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Journal of Power Sources 131 (2004) 147–154
JOURNAL OF POWER SOURCES
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Influence of cathode gas diffusion media on the performance of the PEMFCs

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Abstract

The influence of gas diffusion media (GDM), i.e. carbon paper, on PEMFCs was studied. The study was based on GDM thickness pore size distribution, air-permeability, electronic resistance and hydrophobicity. Cell performances were correlated with the physical properties of the GDM and reasonable agreements were made based on the oxygen-gain which was regarded as an index of mass transfer in the cathode when the reactant was changed from neat oxygen to air. The results show that gas permeability and pore size diameter of the GDM are the important factors in the performance of the cell compared to all other physical properties. When the mean pore size diameter is in the range of about 25–40 μm, thickness of the GDM and its gas permeability play crucial role in lowering oxygen-gain. GDM with larger pore size shows severe flooding in cathodes compared to GDM with smaller pore diameter. Optimized Teflon content in the GDM was found to be 20% whereas above this content gas permeability of the GDM decreased substantially due to decreased porosity.

Keywords: Proton exchange membrane fuel cells; Gas diffusion media; Oxygen-gain; Air-permeability; Pore size distribution; Hydrophobicity

1. Introduction

PEMFC efficiency is high when operated with hydrogen and neat oxygen, but commercialization of fuel cell requires operation with air at ambient pressures. But when air is used the decrease of performance is obvious due to decreased partial pressure which is further reduced by humidification, and finally the performance declines due to blanketing effect of nitrogen in the oxidant. All of these facts make the cell determinantal to several millivolts [1–4]. Also PEMFC loss due to mass transport is high compared to all other losses, particularly when air is used. The challenging future of enhancing the performance is on the diffusion media used to fabricate MEA.

GDMs have the role of reactant permeation from flow fields to catalytic sites by through-plane and in-plane gas access, product permeation from the catalytic layer to flow fields, and electronic and thermal conductivity. Those properties depend on the pore size distribution, thickness, hydrophobic content and carbonization or graphitization conditions of diffusion media [5]. In general, a GDM which is good in gas permeation has a problem in mechanical strength. On the contrary, another GDM is high in mechanical strength but inferior in gas permeation, etc. Thus, the substrate thickness and most probably the mechanical strength is necessary in working of wet proof treatment of the substrate. These parameters are significant factors to be optimized for better cell performances.

The term of gas diffusion media (GDM) is referred to the material where no electrochemical reaction takes place and are positioned adjacent to both side of catalyst-coated membrane for membrane and electrode assembly (MEA) fabrication. Unlike GDM, gas diffusion electrode (GDE) are the catalyst coated diffusion media which is bonded with the membrane to form MEA where the pore structure, permeability to reactants and products and even the structure of the catalytic layer are affected by coating of the catalyst on the diffusion media in GDE [6,7].

Literature study shows that most of the research was restricted by considering only few diffusion media and was extremely employed in the application of carbon layer/microporous layer (MPL) to the GDMs. This shows that diffusion media are not contemplated as a vital source of efficiency loss, even though they determine the permeability of reactants to the catalyst sites. Without proper evaluation and selection of GDM, application of microporous layer and efficient catalyst layer on them would be ineffective.

This publication demonstrates the significance of selection of the gas diffusion media for PEMFCs by evaluating various GDM and shows how the physical properties of GDM affect the cell performance.

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doi:10.1016/j.jpowsour.2004.01.030

2. Experimental

2.1. Electrode preparation

Catalyst ink was prepared by mixing 20% Pt/Vulcan XC-72 catalyst (E-TEK) with isopropyl alcohol (HPLC grade) and then the mixture was ultrasonicated for 1 h. Finally 5 wt.% Nafion® solution supplied by Dupont, Inc. was added to the catalyst ink which was sonicated again for 1 h. These catalyst inks were spray-coated on the pre-treated Nafion® 115 membrane hold in the clamps using an automated spraying machine. A catalyst loading of 0.4 and 0.3 mg Pt/cm^2 were coated on cathode and anode, respectively. Gas diffusion media, i.e. carbon papers with different physical properties were bought from two manufacturers and their physical properties are summarized in Table 1. In this study different GDM were used for the cathodes, but only one GDM, T2, was used for the anodes throughout the experiments. The Teflon content of GDM was 20 wt.% unless specified otherwise. The catalyst-coated membrane was finally kept inside the polythene bag and dried at room temperature to avoid the formation of cracks prior to hot pressing with GDM at 140 °C for 90 s to form an MEA.

2.2. Operating conditions and electrochemical measurements

Single cells were tested using a home-made assembly of graphite block and header made with duralumin. The ribs and the channels in the graphite block formed a semi serpentine flow field and their width and depth were 1 mm. MEAs of 25 cm^2 electrode area were assembled with graphite block and header and all the cells were tested at a cell temperature of 80 °C, and cathode and anode humidification temperature of 65 and 80 °C, respectively. The stoichiometries of the fuel and oxidant were 1.5 and 2.2, respectively.

