

Functionally graded nano-porous gas diffusion layer for proton exchange membrane fuel cells under low relative humidity conditions

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Abstract

Gas diffusion layers (GDLs) were fabricated using commercially available carbon paper as macro-porous layer substrate. Functionally graded nano-porous layers were designed by combining carbon nano-fibers with nano-chain type Pureblack carbon (75:25–0:100 wt.%) in the *z*-direction towards the catalyst layer and Teflon content (say 15–30 wt.%) to obtain variation in pore diameter and also hydrophobicity. On the top of the nano-porous layer, a thin layer of hydrophilic inorganic oxide (fumed silica) was also deposited to retain moisture content to maintain the electrolyte wet, especially when the fuel cell is working at lower relative humidity (RH) conditions, which is typical for automotive applications. The surface morphology, contact angle, bulk characteristics and pore size distribution of the layered GDLs were examined using FESEM, Goniometer, Interferometer and Hg Porosimeter, respectively. The GDLs assembled into MEAs were evaluated in single cell PEMFC under various operating conditions (temperature and RH) using H₂/O₂ and H₂/air as reactants. It was observed that the functionally graded nano-porous GDLs with hydrophilic layer showed an excellent fuel cell performance with a peak power density of about 0.46 W/cm² at 85 °C using H₂ and air at 50% RH. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Gas diffusion layers; Functionally graded; Pureblack[®] carbon; Carbon nano-fibers; Surface morphology; Pore size distribution

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising alternative power sources for various applications due to their higher power densities and environmental benefits. However, the power density values are reduced due to mass transport limitations mainly at the cathode, when air is used. To improve the performance of the PEMFCs, it is critical to balance the properties of the gas flow characteristics in the MEA. Gas diffusion layer (GDL) is one of the critical components of a fuel cell that has the ability to influence the H₂/air system performance at high current density region. The water retaining (hydrophilicity) and water expelling (hydrophobicity) properties of the GDLs have to be watchfully balanced to achieve optimum performance of the fuel cell without flooding when it operates under the 100% relative humidity (RH) conditions of reactant gases [1–6]. The hydrophilicity of the gas diffusion lay-

ers can also avoid drying of electrolyte in lower RH conditions. In general, GDLs are fabricated by coating a macro-porous layer with hydrophobic micro-porous layer. The GDLs are fabricated using commercially available carbon paper (non-woven) or carbon cloth (woven) made of carbon-fiber-based porous materials as a macro-porous layer. Fuel cell performance of GDLs fabricated with carbon paper and carbon-cloth-based macro-porous layers is well studied in the literature [7]. Many strategies are currently emerging to design and develop purpose-built GDLs incorporating various carbon materials for specific operating conditions of fuel cells [8–12]. The influence of the role of pore size as well as porosity distribution of the micro-porous layer on the performance is reported [13–17]. In addition, the effect of GDL fabrication process with various amounts of hydrophobic agent in the micro-porous layer could also influence the fuel cell performance [18,19].

The objective of the present study is to design and develop functionally graded four layered nano-porous gas diffusion layer with varying pore sizes, hydrophobicity and hydrophilicity along the direction of flow of gases (*z*-direction) and evaluating in single cell PEMFCs under various RH conditions using H₂/air.

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The structural variation created by the pore sizes is aimed not only to maintain moisture and to expel the excess water, but also to enhance the utilization of gases at the catalyst surfaces and thereby to minimize mass transfer polarization.

2. Experimental

2.1. Gas diffusion layer

Gas diffusion layers were fabricated with teflonized non-woven carbon paper (P50T, Ballard Applied Materials) as a substrate. Hydrophobic characteristic of the micro-porous layers was provided by TE5839 Teflon suspension (Dupont). Nano-fibrous type carbon (VGCF-H available from Showa Denko America Inc., New York) was mixed with nano-chain PUREBLACK® 205-110 Carbon (available from Superior Graphite Co., Chicago, IL, USA) to provide improved mechanical strength and adhesion of the micro-porous layer with the macro-porous layer. In order to fabricate the four layered micro-porous layers, slurry of carbons with PTFE dispersion in a mixture of isopropanol and de-ionized water mixture (80:20 volume ratio) was prepared by ultrasonication followed by magnetic stirring. Table 1 gives compositions of Pureback carbon, nano-fibrous carbon and PTFE contents in the four layered micro-porous layer. For comparison purposes, a single layered micro-porous layer based GDLs were also fabricated with a composition of 75% Pureback carbon and 25% nano-fibrous carbon (VGCF) using a similar procedure. The slurry was applied on to the carbon paper using micro-spraying technique. Subsequently, carbon paper with the micro porous layer was heated at 120 °C for an hour and then sintered at 350 °C in air for about an hour. The carbon loading for the micro-porous layer was approximately 3 mg/cm².

