



# The use of a novel water porosimeter to predict the water handling behaviour of gas diffusion media used in polymer electrolyte fuel cells

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## ABSTRACT

A novel water porosimeter and its use in determining the capillarity of gas diffusion layers are described. It is found that, in accordance with the Washburn equation, the pressure required to force water into the gas diffusion layer depends on the cosine of the contact angle of water with the surface of the pore. Negative pressure is required to withdraw water from the gas diffusion layer, even when the surface is hydrophobic. The negative pressure required is found to be independent of surface contact angle. It is shown that the performance of gas diffusion layers in an operating fuel cell can be qualitatively predicted from the capillary pressure curves obtained. The advantages of the use of water porosimetry over the use of either mercury porosimetry or porosimetry using wetting fluids are discussed.

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## 1. Introduction

Water could be considered the key substance in a polymer electrolyte fuel cell. Its presence, guaranteed by the oxygen reduction reaction, is required by the ionomeric membrane but its presence in excess in the gas diffusion layer can be extremely detrimental to performance. The understanding of the interaction of water with fuel cell components is therefore an important area of study. It is important, both in the search for new, improved materials [1] and in the development of reliable models to predict and explain fuel cell performance [2,3].

Despite this importance there are relatively few studies of the interaction of water with gas diffusion layers (GDLs). Fowler and co-workers [4] used a wetting fluid to study the capillarity of a number of commercial GDLs. These data were then compared to mercury porosimetry data and the behaviour of water inferred from the behaviour of the other fluids by scaling according to a contact angle. The work presented below will show that this is an error-prone technique. There is evidence of this in the original paper: the pore size determined by the mercury porosimetry (9  $\mu\text{m}$ ), whilst agreeing with capillary flow porometry data [1,5], is very much less than the physical size of the pores when imaged by SEM [6]. Using the same wetting fluid technique, a very detailed study of

one GDL type has been carried out by Mench and co-workers [7–9]. In it they demonstrated that the commonly used capillary pressure correlations are inappropriate for the type of porous media used as GDLs. This is hardly surprising as the correlations were developed for geological samples [10]. The fact that their results could only be expressed as an empirical correlation shows the value of measurement of these properties, as opposed to simulation.

A porosimeter similar to the one used in this work has been applied by the group of Schwartz [11] to study the capillarity of GDLs using water. A key finding was that severe hysteresis was observed. The determination of hysteresis behaviour is impossible using the methods of Fowler and Mench. Nguyen [12] has also used a similar porosimeter and obtained similar imbibition results, however his group observed no hysteresis.

The modelling of fuel cell performance is well developed [2,3], however most of the state of the art models still describe the behaviour of water in the GDL using the correlations that Mench [7] showed to be inappropriate. The predictions of the models will therefore be wrong under conditions that produce liquid water in the GDL. It has been shown by workers at Honda [13] that, even with highly detailed characterisation of the GDL, simulation of the capillary pressure curve is difficult.

It is therefore clear that more experimental measurements of the interaction of water with GDL materials are required, along with a simultaneous advancement of the fundamental understanding of how water behaves in these complex, hydrophobic pore spaces.

Porosimetry is the analysis of the pore space of a porous medium through the intrusion of a non-wetting fluid. Conventionally the fluid used is mercury and this technique, mercury intrusion

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porosimetry, is a well established analytical technique [14]. In the current work the non-wetting fluid is water, as this is directly relevant to fuel cell operation, and the many assumptions involved in the interpretation of mercury porosimetry data can be avoided.

As will be shown below, even when the mechanisms behind the water–GDL interaction are poorly understood, the data themselves can be used a predictor of the performance in an operating fuel cell.

## 2. Experimental

The concept of the water porosimeter is that the sample is held between a hydrophilic porous membrane and a hydrophobic porous membrane. Water is added to and removed from this sandwich through the hydrophilic side with air moving in and out of the sample through the hydrophobic membrane on the opposite side. The water is added at a range of pressures that ensure that the hydrophilic membrane is always full of water and the hydrophobic membrane always empty. Any water added is therefore present in the sample under test. The capillary pressure curve for the sample can thus be generated.