Current–voltage curves were measured galvanostatically with an electronic loader (Daegil Electronics). Impedance spectra were recorded with a Zahner IM 6 instrument at 0.85 V in the frequency range 10 mHz to 100 kHz. For this study the anode served as a counter electrode and reference electrode. To interpret these data, it was assumed that the anode impedances at all current densities were negligible [8].

2.3. Diffusion measurements

Air-permeability through the plane (along the *z* direction) of the gas diffusion media was measured using a home-made apparatus with manometer. The difference in the water column of the manometer gives the pressure drop at an air flow rate of 10 SLPM. The area of the sample exposed to air permeation was 2.4 cm^2.

2.4. Electrical resistance measurements

Through-plane resistance of the GDM was measured by EG&G PAR Model 270 using copper plates. GDM was inserted in between the two plates where the upper plate leads were connected to reference and counter electrode and the lead from the bottom plate was attached to the working electrode. The resistance measured was the total resistance excreted by the bulk of the material and contact resistance of GDM with the metal plates. This through-plane resistance along the *z* direction revealed the GDM electrical conductivity when it was compressed.

2.5. Physical characteristics

Scanning electron microscopy (Hitachi S-4200) was used to observe the morphology of GDM and Micromeritics auto pore IV was employed to obtain porosimetry data of the gas diffusion media.

3. Results and discussion

3.1. Effect of physical properties of GDM

For this study gas diffusion media were bought from two manufacturers which included wide variety of materials having different physical properties. Since the disclosure of the details of the materials with the manufacturer name is not permissible, the name was designated as A and B. The physical properties of the various GDM from these manufacturers are shown in Table 1.

Gas diffusion materials from the manufacturer A are classified as T1, T2, T3 and T4. The details of the diffusion media can be seen from Table 1. They are made of the same

Table 1
Physical properties of various gas diffusion media

Gas diffusion media	Uncompressed thickness (μm)	True density (g/cm^3)	Mean pore diameter[a] (μm)	Gas permeation rate (ml/min cm^2 Pa)
T1	108	0.65	26	47.4
T2	175	0.74	40	26.5
T3	290	0.74	33	14.7
T4	386	0.74	30	11.8
P1	428	0.50	65	24.9
P2	303	0.52	86	19.3
P3	312	0.44	40	85.0

[a] Mercury porosimetry analysis.

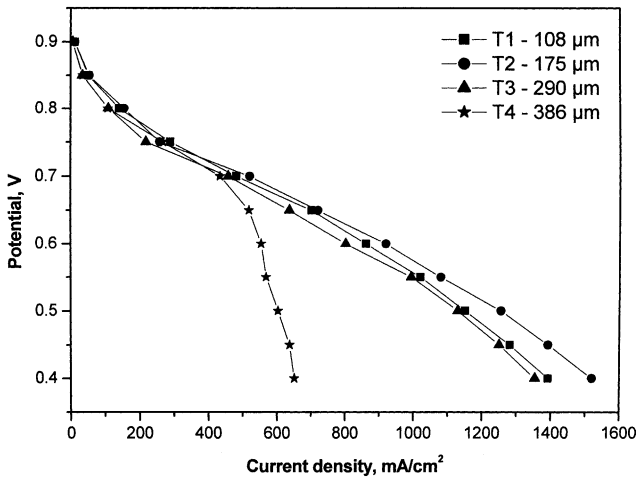

Fig. 1. Polarization curves of cells with different cathode gas diffusion media; H_2/O_2.

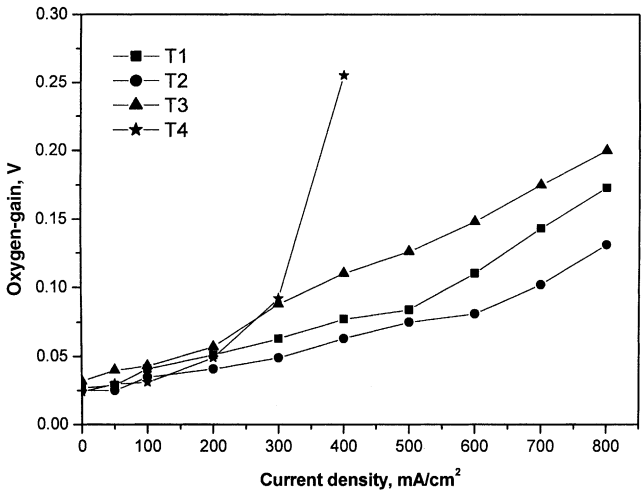

Fig. 3. Oxygen-gain vs. current density for different gas diffusion media.