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 as illustrated in our earlier publication [20].

The GDL sample's wetting characteristics such as, contact angle measurement of a droplet of water and ethanol mixture (1:1 ratio) with the layers was evaluated by NRL CA Goniometer (Ramehart 100). The percentage variation in the droplet dimension was monitored for all the GDL samples at an interval

of 5 min. The pore diameter and pore size distribution of the single and four layered GDL samples were measured by using PoreMaster-60 GT in both low and high pressure modes by Hg intrusion method in a fixed speed mode.

2.2. Catalyst coated membrane

Catalyst-coated membranes (CCM) with 5 cm² 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 Ion Power Inc., New Castle, DE, USA (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 per cm², 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 fuel cell performance for various GDLs was evaluated at various temperatures (70 and 85 °C) and RH conditions (50, 75 and 100% RH) using Greenlight Test Station (G50 Fuel cell system, Hydrogenics, Vancouver, Canada) with H₂/air as well as H₂/O₂ under ambient pressure by galvanostatic polarization. The gas flow rates were fixed at 200 and 400 SCCM for hydrogen and air (also for O₂), respectively. The steady state voltage values were collected by holding the cell at each current density values for 60 s. The RH of the reactant gases was maintained at various values (50, 75 and 100%) by controlling the humidity bottle temperatures.

Table 1
Composition of functionally graded GDL (four layers) and their characteristic Z-range profile from interferometry

Sample	Carbon composition (%)		Teflon (%)	Silica (mg/cm ²)	Z-range profile (μm)
	VGCF	Pureblack			
Carbon paper (GDL substrate)	–	–	18	–	136
Layer 1	75	25	30	–	193
Layer 2	50	50	25	–	127
Layer 3	25	75	20	–	120
Layer 4	0	100	15	–	126
Layer 4 + SiO ₂	0	0	0	0.25	212

3. Results and discussion

The scanning electron micrograph of the functionally graded gas diffusion layers obtained by the successive coating of varying composition of carbon fibre and pure black carbon are shown in Fig. 1a–f. Refinement of the interconnecting pores and the channels they provide for gas flow, is evident from the above figures. The carbon fibres (1a) which are visible (in the range of microns) as straight strands show an increasing connectivity through three-dimensional pores formed by the coatings. It is interesting to observe the multi-directional gas flow channels ending in well defined nano-pores near the electrode. The graded pore dimension and the nano-porous pattern at the electrode contributed to higher surface area of contact between the gases and the electrocatalyst. The diminishing scale of the micrographs through Fig. 1a–f and the well defined multi-directional flow channels demonstrate efficient distribution of the gases on the electrocatalyst of the membrane. This leads to minimum hindrance for the gas to flow from the flow channels through

the macro-porous layer and reduced mass transport polarization losses at the catalyst surface. The GDL's micrographs showed homogenous carbon distribution pattern and crack-free micro-porous layer favoring uniform gas distribution. The SEM images confirm that the presence of carbon nano-fibers leads to mechanical reinforcement of the micro-porous layer. 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 purpose of adding nano-fibrous carbon to Pureblack was to impart structural integrity to the micro-porous layer of the GDL and also to manifest larger pores as evidenced from our earlier study [20]. The structural robustness and the effectiveness of adhesion of the microporous layer to the macro-porous layer were attained by subjecting the GDLs to ultrasonication.

