
Article:
Orogbemi, O.M., Ingham, D.B., Ismail, M.S. et al. (3 more authors) (2016) The effects of the composition of microporous layers on the permeability of gas diffusion layers used in polymer electrolyte fuel cells. International Journal of Hydrogen Energy, 41 (46). pp. 21345-21351. ISSN 0360-3199

https://doi.org/10.1016/j.ijhydene.2016.09.160

Title Page

Title:

The effects of the composition of microporous layers on the permeability of gas diffusion layers used in polymer electrolyte fuel cells

Authors

O. M. Orogbemi*, D. B. Ingham, M.S. Ismail, K. Hughes, L. Ma, M. Pourkashanian

Energy 2050, Department of Mechanical Engineering, University of Sheffield, Sheffield S3 7RD, Sheffield. United Kingdom

*Corresponding author, Tel: +44 114 215 7220

Email address: omorogbemi1@sheffield.ac.uk (O. M. Orogbemi)

Abstract

The effects of the composition of the microporous layer (MPL) on the through-plane permeability of the gas diffusion layers (GDLs) used in polymer electrolyte fuel cells (PEFCs) have been thoroughly experimentally investigated in this paper. For a given PTFE loading in the MPL, the GDL permeability was found to decrease with increasing carbon loading and this is due to the increase in the thickness of the MPL. For all the investigated carbon loadings of the MPL, the permeability values of the GDLs were found to have common trends for the PTFE loadings ranging from 10 to 50 % (by weight): the GDL permeability increases when the PTFE loading in the MPL is increased from 20 to 50 %; the GDL permeability decreases when the PTFE loading in the MPL is increased from 10 to 20 %; and the GDL permeability is a minimum at 20 % PTFE loading present in the MPL. On the other hand, the permeability of the GDL was found to depend on the carbon loading of the MPL in the PTFE range 0-10 %. The effects of the MPL composition on the MPL permeability were found to be similar to those on the GDL permeability. However, the permeability values of the MPLs of the same composition, which were supposed to be ideally the same, were found to significantly vary. This was attributed to the MPL penetration into the body of the carbon substrates.

Keywords: PEFCs; Gas diffusion layer; Microporous layer; Gas permeability; PTFE loading; Carbon loading.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are a promising clean power conversion technology for a wide range of portable, automotive and stationary applications and this is in particular due to its high efficiency and low-temperature start-up [1-2]. A gas diffusion layer (GDL) is one of the main components used in PEFCs as it acts as a multifunctional component. Namely, it distributes the reactant gases to the catalyst layer where the reaction takes place; it improves the electrical contact with the catalyst layer; and it drives the liquid water away from the catalyst layer [3-5]. To efficiently perform the above functions, the GDL is usually wet-proofed [3-7]. Further, it is normally coated with the so-called micro-porous layer (MPL) on the side facing the catalyst layer in order to enhance the electrical contact with the catalyst layer and properly handle the liquid water emerging from the cathode catalyst layer [1-2,9-10]. The MPL is a mixture that typically consists of carbon black and PTFE particles [1, 11].

The effects of the MPL and its composition on the performance of PEFCs have been investigated by many researchers [3-4, 7-8, 12]. The areas of research in this regard are typically on the effects of the loading of the wet-proofing agent [13-17], and the type of carbon black [16, 18]. Ismail et al. [19] found that the through-plane permeability of the GDL increases as the PTFE loading in the MPL increases from 25 to 50 %. This was justified by the findings obtained by Uchida et al. [15]. Park et al. [18] found that a maximum fuel cell performance is obtained with an MPL carbon loading of 0.5 mg cm^{-2}. Jordan et al. [7] reported that the better fuel cell performance is achieved when the loading of the Acetylene Black carbon is between 1.25 and 1.9 mg cm^{-2}. Also, they found that the PEFC performs better with the sintered MPL loaded with Acetylene Black carbon than with Vulcan XC-72R and this is mainly due to the uniform distribution of the PTFE loading in the MPL loaded

with Acetylene Black carbon. Similarly, it has been shown that the performance of the PEFC is highly sensitive to the PTFE loading either in the carbon substrate or in the MPL [19-21].