carbon fibers and have the same Teflon content of 20 wt.% and thus they have almost the same physical properties except thickness and thus gas permeability. This material was used as cathode gas diffusion media and their polarization curves for neat oxygen and air can be seen from the Figs. 1 and 2. In all the experiments, T2 was used as a GDM for the anode. The GDM showed same trend with pure oxygen and air. The cell performance was almost similar at low current density region. But as the current density was increased, T1 exhibits slightly higher mass transport hindrance than T2. This might be because thinner GDM are vulnerable to water flooding than thicker ones [9]. Maximum performance was observed for T2 in the entire current density range whereas T3 with thickness of 290 μm showed a slightly higher activation, ohmic and mass transfer resistance. In the case of T4 severe flooding started earlier in the ohmic region itself. It may be due to low gas permeation as the thickness of the GDM increases and oxygen diffusion could be possibly affected by condensation of water clogging the pores. In Fig. 3 increase of oxygen-gain (the voltage difference between the cell voltage obtained from oxygen operation and air operation) from T2 to T4 was observed as a result of effect of GDM. Since the pore size distribution does not vary widely, those results could be attributed to that there is limitation of oxygen diffusion in the thicker gas diffusion media.

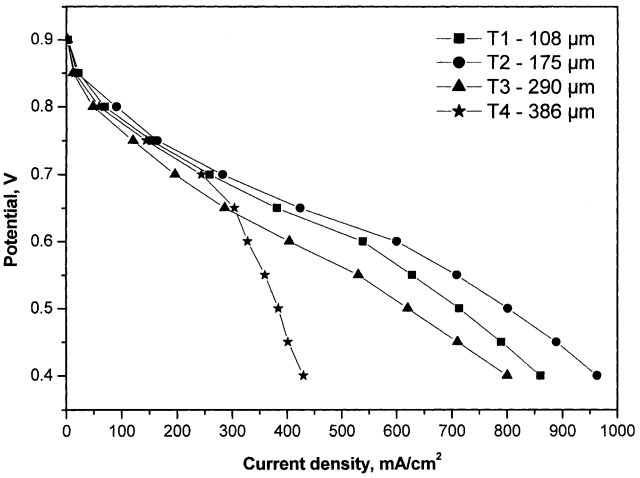

Fig. 2. Polarization curves of cells with different cathode gas diffusion media; H_2/air.

Fig. 4 shows scanning electron micrographs of the GDM. From T1 to T4 the surface morphology of the pores seems to be slightly decreased with increasing thickness. That might be due to the Teflon coverage on the surface of the GDM though they all have the same Teflon content of 20 wt.%. Pore size distribution determined by mercury porosimetry revealed (Fig. 5) that the pore size in the range of 22–32 μm predominates in all this class of materials, but the difference exists in the interconnected pore volume which is a function of pore diameter and porosity of the GDM. The mean pore diameters of T1 and T2 are about 26 and 40 μm whereas T3 and T4 lie in this range. The through-plane electric resistance values of the GDM were initially high and they decreased when they were compressed as shown in Fig. 6. In general the bulk property of these materials showed 40% reduction as compression force increased to fivefold. This experiment shows that there is the optimum thickness for diffusion materials above which they act as a diffusional barrier to the oxygen reactant by causing accumulation of nitrogen blanket within the pores, especially when air is used as an oxidant.

The particulars of the diffusion materials purchased from manufacturer B can be seen from Table 1. The density of the material of P1, P2 and P3 are 0.50, 0.52 and 0.44 g/cm^3, respectively. Since the density of these materials differ from one another, the evaluation of this material based on thickness was not suitable. Polarization characteristic of this material shows invariable performance in the low current density region (Fig. 7) irrespective of the permeability of the