Fig. 2 shows the SEM of the cross-section of the structurally/functionally graded micro-porous layers based GDL. As seen from Fig. 2, the four layered micro-porous layer show a thickness of about 50 to 60 microns. The GDL cross-section

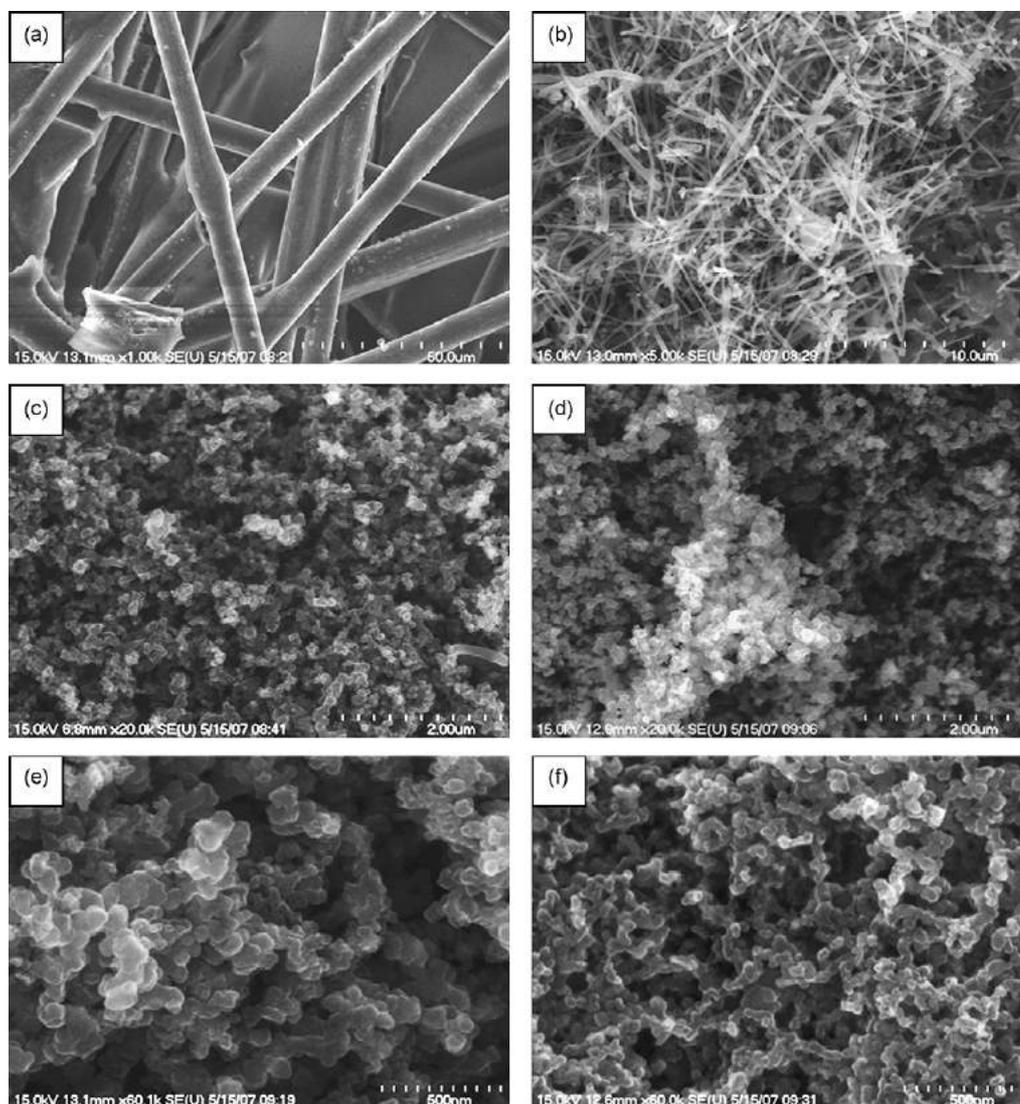


Fig. 1. Scanning electron micrographs of (a) macro-porous layer carbon paper substrate and micro-porous layers 1–4 with various compositions (%) of Pureblack nano-chain: VGCF carbons (b) 25:75, (c) 50:50, (d) 75:25, (e) 100:0, and (f) fumed silica coated micro-porous layer 4.