The apparatus used for this work is depicted in Fig. 1. The sample is compressed in a fixture consisting of two aluminium alloy end plates, one of which has a pneumatic piston mounted in it. This piston can exert compressive loads on the sample of up to 100 psi and thus the sample can be tested under the same degree of compression that would be used in an operating fuel cell. Water is introduced through the end plate without the piston and is distributed across the surface of the plate by a network of channels machined into the plate's face. A hydrophilic membrane (Hybond N 0.45  $\mu\text{m}$  pore diameter, Amersham Life Sciences) is sealed over these channels using silicone sealant. The sample (12 cm  $\times$  12 cm) is placed on top of this hydrophilic membrane inside a silicone gasket mounted in the end plate. Sealing onto this gasket is a porous PTFE membrane, which is designed to allow air to escape from the apparatus but to be highly resistant to water. The water entering the apparatus is therefore forced into the sample. The PTFE membrane is constructed from four layers of 0.07  $\mu\text{m}$  pore size expanded PTFE (Tetratex 1316 Donaldson) laminated together by hot bonding a window frame of polyethylene around the perimeter. The polyethylene seals the edges of the porous PTFE and protects them from damage by the seal. A sintered porous metal plate is placed on top of the porous PTFE. This can transfer the compression of the piston and thus compress the GDL sample and seal the fixture, whilst still allowing gas to escape from the cell. Tests have shown that the maximum pressure achievable before water penetrates the porous PTFE and invalidates the test is 65 psi. This means, in practice, that

all the porosity in the fibrous portion of a GDL, however hydrophobic, can be accessed, but any porosity contained in a porous carbon fill cannot.

This fixture is similar in concept to the one used by Schwartz and co-workers [11], but has the additional capability of varying the sample compression in a controlled way. Sample preparation is also considerably easier. Recent work by Nguyen [12] uses a fixture very similar to the one in this work, however the sample compression was not well controlled. As the behaviour of GDLs in the cell is well known to vary with compression, the authors feel that it is essential to study GDLs under realistic loads.

The water is introduced to the fixture using a programmable syringe pump (PHD 200 Infuse-Withdraw, Harvard Apparatus). The pressure of the water was measured using a pressure transducer (0–100 psi, accuracy 0.06 psi, Druck PDCR 1830, GE Sensing). The pressure transducer was mounted on the lower portion of a vertical side tee, the upper portion of the tee had a valve through which water could be added to ensure no air bubbles were present in the apparatus at the start of the experiment.

To generate the capillary pressure curves of a sample, water was injected into the porosimeter at a low, constant rate until a pre-defined maximum pressure was reached. Subsequently water was withdrawn at the same rate until a minimum pressure limit was achieved. The negative pressure limit was determined by the bubble point of the hydrophilic membrane, which was around 4 psi, so most data were collected down to around  $-2$  psig. The water breakthrough pressure of the porous PTFE was around 65 psi, but generally the form of the pressure/volume curve showed that there was no porosity accessible at pressures in excess of 5 psi.

It was shown that the data did not depend on the rate of imbibition–drainage over the range studied. All data were collected at 0.1 ml  $\text{min}^{-1}$ , unless otherwise stated.

It was generally observed that it was harder to intrude water for the first time compared to all subsequent cycles. If only one imbibition–drainage cycle is shown, this is the second cycle, and is representative of the equilibrium state of the sample.

## 3. Results and discussion

### 3.1. Water porosimetry

Fig. 2 shows the first imbibition–drainage cycle obtained for a typical wet-proofed GDL. Since the pump runs at a constant rate the volume axis can also be thought of as representing time. Starting from zero volume, or time, the initial portion of the curve has a capillary pressure of zero. This corresponds to the filling of the

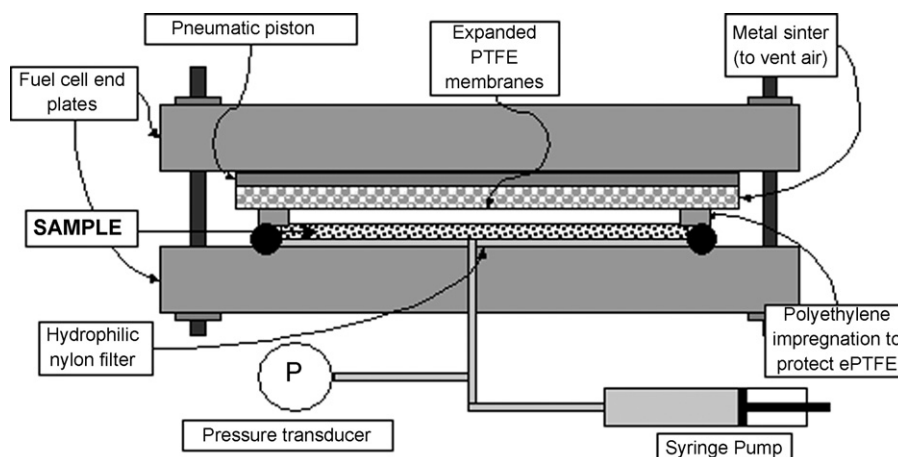


Fig. 1. Schematic of the water porosimeter.