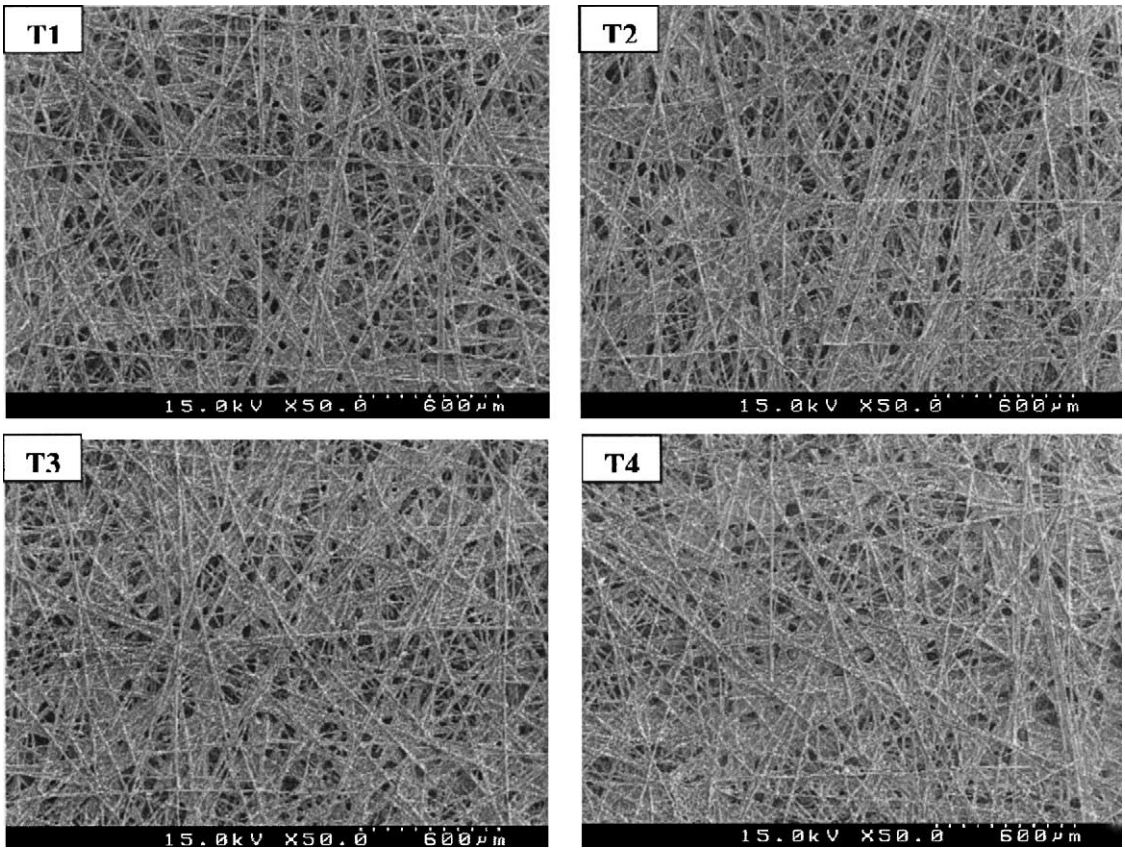

Fig. 4. Scanning electron micrographs of manufacturer A gas diffusion media, 20% PTFE.

GDM to air. At high current density region P1 and P2 shows mass transfer limitation. In case of P3, the mass transfer limitation was not observed.

This can be elucidated from the SEM images as shown in Fig. 8. P1 is a felt where the orientations of carbon fibers are irregular in structure whereas in case of P2 the carbon fibers are somehow linear with less pore structure. The surface morphology of carbon fiber in P3 is irregular in network. This rationalizes the difference in pore size distribution of the GDM which are quite different from one another. P1 shows the pore size distribution (Fig. 9) predominates in two regions: one is at 5 μm and the other is at 60 μm. P2 exhibits broad range from 60 to 90 μm and P3 in the range of about 45–60 μm. Gas diffusion media P1 and P2 have larger mean

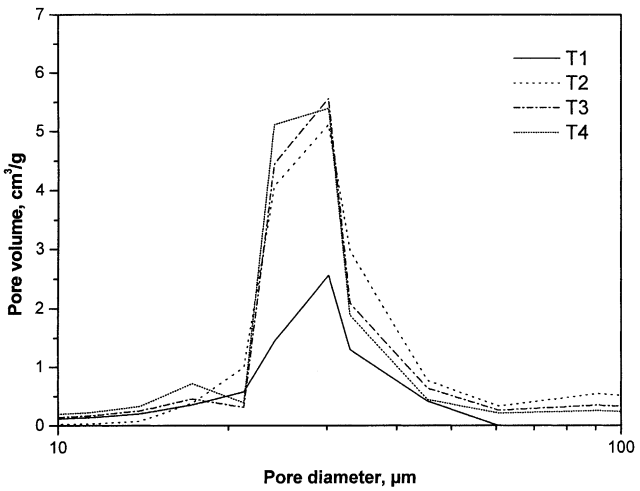

Fig. 5. Pore size distribution of manufacturer A gas diffusion media.

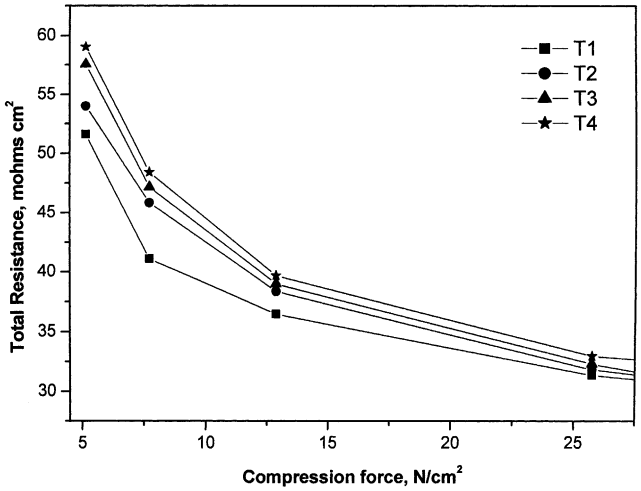

Fig. 6. Gas diffusion media resistance as a function of compression force.