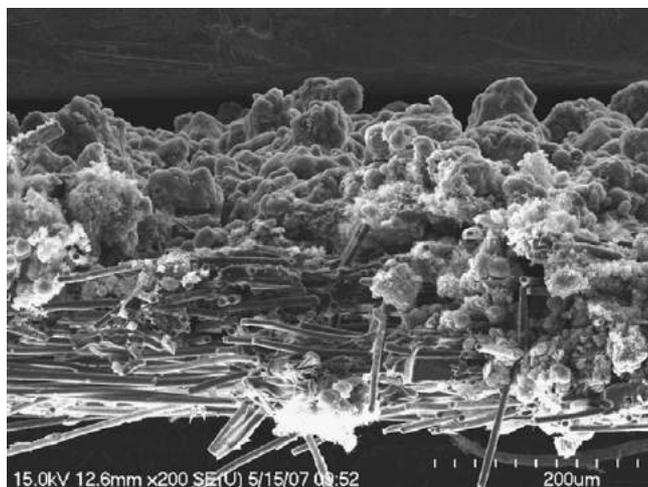


Fig. 2. Cross-sectional view of four layered gas diffusion layer using various compositions of Pureblack + nano-fibrous carbon based micro-porous layer by scanning electron microscope.

image shows no carbon bleed-through from the micro-porous layer to the uncoated side of the macro-porous carbon paper substrate and keeping the pores in the macro-porous layer unblocked. The structural and functional gradation and the

porous features in the cross-section highlight the combination of mechanical robustness of the nano-chain and nano-fibrous carbon.

The interferometric surface profiles of the carbon paper and the four layers of mixture of the carbon Pureblack and VGCF are shown in Fig. 3a–f. The higher amount of VGCF (75 wt.%) of the total carbon loading in layer 1 is well reflected in the surface profile (Fig. 3b) by the depth variation due to its fibrous nature compared to that in the macro-porous layer in Fig. 3a. The increasing percentage of the Pureblack resulted in almost uniform depth profile in the subsequent layers of 2, 3 and 4. The cavity filling characteristics of the pure black carbon is evident in Fig. 3c–e, respectively. Due to the hydrophilic characteristic of the fumed silica layer on top of the 4th layer contributed towards volume increase and the depth profile and it is reflected in Fig. 3f as enhanced variation up to about 212 μm . Table 1 summarizes the composition of the graded four layers and their Z-range profiles. The depth profile values can be explained based on the fact that the depth of the open channel of the macro pores is less (Fig. 3a) and gives low Z-range values (136 μm) due to the least interference of the reflected rays on open structures. Fig. 3b shows a high Z-range profile (193 μm) due to effective closing of the open pores by the carbon pure black in layer-1 and hence