As stated earlier, the literature has shown that the permeability of the GDL increases with increasing PTFE loading in the MPL [21-22]. However, such a results was drawn from either a single value for the carbon loading and/or a limited number of PTFE loadings. In this paper, the sensitivity of the through-plane permeability of the GDL to a wide spectrum of MPL carbon and PTFE loadings has been investigated for the first time. This spectrum represents 30 different MPL compositions that result from 5 different carbon loading (ranging from 0.5 mg cm^{-2}) and 6 different PTFE loadings (ranging from 0 to 50%). This research is important because obtaining accurate values for the permeability of the porous media of the membrane electrode assembly (MEA) is essential to obtain realistic saturation profiles in the modelled PEFCs.

2. Materials and methods

The carbon substrate used to prepare the coated GDLs was SGL 10BA which was provided by SGL Carbon GmbH (Meitingen, Germany). The carbon powder and the PTFE dispersion used in the MPL ink were Ketjenblack EC-300J (AkzoNobel, the Netherlands) and 60 wt. % PTFE (Sigma-Aldrich, UK), respectively.

For the purpose of this study, 30 sets of MPL-coated GDL samples, representing 30 realistic MPL compositions, were prepared. Each set consists of 6 samples.

The composition of the MPL was varied by varying the amounts of the carbon black and PTFE used to prepare the MPL ink. Namely, the carbon black loading was set first and subsequently the amount of PTFE was set as a weight percentage of the entire MPL weight. The carbon loadings covered were: 0.5, 1.0, 1.5, 2.0 and 2.5 mg cm^{-2}. For each carbon

loading, the PTFE loading was set to represent 0, 10, 20, 30, 40 and 50 wt. % of the weight of the formed MPL. It should be note that, by measuring the masses of the GDL samples before and after MPL coating, the actual mass of the MPL loadings were found to be more or less the same as the desired ones. For example, for 2.0 mg cm^{-2} carbon loading and a 50 wt. % PTFE loading, the PTFE loading in the units of mg cm^{-2} is 2.0 and therefore the entire MPL loading is 4 mg cm^{-2}.

The calculated amount of carbon black and the PTFE dispersion were manually mixed until a paste-like material was formed. Isopropyl alcohol was added to the formed mixture and the resulting slurry was placed in an ultrasonic bath (U300H, Ultrawave Ltd, UK), with a power 35 W, until an ink with a good dispersion was formed. Using nitrogen, the ink was then manually sprayed onto the samples of the carbon substrates attached to a heated plate [22]. The spray gun used was 100LG (Badger, USA). The temperature of the plate was set to about 80 □ in order to evaporate the alcoholic components as the ink was applied to the substrate. The samples of the carbon substrates were cut out from the main sheet and made circular with a 2.50 cm diameter [20]. The MPL-coated GDLs were then heat-treated to a temperature 120 ℃ for 1 hour, at 280 ℃ for 30 minutes and finally sintered at 350 ℃ for 30 minutes using nitrogen gas to uniformly distribute the PTFE particles throughout the MPL [8, 13-14]. The thickness of the GDL samples was measured both before and after the MPL-coating using a micrometre. Each sample was measured at 4-equally-spaced positions within it to provide a representative average value of the thickness of the sample.

The experimental setup of this work has been previously used in [19-20] for investigating the through-plane permeability, see Fig. 1. As shown in Fig. 1, the setup consists of upper and lower fixtures, with the sample fixed between the two fixtures as described in [22]. Nitrogen flows through the sample and the pressure drop across the sample was measured at 7 equally-

spaced flow rates. The flow controller used was an HFC-202 (Teledyne Hastings, UK) with a range of 0.0-0.5 SLPM and the differential pressure sensor used was aPX653 (Omega, UK) with a range of ±12.5 Pa.