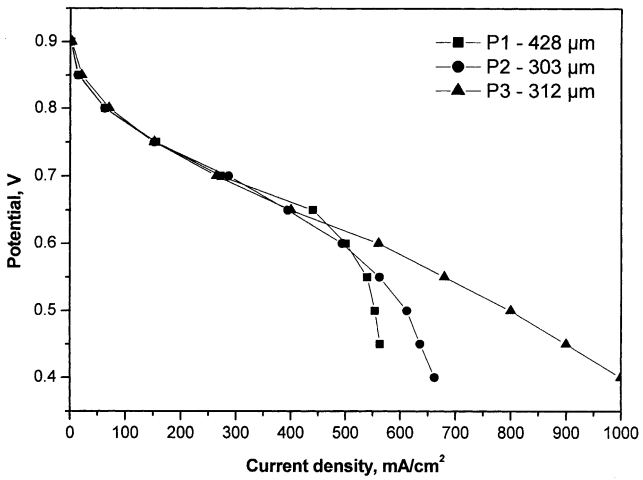

Fig. 7. *i–V* characteristics of cells with different cathode gas diffusion media; H_2/air.

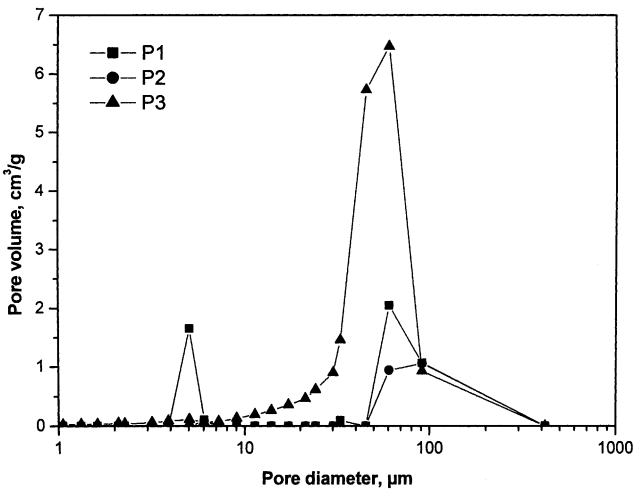

Fig. 9. Pore size distribution of various gas diffusion media.

pore diameters of about 65 and 86 μm which may be the cause for severe flooding in cathodes. The reason behind this is that water generated from the electrochemical reaction and electro osmotic drag will create a certain hydraulic pressure at the interface between hydrophobic GDM and hydrophilic catalytic layer [10]. Under this condition, the water will try to pass through the pore but the hydrophobic pore will resist this intrusion. As a consequence water droplet will form at the interface, which is in some form proportional in size to the diameter of the pore.

Electrical resistance measured as a function of compression force shows (Fig. 10) that P3 has the lowest resistance at initial compression compared to all other gas diffusion media and also the reduction of resistance with compression

