20] Y.W.C. Yang, T.F. Hung, J. Huang, F.L. Yang, *J. Power Sources* 173 (2007) 183–188.
- [21] J. Yu, Y. Yoshikawa, T. Matsuura, M.N. Islam, M. Hori, *Electrochem. Solid-State Lett.* 8 (2005)A152–A155.
- [22] A.M. Kannan, L. Munukutla, *J. Power Sources* 167 (2007) 330–335.