[Insert Fig. 1]

Data analysis

Low flow rates were used and therefore the inertial losses were assumed negligible. Consequently, Darcy's Law was used to solve for the permeability of the GDL sample before and after the MPL-coating [20]:

$$\frac{\Delta p}{L} = \frac{\mu}{k} v \qquad (1)$$

where Δp is the pressure drop across the sample, L is the thickness of the sample, μ is the dynamic viscosity of nitrogen estimated at the test temperature (about 20 ⍰), k is the gas permeability of the GDL sample calculated at the test temperature and v is the velocity of the flowing gas. Fig. 2 shows a typical pressure gradient-velocity experimental data. To estimate the permeability, these experimental data were curve-fitted to Equation (1).

[Insert Fig. 2]

The through-plane gas permeability of the MPLs can be estimated making use of the assumption that the pressure drop across the entire sandwich is an algebraic summation of the pressure drops across the MPL and the carbon substrate. To this end, the following equation can be used to solve for the permeability of the MPL [19]:

$$k_{MPL} = \frac{L_{MPL}}{\frac{L_{cGDL}}{k_{cGDL}} - \frac{L_{nGDL}}{k_{nGDL}}} \qquad (2)$$

where k_{MPL}, k_{cGDL} and k_{nGDL} are the gas permeability coefficients for the microporous layer, the MPL-coated GDL and the carbon substrate, respectively; and L_{MPL}, L_{cGDL} and L_{nGDL} are the thicknesses of the microporous layer, the MPL-coated GDL and the carbon substrate, respectively. To determine the thickness of the MPL, cross-section scanning images were used. Notably, in these images, the thickness of the MPL varies widely. Therefore, the thickness of the MPL was estimated at as many points as possible in order to have a well-representative value of the MPL thickness; see, for example, Fig. 3.

[Insert Fig. 3]

3. Results and discussion

Effects of carbon loading

Fig. 4 shows the through-plane gas permeability of the MPL-coated GDLs as a function of the carbon loading of the MPL. It should be noted that the PTFE loading is kept constant at 20 wt% in this work, a value frequently utilised in the literature [14-16]. As anticipated, the figure shows that the permeability of the carbon substrate (1.78×10^{-11} m^2) reduces by an order of magnitude when coated with an MPL containing as low as 0.5 mg cm^{-2} of carbon loadings. The subsequent increase in the carbon loading of the MPL results in gradual and significantly less decrease in the permeability of the GDL. The initial sharp decrease in the permeability is mainly attributed to the addition of substantially low-porosity MPL. On the other hand, the subsequent decrease in the permeability with increasing carbon loading is mainly due to the increase in the thickness of the MPL. Similar results were obtained in [14-16].

[Insert Fig. 4]

Effects of PTFE loading

Fig. 5 shows the estimated through-plane permeability of the MPL-coated GDLs as a function of the PTFE loading for the various considered carbon loadings, namely 0.5, 1.0, 1.5, 2.0 and 2.5 mg cm^{-2} in the MPL. All the curves show three common trends for all the carbon loadings investigated. The first one of these common trends is that, after 20 % PTFE loading, the permeability increases with increasing PTFE loading in the MPL. This has been justified in the literature by stating that the relatively large PTFE particles cannot penetrate the relatively small pores within the carbon agglomerate but the larger pores between these agglomerates. This increases the sizes of the agglomerates and consequently increases the porosity of the carbon-PTFE mixture [11, 15, 18-20]. This has been confirmed by the pore size distribution (PID) measurements, conducted by Uchida et al. [15], which show that the pore size increases as PTFE loading in the carbon-PTFE mixture increases. The second common trend is that the permeability of the GDL decreases when the PTFE loading in the MPL is increased from 10 to 20 %. This can be explained by stating that (i) the increase in the PTFE loading increases the thickness of the MPL, and (ii) the PTFE loading is not sufficiently high to make its 'positive' porosity-increasing effect overcome its 'negative' thickness-increasing effect. Note that by 'positive' effect we mean that it increases the permeability and by 'negative' effect we mean that it decreases the permeability. The last common trend is that the gas permeability of the coated GDL is a minimum with a 20 wt. % PTFE loading in the MPL.