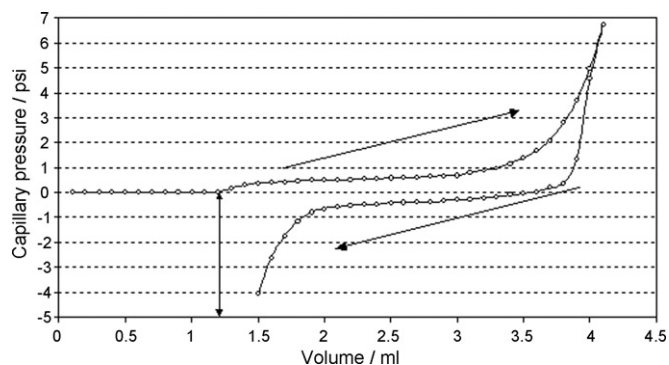


Fig. 2. Capillary pressure curve for a wet-proofed GDL. The vertical arrow denotes the start of the filling of the pores of the GDL.

hydrophilic membrane. A clear inflection point at 1.2 ml, marked in the figure by an arrow, denotes when the water starts to enter the GDL. From this point onwards the pressure/volume relationship is therefore characteristic of the GDL under test. The positive pressure required to force water into the structure gives a measure of the hydrophobicity of the pore space. After 3.8 ml of water have been injected into the text fixture the pressure rises steeply showing that there is no more porosity accessible at these pressures. The water uptake of the sample is therefore 2.6 ml. From the sample density and the compression vs. thickness relationship for this material it was calculated that this corresponds to filling 80% of the total porosity of the sample.

It was found that GDLs which were solely based on fibres would fill completely during the experiment, whether wet-proofed or not. For GDLs that contained a carbon fill, such as this one, complete filling would only occur if the fill was hydrophilic in nature. This shows that hydrophobic porosity within carbon fills does not fill with water in the pressure range studied in this work. This is expected due to the very small size of these pores (typically <100 nm).

The drainage curve shows marked hysteresis. This is in agreement with Schwartz [11], but in stark contrast to Nguyen [12] who observed good agreement between the imbibition and drainage curves. Hysteresis has been observed for every sample tested to date.

The extent of the hysteresis is surprising. Almost all the imbibed water requires a negative pressure to be removed from the sample. Despite the fact that pressure has been applied to force water into the pores, pressure also has to be applied to remove the water. The positive pressure of the imbibition curve shows that the GDL is hydrophobic and yet it does not spontaneously dewet, a counter-intuitive result. One possible explanation is that the wet-proofing of the GDL is imperfect and that the water once inside the pore space can attach to unwet-proofed hydrophilic sites and pressure is required to break this attraction. However, this phenomenon was observed for such a wide range of samples, wet-proofed to differing extents, using different methods, that it is unlikely that this is the explanation. This will be discussed in more detail below.

A more likely explanation is that the hysteresis is related to the pore shape. In a fibrous material the pores are very different in shape to the uniform cylindrical shape often assumed. It has been shown both theoretically [15] and experimentally [16] that the non-parallel pore walls found in fibrous media have a profound affect on the interaction with fluids. In particular, it has been shown that wetting fluids would require positive pressure to enter fibrous media, despite a contact angle of less than  $90^\circ$  [15,16]. This finding has been repeated with rock samples by Anderson [17] who observed that contact angles of less than  $50^\circ$  were required for spontaneous imbibition. The drainage curve of a hydrophobic medium is equivalent to the imbibition curve of a wetting fluid;