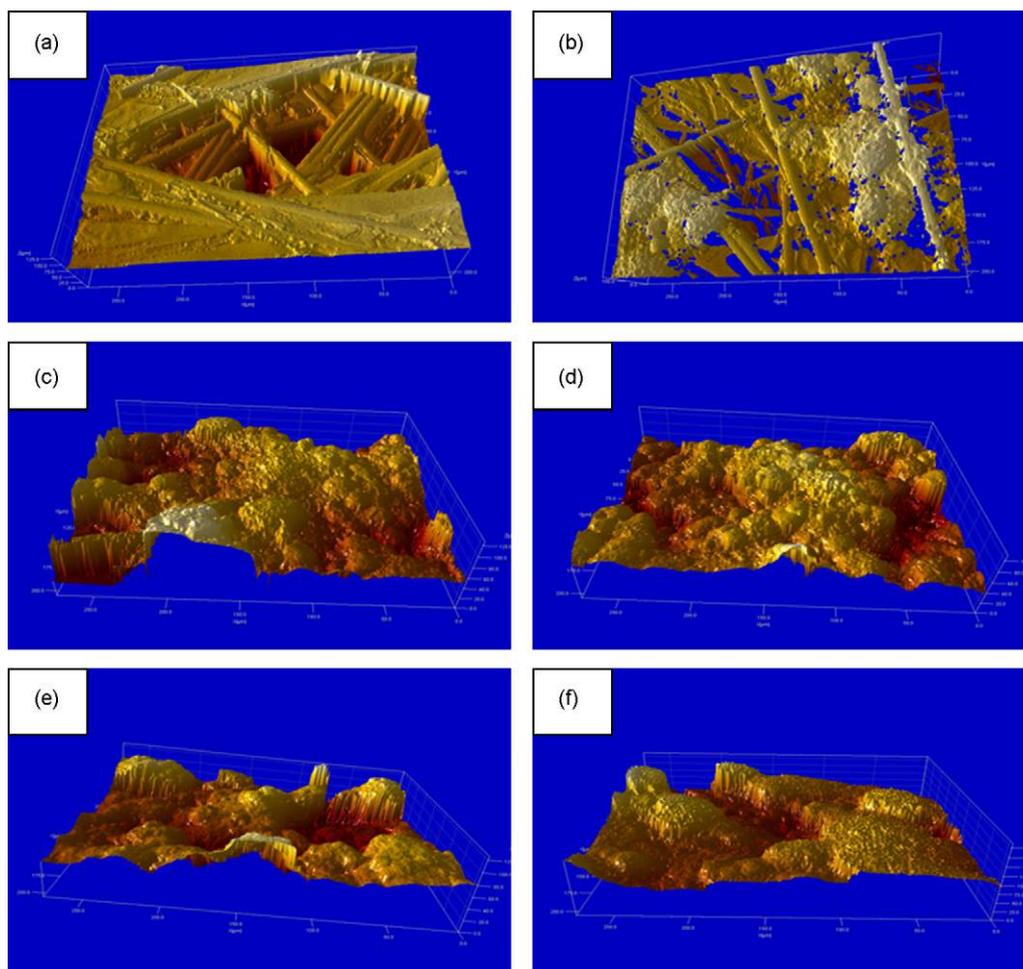


Fig. 3. Interferometry images of (a) macro-porous layer carbon paper substrate, micro-porous layers 1–4 with various compositions (%) of Pureblack nano-chain: VGCF carbons (b) 25:75, (c) 50:50, (d) 75:25, (e) 100:0, and (f) fumed silica coated four layered micro-porous layer.

to the effective interference in the cavities. Further, the layers with increasing percentages of carbon Pureblack smoothens the surfaces by the size refinement of the pores and hence the Z-range values register marginal changes in values. The spray of fumed silica shows large change in the depth profile (212 μm), due to the hydrophilic nature of silica, which itself is porous and characterized with large number of closed and open pores.

The wetting angle profiles using water–ethanol (1:1 ratio) are given in Fig. 4 for layers 1–4 in the micro-porous layers for the functionally graded GDL. Ethanol was mixed with water to improve the wetting characteristics, as pure water alone could not be used for wetting angle measurements. However, the wetting angle could not be measured for fumed silica coated micro-porous layer, as the water–ethanol drop gets absorbed quickly into the micro-porous layer of the highly hydrophilic surface. The wetting angle is the angle that the tangent makes with the point of contact of the drop [9] with the surface under study; the surface characteristics and its constituents influence this property. The contact angles and the Z-range profiles bring to fore front the fact that more corrugated the surface is, lesser

is the contact angle and higher the fineness of the layer, greater is the contact angle. This can be explained based on two aspects of our layers, namely, surface roughness which is caused by the nano-fiber content of the layers and smoothness which is contributed by the pure black carbon in our coatings. Hence layer with high Z-range profile (layer 1) will tend to show low contact angle (133.7°), where as the layer with low Z-range profile (layer 3) is exhibiting high contact angle (140.8°). Obviously, any layer that gives rise to an in-between Z-range profile (layer 4) is expected to yield an in-between value of the contact angle in the inverse order and our experimental results support this point.

Fig. 5 compares the pore size distribution data measured by Hg porosimetry in low and high pressure modes for one layered and four layered micro-porous layer GDLs fabricated using Pureblack nano-chain and nano-fibrous carbons. As observed from the pore size distribution data in Fig. 5, the GDL with functionally graded four different compositions of Pureblack and nano-fibrous carbons in the micro-porous layer show pores with 0.075, 0.55, 15, 40 and 225 μm diameters. However, the