Interestingly, the PTFE loading is sensitive to the carbon loading in the PTFE loading range from 0 to 10 %. Namely, the permeability in this range: (i) decreases for the 0.5 mg cm^{-2} carbon loading, (ii) remains almost the same for 1.0 mg cm^{-2} carbon loading, and (iii) increases for the 1.5, 2.0 and 2.5 mg cm^{-2} carbon loadings. Apparently, the 0.5 mg cm^{-2}

carbon loading is not sufficiently high to completely cover the large pores on the surface of the carbon substrate. Fig. 6 shows that, with 0.5 mg cm^{-2}, the skeleton of the carbon substrate can be clearly seen. This also justifies the large gap between the permeability values of the GDL coated with 0.5 mg cm^{-2} and those coated with higher carbon loadings. Therefore, adding some PTFE material to the carbon black reduces the size of the above large pores and consequently decreases the permeability. For relatively large carbon loadings, i.e. 1.5, 2.0 and 2.5 mg cm^{-2}, it appears that the carbon loading is sufficiently high to completely cover the large pores on the surface of the substrates and to 'absorb' the relatively low added PTFE amount. As explained above, the added PTFE particles increase the porosity, and consequently the permeability of the MPL. Apparently, the 1.0 mg cm^{-2} carbon loading is the loading at which the above competing effects of the 10 % PTFE loading are counterbalanced. However, the authors think that the above justification for the trends in the PTFE loading range from 0-10 % require some supporting evidences and therefore further complementary investigation is required.

[Insert Fig. 5 and Fig. 6]

Through-plane gas permeability of MPLs

As described in Section 2, Equation (2) was used to calculate the through-plane permeability of the MPLs of the coated GDLs. Fig. 7 shows the calculated MPL permeability values as a function of PTFE loading for all the carbon loadings investigated. As anticipated, the trends of the permeability curves of the MPLs are, in general, in accordance with those of the MPL-coated GDLs. It should be noted that the permeability values of the MPLs, which have the same PTFE loading, must be ideally the same as the composition is the same for all the above MPLs. For example, the MPLs with 20 % PTFE loading must all have ideally the same permeability value as the weight compositions of those MPLs are all the same, i.e. 20% PTFE

and 80% carbon black. However, this is not the case for the MPL permeability values shown in Fig. 7. Namely, there is a significant variation in the permeability values for the MPLs of the same composition. This is most likely to be due to the significant penetration of the MPL material into the body of the carbon substrates. The accurate estimation of the MPL penetration and subsequently the permeability of the MPL may be a topic of a future work.

[Insert Fig. 7]

4. Conclusions

The effects of the composition of the MPL on the permeability of the GDLs have been experimentally investigated in this paper. As anticipated, for a given PTFE loading, the permeability was found to decrease with increasing carbon loading and this is mainly due to the increase in the thickness of the MPL. The trends and observations associated with the effects of the PTFE loading of the MPL on the through-plane permeability of the GDL can be summarised as follows:

- For all the investigated carbon loadings, the permeability of the GDL was found to be a minimum at 20% PTFE loading in the MPL.
- For all the investigated carbon loadings, the GDL permeability was found to increase when the PTFE loading of the MPL is increased from 20 to 50%. This was attributed to the increase in the porosity of the MPL induced by the large PTFE particles.
- For all the investigated carbon loadings, the GDL permeability was found to decrease when the MPL PTFE loading is increased from 10 to 20% and this is most likely due to the increase in the MPL thickness which results in higher mass transport resistance.
- The effects of the PTFE loading of the MPL on the GDL permeability depends on the carbon loading in the PTFE range 0-10%: (i) for a carbon loading of 0.5 mg cm^{-2}, the GDL permeability decreases with increasing MPL PTFE loading, (ii) for a carbon

loading of 1.0 mg cm^{-2}, the GDL permeability remain almost the same, and (iii) for a carbon loading of 1.5-2.5 mg cm^{-2}, the GDL permeability increases with increasing PTFE loading. These results were explained in the text considering the competing effects of (a) the MPL coverage of the surface of the carbon substrate, and (b) the increase of the MPL porosity due to the addition of the PTFE particles.

Finally, the through-plane permeability of the MPLs of all the cases were estimated. As anticipated, the were found to follow the same trends as those of the MPL-coated GDLs. Interestingly, the permeability values of the MPLs of the same composition were found to significantly vary. This was attributed to the MPL penetration into the body of the carbon substrates.