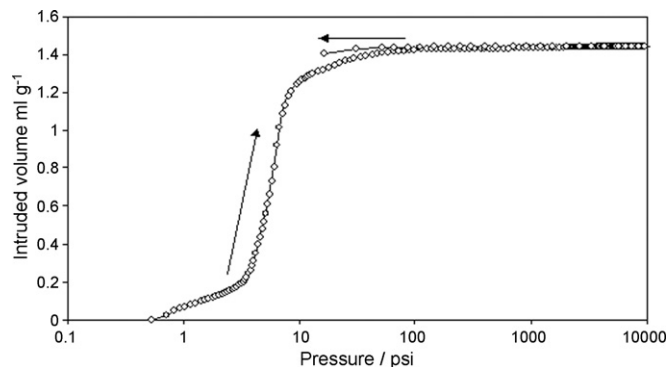
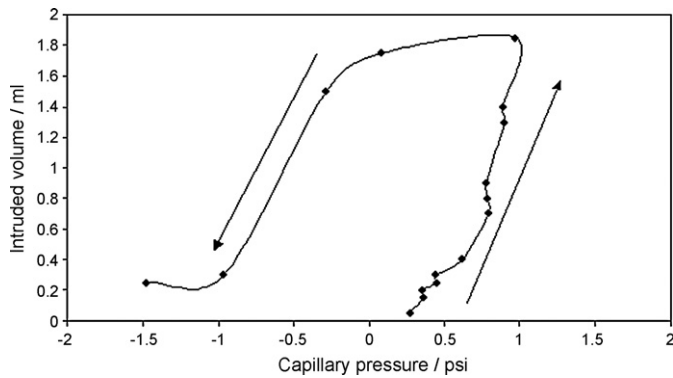


Fig. 3. Mercury porosimetry imbibition–drainage cycle for TGP-H-060.

air is considered to be the wetting fluid. The observed requirement to apply a negative pressure on the water, a positive pressure to the air, is therefore in agreement with existing observations and theory.

It is instructive to examine the results of Fig. 2 in the light of teachings of the extensive mercury porosimetry literature. Since mercury porosimetry is the intrusion of a non-wetting fluid into a porous solid, and thus is analogous to the current work, the processes at work should be the same and therefore so should the interpretation of results. The initial difference is that the drainage curve would be unobtainable using mercury since commercial mercury porosimeters do not measure negative capillary pressures. The sample is initially evacuated and then mercury added and withdrawn through the application of positive pressure, the drainage curve therefore ends at atmospheric pressure. Thus in a mercury porosimetry experiment, analogous to the water porosimetry of Fig. 2, no drainage of the non-wetting phase would be observed. An example of this can be seen in Fig. 3, which shows a mercury porosimetry imbibition–drainage for a commercial GDL (Toray TGP-H-060). It can be seen that the drainage curve stops at a higher pressure than the mercury imbibition pressure and so the drainage properties are impossible to measure. Examples of this for other fibrous media can be seen in the literature [18]. This shows that the water porosimeter is a more powerful tool for studying GDLs than the more common mercury porosimeter. It is common in mercury porosimetry for the drained volume to be significantly less than the imbibed volume. In cases, unlike Fig. 3, when the pressure can be lowered to less than the imbibition pressure this is interpreted as entrapment of the mercury as a result of the connectivity of the non-wetting fluid phase being lost during drainage, the so-called “snap-off”. The result in Fig. 2 suggests that this is not necessarily the case. Where the experiment of Fig. 2 to have been stopped at zero pressure, it would have been assumed that almost all the water has been retained within the GDL due to “snap-off”. However, the ability to remove almost all the water at negative pressures shows that connectivity has not been lost and the water which has not come out of the pores at zero pressure can be removed. This possibility does not seem to have been considered in the mercury porosimetry literature and therefore it is likely that at least some of the interpretation of results in this literature is wrong.

When the drainage of mercury does occur at a positive pressure, but at a drainage pressure less than the imbibition pressure, it is often assigned to the “contact angle hysteresis”, *i.e.* the supposition that the advancing and receding contact angles are different. Many authors have pointed out that this is thermodynamically unfeasible and shown that hysteresis can be caused by a variety of structural effects [14,19]. The water porosimetry results presented here appear to show an extreme case of this structure-induced hysteresis.



**Fig. 4.** Capillary pressure curve for TGP-H-060 10% PTFE measured using a static water column.

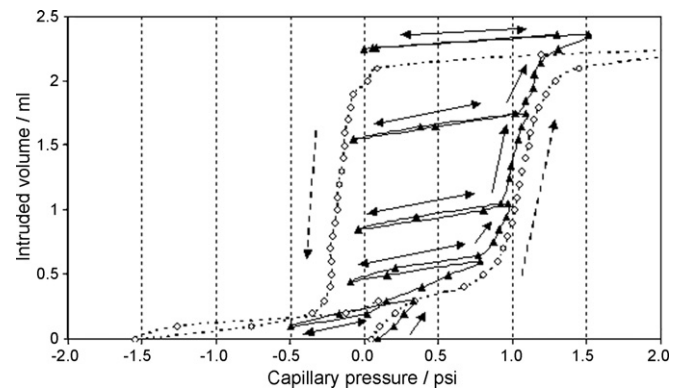
In Fig. 2 it is not clear where to assign the break point on the drainage curve. It is impossible to determine whether the steeply curving portion at below 2 ml corresponds to strongly held water being withdrawn from the GDL or water being withdrawn from the hydrophilic membrane. This means that between 0.8 ml and 0.3 ml of water is retained within the sample at the most negative pressure measured. This could either be held on strongly hydrophilic sites or entrapped within the structure due to “snap-off”.