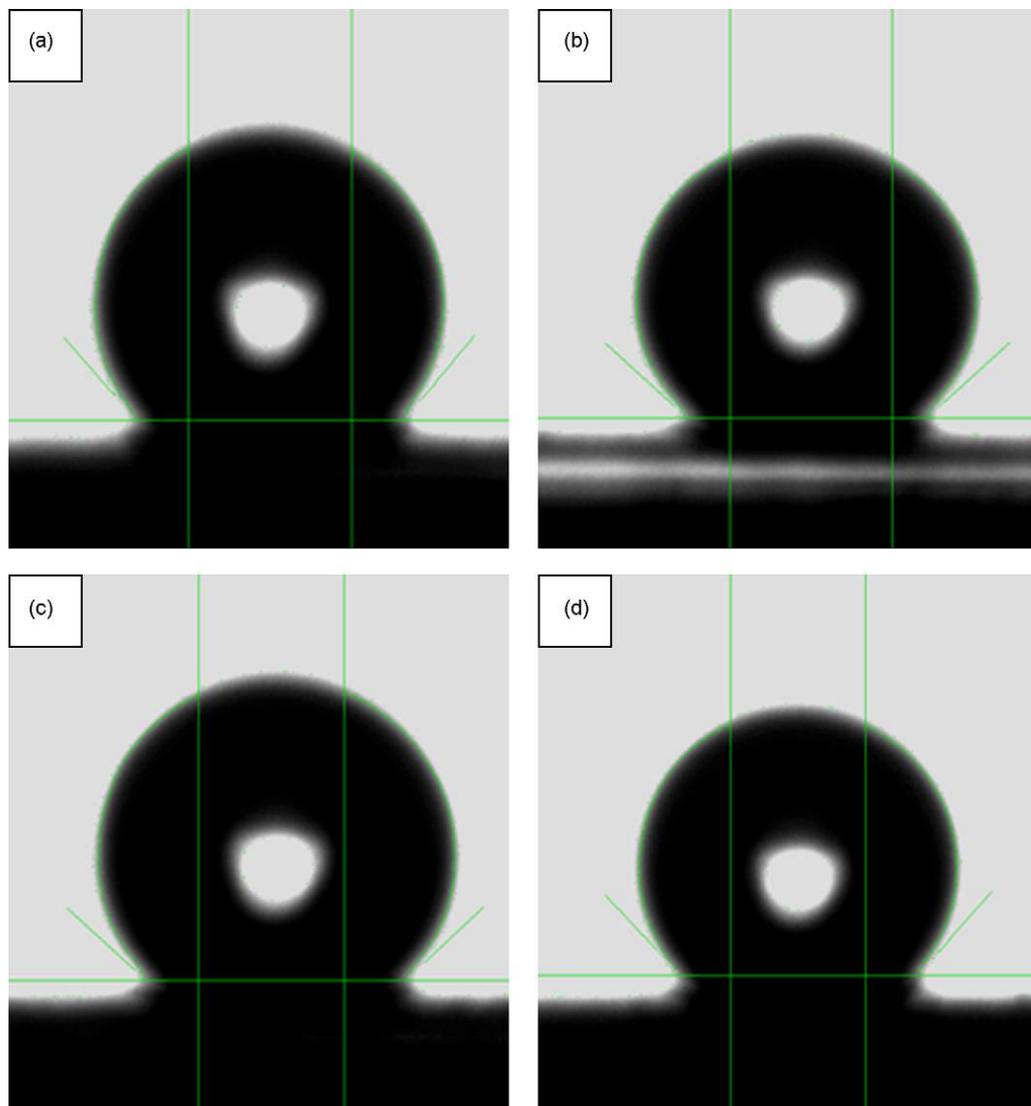


Fig. 4. Contact angle images as measured on the micro-porous layers of the functionally graded GDL; layer 1, (b) layer 2, (c) layer 3 and (d) layer 4.

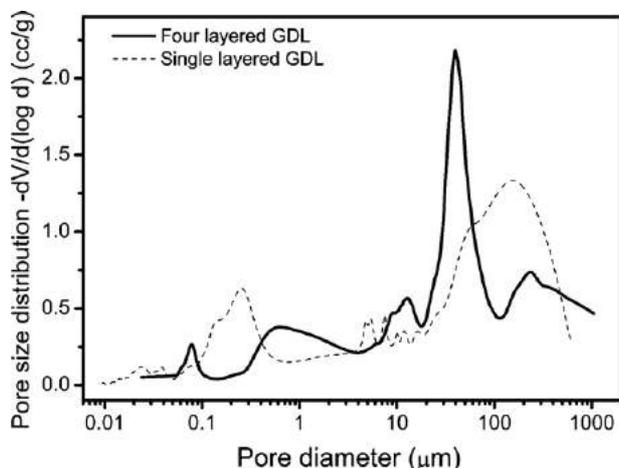


Fig. 5. Pore size distribution data as measured using Hg porosimetry for a single and four layered GDL samples with Pureblack + nano-fibrous carbon based micro-porous layers.