Acknowledgment

The first author gratefully acknowledges the Management of Federal College of Education, Obudu, through Tertiary Education Trust Fund (TETFund AST & D) intervention, Nigeria, for their financial support. Also, the authors would like to thank SGL Technologies GmbH, Germany for providing the GDL sample material. The technical supports of Paul Crosby for the experimental work carried out in this study is gratefully acknowledged.

Nomenclature

L GDL sample thickness / m

k Permeability / m^2

p Pressure / Pa

v Gas velocity / m s^{-1}

μ Fluid dynamic viscosity / Pa s

References

[1] Barbir F. PEM Fuel Cells: Theory and Practice. 2012, 2nd Edition, Academic Press, California, USA.

[2] Owejan JP, Trabold TA, Jacobson DL, Arif M, Kandlikar SG. Effects of flow field and diffusion layer properties on water accumulation in a PEM fuel cell. Int J Hydrogen Energy 2007; 32: 4489-02.

[3] Ramasamy RP, Kumbur EC, Mench MM, Liu W, Moore D, Murthy M. Investigation of micro- and micro-porous layer interaction in polymer electrolyte fuel cells. Int J Hydrogen Energy 2008; 33: 3351-67.

[4] Velayutham G, Kaushik J, Rajalakshmi N, Dhathathreyan KS. Effect of PTFE content in gas diffusion media and microlayer on the performance of PEMFC tested under ambient pressure. Fuel Cells 2007; 4: 314-18.

[5] Tadbir MA, Hannach ME, Kjeang E, Bahrami M. An analytical relationship for calculating the effective diffusivity of micro-porous layers. Int J Hydrogen Energy 2015; 40:10242-50.

[6] Nguyen TV, Ahosseini A, Wang X, Yarlagadda V, Kwong A, Weber AZ, Deevanhxay P, Tsushima S, Hirai S. Hydrophobic gas-diffusion media for polymer-electrolyte fuel cells by direct fluorination. J The Electrochemical Soc. 2015; 162:F1451-60.

[7] Jordan LR, Shukla AK, Behrsing T, Avery NR, Forsyth M. Effect of diffusion-layer morphology on the performance of polymer electrolyte fuel cells operating at atmospheric pressure. J Applied Electrochemistry 2000; 30: 641-46.

[8] Antolini E, Passos RR, Ticianeli EA. Effect 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.

[9] Ismail MS, Ingham DB, Hughes KJ, Ma L, Pourkashanian M. Effective diffusivity of polymer electrolyte fuel cell gas diffusion layers: An overview and numerical study. Int J Hydrogen Energy 2015; 40:10994-10.

[10] Schweiss R. Benefits of membrane electrode assemblies with asymmetrical GDL configurations for PEM fuel cells. Fuel cells 2016; 16: 100-6.

[11] Su H, Sita C, Pasupathi S. The effect of gas diffusion layer PTFE content on the performance of high temperature proton exchange membrane fuel cell. Int J Electrochem. Sci 2016; 11:2919-2926.

[12] Giorgi L, Antolini E, Pozio A, Passalacqua E. Influence of the PTFE content in the diffusion layer of low-Pt loading electrodes for polymer electrolyte fuel cells. Eletcrochimica Acta 1998; 43: 3675 – 80.

[13] Kim YS, Peck DH, Kim SK, Jung DH, Lim S, Kim SH. Effects of the microstructure and powder compositions of a microporous layer for the anode on the performance of high concentration methanol fuel cell. Int J Hydrogen Energy 2013; 38: 7159-68.

[14] Kitahara T, Kinomi T, Nakajima H. Microporous layer coated gas diffusion layers for enhanced performance of polymer electrolyte fuel cells. J Power Sources 2010; 195: 2202-11.

[15] Uchida M, Aoyama Y, Eda N, Ohta A. Investigation of the microstructure in the Catalyst layer and effects of both Perfluorosulfonate Ionomer and PTFE-loaded carbon on the catalyst layer of polymer electrolyte fuel cells. J Electrochemical Society 1995; 142: 4143-49.