Due to the parallels with mercury porosimetry discussed above, all subsequent figures will be presented using the convention of pressure along the X-axis with volume on the Y, *i.e.* the transpose of Fig. 2. When this is done the volume required to fill the hydrophilic membrane (*e.g.* 1.2 ml in the case of Fig. 2) is subtracted from the measured volume to give an intruded volume, which reflects the amount of water in the GDL sample.

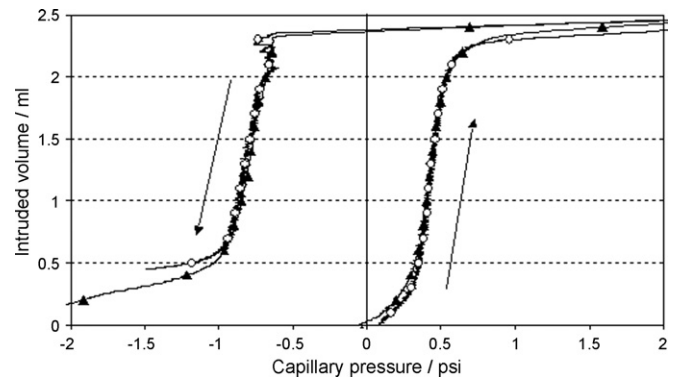
That this marked hysteresis is seen in the present work and in that of Schwartz [11], whilst it is absent from the very similar work of Nguyen [12] is puzzling. Nguyen raised three possible explanations for this discrepancy. Firstly the GDLs used were slightly different, secondly the Nguyen technique measured the equilibrium pressures rather than a quasi-equilibrium state using a low-flow rate. The third difference was that Nguyen used a smaller capillary pressure range.

The first two points are addressed in Fig. 4. This shows a capillary pressure curve for the same GDL used in the Nguyen work, Toray TGP-H-060 with 10% PTFE, although the samples may differ slightly due to different in-house wet-proofing procedures. To address the second point, the data in Fig. 4 were obtained using a static water column to measure both the pressure and volume uptake, as opposed to the syringe pump and transducer. Each point was recorded after holding at constant head for at least 10 min. Although the quality of the data is poor, it is clear that the hysteresis is still present. Nguyen’s third proposal, the possibility of the extent of pore filling changing the hysteresis is often observed in the mercury porosimetry literature, however Fig. 5 shows that this is not occurring in this case. Fig. 5 shows two capillary pressure curves for a single Toray TGP-H-060 sample. In one case the sample was completely filled in a single imbibition step, the usual procedure. The data show the broad hysteresis loop. The second curve was generated by stopping imbibition several times and reversing the direction of the syringe pump until a negative capillary pressure was measured. Whenever the pump direction was reversed, irrespective of the extent to which the sample had been filled, the severe hysteresis was observed. The pressure could be reduced to below zero with almost no drainage occurring.

In order to confirm that the results presented in this work can be considered representative of the equilibrium situation a capillary pressure curve was measured at a flow rate 10 times slower than the standard one. It is shown in Fig. 6 that this large change in the



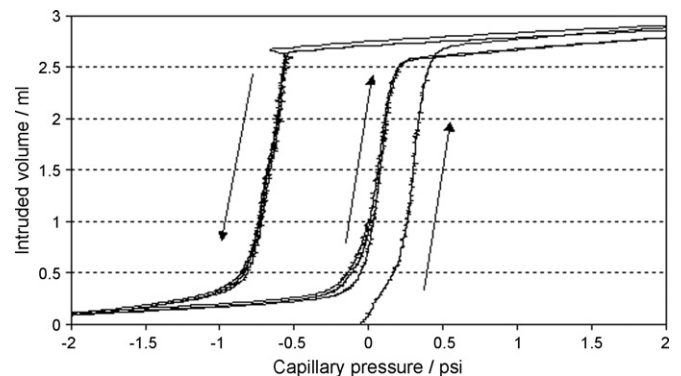
**Fig. 5.** Capillary pressure curves for TGP-H-060 10% PTFE showing that the extent of hysteresis is independent of whether the sample is filled in one step (○) or by several partial imbibition–drainage (▲) cycles.