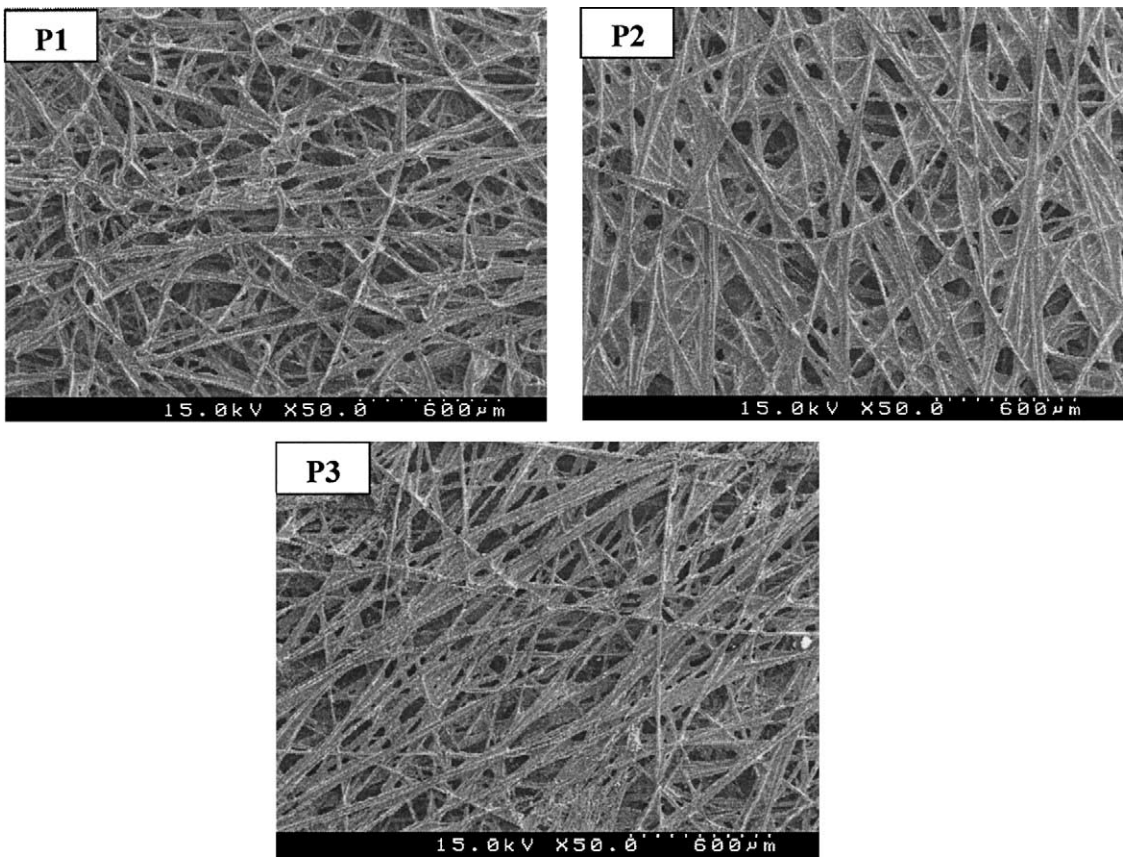

Fig. 8. SEM images of manufacturer B gas diffusion media, 20% PTFE.

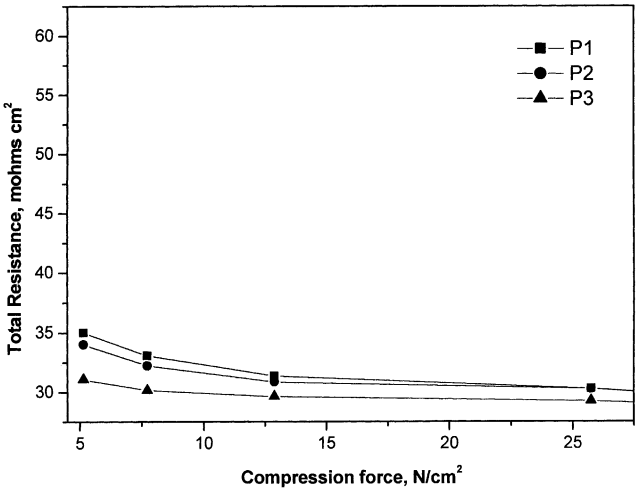

Fig. 10. Gas diffusion media resistance as a function of compression force.

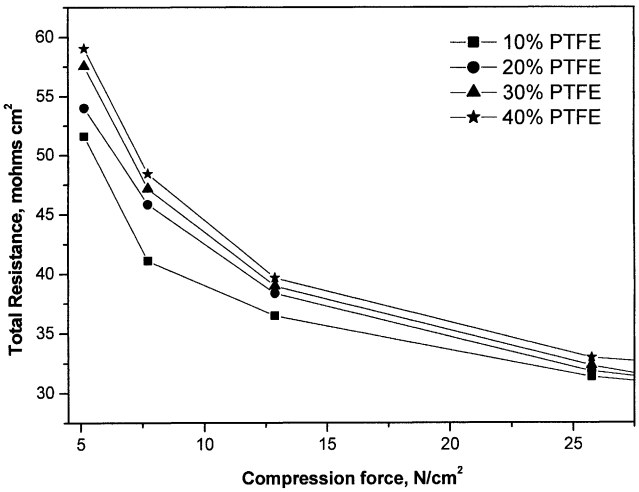

Fig. 12. Resistance vs. compression force.

force for this materials were negligible compared to other GDM, enabling that when assembling MEA the requirement of higher torque is not mandatory to reduce the resistance.