[16] Park S, Lee JW, Popov BN. Effect of carbon loading in microporous layer on PEM fuel cell performance. J Power Sources 2006; 163: 357-63.

[17] Ihonen J, Mikkola M, Linbergh G. Flooding of gas diffusion backing in PEFCs physical and electrochemical characterization. J. The Electrochemical Society 2004;151: A1152-61.

[18] Park S, Lee JW, Popov BN. A review of gas diffusion layer in PEM fuel cells: Materials and designs. Int J Hydrogen Energy 2012; 37: 5850-65.

[19] Ismail MS, Damjanovic T, Hughes K, Ingham DB, Ma L, Pourkashanian M, Rosli M. Through-plane permeability for untreated and PTFE-treated gas diffusion layers in proton exchange membrane fuel cells. J Fuel Cell Science and Technology 2010; 07:0510161-7

[20] Ismail MS, Borman D, Damjanovic TD, Ingham DB, Pourkashanian M. On the through plane permeability of microporous layer-coated gas diffusion layers used in proton exchange membrane fuel cells. Int J Hydrogen Energy 2011; 36: 10392-02.

[21] Chen HH, Chang MH. Effect of cathode microporous layer composition on proton exchange membrane fuel cell performance under different air inlet relative humidity. J Power Sources 2013; 232: 306-9.

[22] Ismail MS, Hughes KJ, Ingham DB, Ma L, Pourkashanian M. Effect of PTFE loading of gas diffusion layers on the performance of proton exchange membrane fuel cells running at high-efficiency operating conditions. Int J Energy Research 2013; 37: 1592-9.

[23] Ye Q, Nguyen T. Three-dimensional simulation of liquid water distribution in a PEMFC with experimentally measured capillary functions. J The Electrochemical Society 2007; 154: B1242-51.

[24] Lee HK, Park JH, Kim DY, Lee TH. A study on the characteristics of the diffusion layer thickness and porosity of the PEMFC. J Power Sources 2004; 131: 200-6.

[25] Shou D, Tang Y, Ye L, Fan J, Ding F. Effective permeability of gas diffusion layer in proton exchange membrane fuel cells. Int J Hydrogen Energy 2013; 38: 10519-26.

[26] Gostick JT, Fowler MW, Pritzker MD, Ioannidis MA, Behra LM. In-plane and through plane gas permeability of carbon fibre electrode backing layers. J Power Sources 2006;162: 228-38.

[27] Ong AL, Bottino A, Capannelli G, Comite A. Effect of preparative parameters on the characteristic of poly (vinylidene fluoride)-based microporus layer for proton exchange membrane fuel cells. J Power Sources 2008; 183: 62-68.

Figure Captions

Fig. 1 A schematic diagram of the experimental setup [19].

Fig. 2 Experimental data for the pressure gradient as a function of the velocity of the flowing gas.

Fig. 3 SEM cross-section images of MPL-coated GDLs: the averaged MPL thicknesses for all cases from a – e are: 0.59, 1.02, 1.48, 1.69 and 2.38 × 10^{-4} m, for carbon loading of 0.5, 1.0, 1.5, 2.0 and 2.5 mg cm^{-2} , respectively.

Fig. 4 (a) An SEM image for a surface of a bare carbon substrate sample before coating, (b) The gas permeability of the GDL before and after coating, and MPL-coated GDL as a function of the carbon loading in the MPL, (c-d) SEM images for surfaces of after GDLs coating of 0.5 and 2.0 mg cm^{-2} carbon loadings, respectively. The PTFE loading is 20 wt% for both the cases.

Fig. 5 (a) The curves representing the gas permeability of the MPL-coated GDLs as a function of PTFE loading for various carbon black loading, and (b) the above curves after excluding the 0.5 mg cm^{-2} carbon loading curve.

Fig. 6 (a-e) SEM images for surfaces of MPL-coated GDLs with 10, 20, 30, 40, 50 wt% PTFE loading, respectively. The carbon loading is 2.0 mg cm^{-2} in all cases.

Fig. 7 (a) The curves representing the gas permeability of the MPL as a function of PTFE loading for various carbon black loading, and (b) the above curves after excluding the 0.5 mg cm^{-2} carbon loading curve.