**Fig. 6.** Capillary pressure curves for a wet-proofed carbon fibre web showing that flow rate has no effect on the results. Flow rates: 0.1 ml min<sup>-1</sup> (○) and 0.01 ml min<sup>-1</sup> (▲).

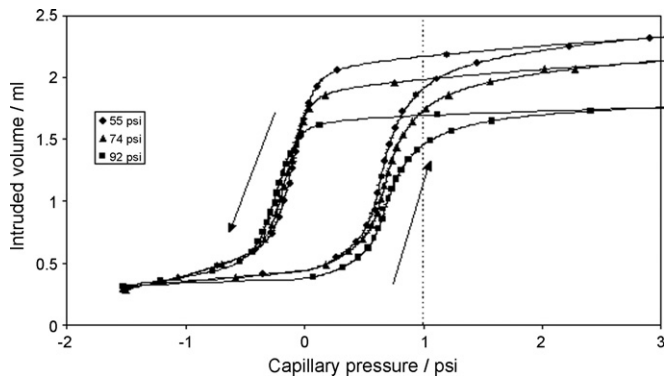
flow rate had no effect on the capillary pressure curve and therefore the faster, more convenient, rate could be used with a high level of confidence.

Fig. 7 shows a set of three imbibition–drainage cycles for a wet-proofed carbon fibre non-woven web. It can be seen that during the first imbibition cycle, which starts at the origin, imbibition occurs at a significantly higher pressure than the second or third cycles, which agree completely. This phenomenon was general: all samples showed a higher imbibition pressure for initial wetting and then displayed stable behaviour. The reduced imbibition pressure for the second and subsequent cycles is assigned to water retained within the structure facilitating wetting. This will occur through

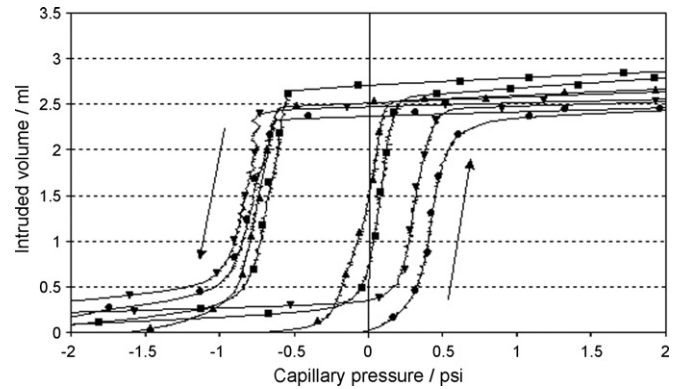


**Fig. 7.** Capillary pressure curves for a wet-proofed carbon fibre non-woven web showing the difference between the primary imbibition and subsequent imbibitions. Primary imbibition curve starts from the origin.





**Fig. 8.** Capillary pressure curves for a carbon-filled wet-proofed carbon fibre non-woven web under differing compressive loads. Data obtained consecutively for the same sample in order of increasing load: 55 psi (●), 74 psi (▲) and 92 psi (■).



**Fig. 9.** The influence of surface treatment on the capillary pressure curves for a fixed type of carbon fibre non-woven web. Solution 1 contact angle = 75° (▲), dispersion 1 contact angle = 90° (■), dispersion 2 contact angle = 103° (▼) and solution 2 contact angle = 105° (●).

two distinct mechanisms. Firstly, any bulk water held within the structure will have a contact angle of 0° with the imbibing water, thus reducing the composite contact angle of the material according to Cassie's law [20]. In addition, any wetting of the carbon surface during the primary imbibition would be reasonably expected to change the surface functionality of that carbon, and thus change its wettability.