single layered GDL shows only two types of pores with 0.25 and 150 μm diameters. It is interesting to note that the single micro-porous layer GDL shows majority of the pores having 150 μm in diameter, whereas the four layered micro-porous layer shows pores with ~ 40 μm diameter, which can be beneficial in retaining the product water when the cell is operating under lower RH conditions. In addition the four layered micro-porous GDL with larger pores (225 μm) can also perform better when the cell is operating at 100% RH conditions without flooding. The silica coated four layered GDLs did not show any significant difference in pore size distribution compared to the one without silica. Therefore, the functionally graded GDLs, with and without silica coating are expected to show superior fuel cell performance at all RH conditions of the reactant gases compared to that with the single layered GDLs. The liquid water flux and liquid saturation with varying pore diameter of GDLs are well studied in the literature [21].

Figs. 6 and 7 show the galvanostatic polarization data at 70 and 85 $^{\circ}\text{C}$ using H_2/air at various RH conditions at ambient pressures for 5 cm^2 active area MEAs with functionally graded micro-porous layered GDLs with and without silica coating. For comparison, fuel performance is also given in Fig. 8 for GDLs with single layered micro-porous layer using H_2/air at various

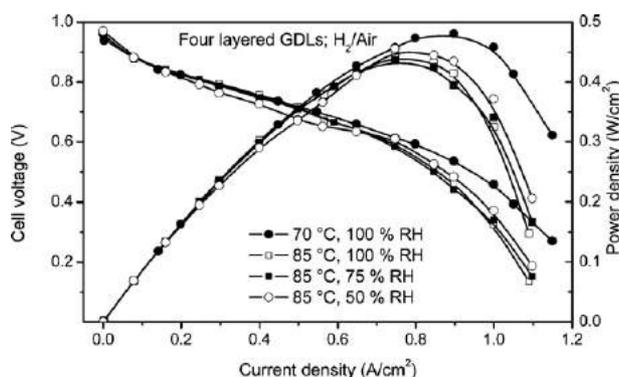


Fig. 6. Fuel cell performance of MEAs with four layered GDLs at various RH conditions at 70 and 85 $^{\circ}\text{C}$ using H_2/air at ambient pressure.

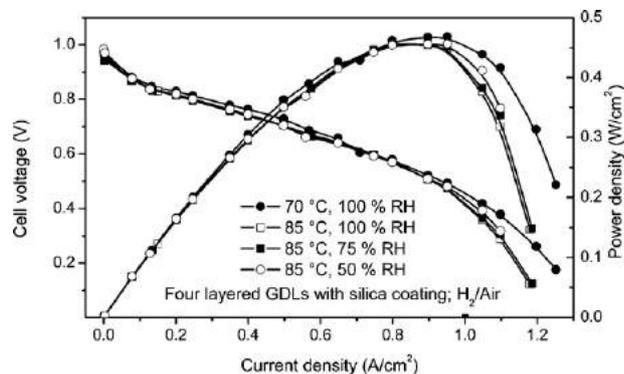


Fig. 7. Fuel cell performance of MEAs with SiO_2 coated four layered GDLs at various RH conditions at 70 and 85 $^{\circ}\text{C}$ using H_2/air at ambient pressure.