3.2. Effect of hydrophobicity

Fig. 11 shows the polarization curves for cells using MEAs with different hydrophobic Teflon content (10–40%) of T2 cathode gas diffusion media from the manufacturer A. As can be seen from the figure that the GDM with 20% PTFE showed the best the performance, which implies that facilitation of mass transport is better than other GDM. Linear portion of the polarization curve corresponds to ohmic resistance decreases for 30% or higher teflonized GDM that may be ascribed to an excess of non-conductor in the GDM. The *i–V* curve of the 40% Teflon in the GDM exhibits resistance in the activation, ohmic and mass transport region. This may be perhaps due to increased electronic resistance

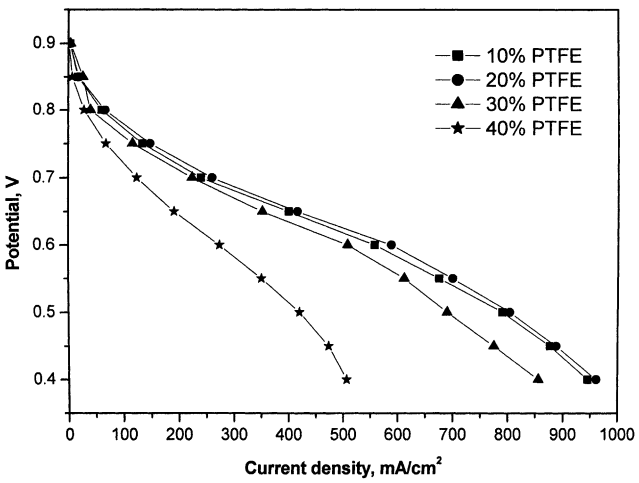

Fig. 11. Polarization curves of cells with various percentages of teflonized manufacturer A-T2 cathode gas diffusion media; H_2/air.

of excessive non conductor (Fig. 12) and decreased porosity by the Teflon clusters causing hindrance for diffusion of oxidant.

This was confirmed by the scanning electron micrograph shown in Fig. 13, where the porosity of the GDM decreased with increasing Teflon content from 10 to 40% gradually. This also reflects the permeability of the air in the diffusion media. For 10 and 20% the gas permeability is high whereas it decreases for 30 and 40% as shown in Table 2. The observed value of gas permeability for 40% is very low compared to all other GDM and is only about 1/3 of 20% teflonized GDM. This shows that the permeability of reactant is significantly affected by the presence of excessive non-conductor in the GDM, which in turn deteriorates the performance of the PEMFC.

Impedance analysis (Fig. 14) reveals that charge transfer resistance is accompanied by the hydrophobic content in the material. The presence of Teflon in the GDM is necessary for mass transport of water. But there is substantial adverse effect when the amount of non-conductor is high. The oxygen-gain curve shown in Fig. 15 implies that as the Teflon content is increased the transfer of oxygen to the catalyst sites decreases due to low permeability of gas diffusion media. 10% teflonized GDM exhibited higher oxygen gain than 20% teflonized GDM even though it exhibited high gas permeability and hence was expected to show a lower oxygen gain. That results could be due to the mass transfer caused by inefficient water removal.

Table 2
Physical properties of various percentages of teflonized manufacturer A-T2 gas diffusion media