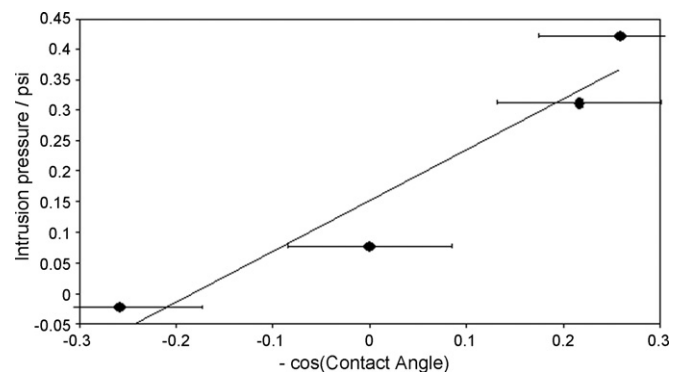
The ability of the instrument built for this work to determine the influence of GDL compression on water handling is demonstrated in Fig. 8. This shows the capillary pressure curves obtained for a single sample of carbon-filled wet-proofed carbon fibre non-woven web at three different compressive loads. The data were obtained consecutively in order of increasing compression. The most marked effect is a reduction in the water uptake. Taking the volume intruded at a capillary pressure of 2 psi to be representative of complete filling, the volumes at 74 psi and 92 psi are 92% and 77% of the volume taken up at 55 psi. The large reduction in pore space at the highest load would most likely result in poor mass transport properties in the cell. The phenomenon of mass transport limitations induced by over-compression of the GDL is well known [1]. The large reduction in the porosity of the GDL at 92 psi would necessarily result in a reduction in the effective diffusivity of oxygen through the GDL. This would be likely to lead to mass transport losses and therefore the results of Fig. 8 suggest that the GDL tested should be compressed at no more than 74 psi to avoid poor fuel cell performance. The pressures of both imbibition and drainage are also affected by the compression, although to a lesser extent than the intruded volume. The pressure of imbibition is increased and the drainage pressure reduced. The fact that both the pressures change in a correlated way is evidence that the hysteresis is induced by the sample's structure. If the negative drainage pressure were caused by hydrophilic sites being accessed in the pore space the drainage pressure would be expected to be independent of compression.

The dependence of the imbibition and drainage pressures on the surface wettability of the pore is shown in Fig. 9. An unfilled carbon fibre non-woven web was treated with four different wet-proofing agents, two solutions and two dispersions. The wettability of the surface of the wet-proofing agent was independently determined by coating a glass slide and measuring the contact angle optically using a Dynamic Adsorption Tester (DAT1100 Fibro Systems AB, Sweden). This gives the contact angle of a non-porous surface of the wet-proofing agent which, due to the contributions of surface roughness and porosity, will be very different from the composite contact angle that would be measured for the GDL itself. The dependence of the imbibition pressure on contact angle is clear, in agreement with intuition, the higher the contact angle the harder it is to force water into the structure. The Washburn equation which gives the capillary pressure,  $P_{\text{capp}}$  necessary for penetration of a

cylindrical pore by a non-wetting fluid is given by [14]

$$P_{\text{capp}} = -\frac{2\gamma \cos \theta}{R}$$

where  $\gamma$  is the fluid surface tension,  $\theta$  the contact angle and  $R$  the pore radius. This equation is often used in the literature to convert imbibition pressures to pore sizes, neglecting the influence of pore shape. Fig. 10 shows that the results are not inconsistent with this relationship. The penetration pressure, defined as the pressure at the inflection point of the imbibition curve, is plotted against  $\cos \theta$  and the dependence is, within the relatively large errors in the contact angle, linear. The non-zero intercept on the  $\cos \theta$  axis is not in agreement with the Washburn equation, however it is close to the accuracy limit of the pressure transducer and therefore may not be correct. The pore size calculated from the results using this simplified model is, however, totally wrong. Whether individual data points are used or the gradient of the  $P$  vs.  $\cos \theta$  line, the pore diameter is calculated to be 30–60  $\mu\text{m}$ , whereas SEM images show the fibre spacing to be around 100–150  $\mu\text{m}$ . This underestimation is in agreement with the effect of the non-parallel pore walls discussed earlier [16]. The additional curvature of the meniscus that the wall curvature causes, results in an increase in the pressure required for penetration, in agreement with the underestimate of pore size. This shows that pore sizes for fibrous media determined solely by porosimetry will be subject to large uncertainty and should be regarded as a measure of “effective pore size”, at best. The use of this “effective pore size” as being a good measure of the characteristic geometric pore size is misleading. The occurrence of this problem in mercury porosimetry was raised in Section 1 of this paper.



**Fig. 10.** The dependence of modal imbibition pressure on the contact angle of the surface treatment agent.

For the three higher values of contact angle, use of the formula in the work of Harriott [16] is invalid and for the lowest contact angle the penetration pressure calculated is too large. The reason for this discrepancy is presumably the fact that pore openings in a non-woven web are either quadrilateral, triangular or more complex and far from the assumed doughnut shape. The non-parallel pore walls can therefore not be used to quantitatively explain the data.