RH conditions at ambient pressures. From Fig. 7, it is worth mentioning that the combination of nano-fibers along with Pureblack nano-chain carbon in the four layered micro-porous layer shows a peak power density value of 0.46 W/cm^2 under the test conditions: with hydrogen/air at ambient pressure, 85 $^{\circ}\text{C}$ and 50% RH. The contributing factor for the enhanced power density value of the functionally graded GDLs compared to that of the single layered GDLs using H_2/air are: formation of favorable pores to minimize polarization loss and providing relatively better gas transport as well as water management characteristics at all operating conditions. Consistent with the intuitive notion based on the nano-sized pores for the functionally graded GDLs compared to that of the single layered GDLs as observed from the pore size distribution data, the polarization data in Fig. 6 (and also Fig. 7) showed exceptionally high power density using H_2 and air at 50% RH at the elevated cell temperature of 85 $^{\circ}\text{C}$. In the present study, functionally graded micro-porous layer with various compositions of nano-fibers along with Pureblack nano-chain along the z -direction offered improvement in the performance at lower as well as 100% RH conditions of the feed gases, with a wider spectrum of nano-sized pores and larger pores, as seen from Fig. 5. In particular, excellent gas diffusion (mass transport) of the functionally graded micro-porous layers is exhibited by the larger pores and superior water management through the nanopores towards the catalyst layers, under lower RH conditions to keep the electrolyte moist. A mathematical model based on capillary theory and multi-gas diffusion theory also favors GDL

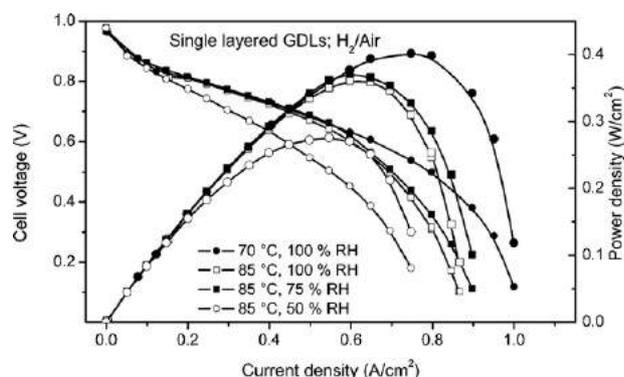


Fig. 8. Fuel cell performance of MEAs with single layered GDLs at various RH conditions at 70 and 85 $^{\circ}\text{C}$ using H_2/air at ambient pressure.

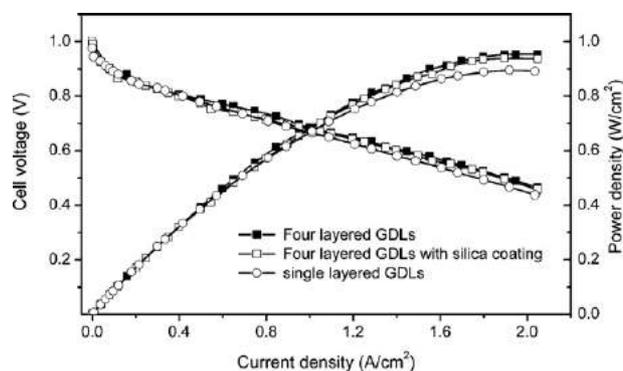


Fig. 9. Fuel cell performance of MEAs with four layered GDLs with and without SiO₂ coating and single layered GDLs at 70 °C using H₂/O₂ at ambient pressure at 100% RH conditions.

with gradient porosity for the liquid water to be discharged out and retaining less liquid in the GDL leading to superior gas diffusion characteristics [22].

Fig. 9 show the polarization data of the MEAs with GDLs containing four layered micro-porous layer with and without SiO₂ and single layered micro-porous layer using H₂/O₂ at 70 °C, 100% RH conditions at ambient pressure. Primarily when oxygen is used with high stoichiometry (400 SCCM at all current density values), there is no significant difference in diffusion limitation in the current density region evaluated in the present study, for the four layered and single layered GDLs. Based on this observation, the enhanced fuel cell performance with air as oxidant could be attributed to the characteristics of the functionally graded GDLs.

4. Conclusions

Functionally graded GDL with four layered micro-porous layer containing various compositions of nano-chain as well as nano-fibrous carbons on the macro-porous carbon paper substrate has been developed and evaluated in the single cell PEMFC under various RH conditions. It is worth mentioning that the gas diffusion layer with pores as small as 75 nm in the micro-porous layer towards the catalyst layer could retain the product water to keep the electrolyte sufficiently moist to sustain the proton conductivity as evidenced from the fuel cell performance at 85 °C, 50% RH using H₂/air. In addition, the functionally graded GDLs were examined by FESEM, Goniometer, Interferometer and Hg Porosimeter for understanding the structure–property relationship. Based on our study, there exists a clear qualitative relationship between the pore diameter values and the fuel cell performance for the single and four layered GDLs.

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