PTFE (%)	Gas permeation rate (ml/min cm² Pa)
10	30.4
20	26.5
30	17.0
40	9.9

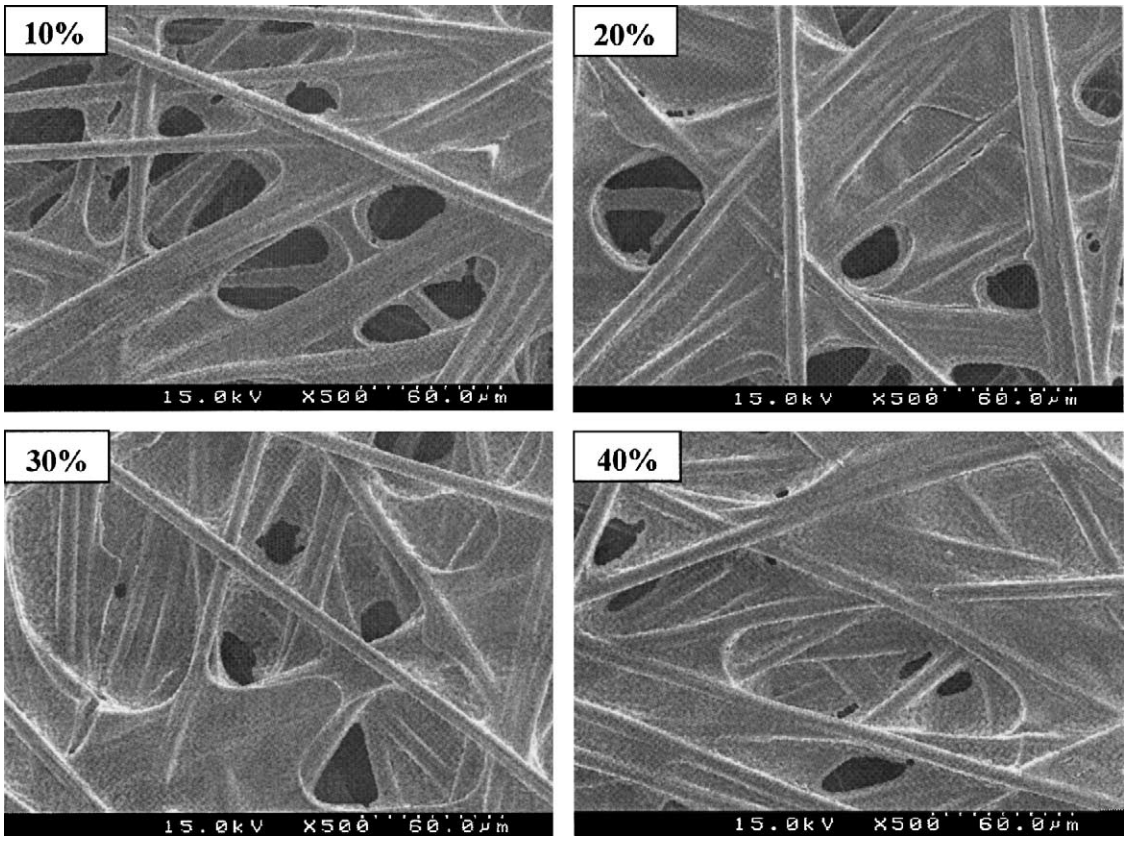

Fig. 13. Scanning electron micrographs of various percentages of teflonized manufacturer A-T2 gas diffusion media.

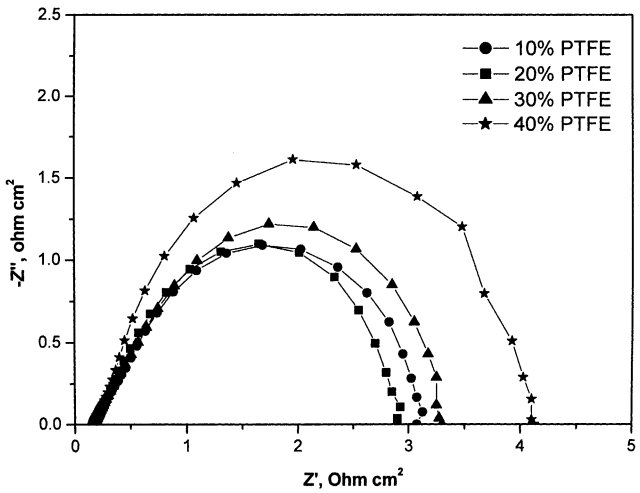

Fig. 14. Impedance analysis at 0.85 V of cells with different PTFE content in the cathodes.

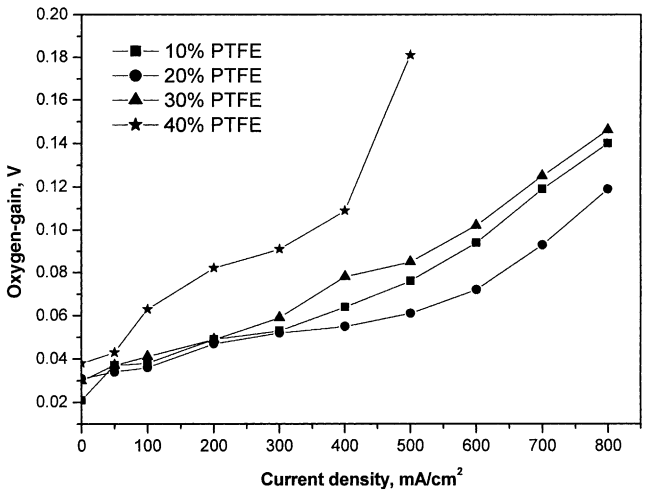

Fig. 15. Mass transfer resistance shown as oxygen-gain as a function of current density.

4. Conclusions

Analysis of the gas diffusion media shows that selection of the material is very important for the cell performances:

- Generally GDM with lower thickness is beneficial due to low gas diffusion loss than materials with higher thickness whereas too thinner GDM are susceptible to mass transfer limitation, contact resistance and weakness in mechanical properties. Therefore, there is an optimum thickness of GDM for the PEMFCs.
- Pore size distribution of the material reveals that GDM with larger mean pore size of above 60 μm negatively affects the cell performance in the high current density

region due to formation of water droplets in the interface of the GDM and active layer. But the significance of pore size distribution is less in the low current density region. This shows that selection of GDM with optimized mean pore diameter is essential.

- From our study, gas permeability of the media is one of the most important factors to be considered when selecting GDM because it has significant effect on the performance and oxygen-gain of the PEMFCs.
- Electronic resistance of the material was found to be different from manufacturer to manufacturer; normally it decreases with decreasing thickness of the material.
- Hydrophobicity of the GDM shows that if a hydrophobic layer is present in low quantity the reactant permeability is affected by poor water removal whereas at higher content there is severe gas diffusional loss. From our experiments, 20% PTFE gave the best performance.

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