The drainage behaviour of the GDLs in Fig. 9 is not affected by the surface contact angle to the same extent. Although there is some variation between the samples it does not depend in any clear way on contact angle and is probably best assigned to sample-to-sample variation. The de-wetting of this structure is therefore not sensitive to a change in contact angle from  $75^\circ$  to  $105^\circ$ , a highly surprising result. This behaviour has, however, been repeated for other GDL materials. The drainage behaviour appears to be more a fingerprint of the structure and is independent of the surface wettability. To the author's knowledge, there is no model in the literature that would predict this, although the failure of the Washburn model has been observed previously for hydrophobic porous silicas [21].

The lack of any effect on contact angle on the dewetting is more evidence that the hysteresis is not caused by attachment to hydrophilic sites as it is highly unlikely that the number of these sites would be the same for four samples wet-proofed to such different extents, especially as the method of wet-proofing was varied significantly. Two of the treatments used aqueous dispersions of fluoropolymers into which the base web was dipped. The sample was then fired to sinter the fluoropolymer. This is the most common method of GDL wet-proofing. The other two treatments were solution-based treatments, one an aqueous solution the other in an organic solvent. For these contrasting routes to all result in the same distribution of uncoated hydrophilic sites is unlikely. The hysteresis is therefore caused by the structure of the pore space. In mercury porosimetry, structural hysteresis takes two distinct forms. Pressure hysteresis, a difference in the imbibition and drainage pressures, drainage occurring at lower pressure than imbibition, and volume hysteresis, the retention of some of the mercury within the sample at the end of a imbibition–drainage cycle [14,20]. The pressure hysteresis is generally assigned to the “ink-bottle” effect. This is the term given to the realisation that the imbibition pressure of the non-wetting fluid is governed by the size of the pore necks, whereas the drainage is governed by the (wider) pore bodies. The drainage therefore occurs at a lower pressure. The difference between the size of the pore neck and the pore body determines the width of the hysteresis loop and the Washburn equation is used to calculate the relevant size distributions. This explanation cannot, however, explain the hysteresis observed in the current work. The drainage occurs at a negative pressure and therefore would require either a negative contact angle for the pore bodies, which is highly unlikely, or a negative pore body radius, which is impossible. Again, the pore shape would appear to be playing a critical role in controlling the capillarity. The non-parallel nature of the pore walls in fibrous media has been shown to cause a “wetting fluid”, *i.e.* one with a contact angle of less than  $90^\circ$ , to not spontaneously imbibe [16,17]. The same is occurring here with air being the wetting fluid; the contact angle for the air being  $180^\circ - \theta$ . The negative pressure to remove the water is therefore not an unprecedented phenomenon.

There is also the possibility that the negative pressure is a result of the fluid phase becoming trapped in a metastable state within the pores of the medium. As a pore dewets the meniscus will shrink as it approaches the pore neck, with a contact angle of more than  $90^\circ$  this is energetically unfavourable. In mercury porosimetry in most cases this energy barrier can clearly be overcome as otherwise no mercury could leave the pores. It has been suggested that the energy required is supplied by the momentum of the draining mercury elsewhere in the structure [22]. It is possible that due to the much lower density of water this does not happen to the same extent and

the energy has to be supplied by the invading phase (air). Whilst this seems reasonable this does not explain the invariance of drainage pressure with changes in contact angle as the energy of the menisci in both the pore neck and pore body will depend on this.

The causes of the volume hysteresis, the retention of the non-wetting phase within the sample at the end of a imbibition–drainage cycle, are related to pore connectivity. For higher connectivities the percolation properties of the pores are better and less mercury is retained. The data displayed in this paper show that, as would be expected, the connectivity of the pore space in the GDLs is good. It appears that the level of water retention is higher in filled materials (*e.g.* Figs. 2 and 8) than in unfilled solely fibrous media (*e.g.* Figs. 5 and 9). The unfilled samples appear to retain almost no water, however the uncertainty in the location of the point of zero filling prevents a detailed analysis.

### 3.2. Prediction of fuel cell performance

The results and discussion of Section 3.1 make it clear that a detailed quantitative prediction of the water handling behaviour of a GDL is currently unobtainable. What is therefore required for MEA and fuel cell developers is an empirical test to distinguish between a “good” GDL and a “bad” GDL. In this context “good” and “bad” refer to the extent of water build up within the GDL during operation at high current density under well-humidified conditions.

Three GDLs were ranked in terms of their propensity to flood when used as the cathode in a direct methanol fuel cell. MEAs were made using the three GDLs with identical catalyst layers and Nafion 115 membrane. The MEAs were then tested at  $60^\circ$  and ambient pressure with 1 M methanol at an initial air flow rate of  $240 \text{ ml min}^{-1}$  for a  $50\text{-cm}^2$  active area. The air flow rate was then reduced gradually until the cathode GDL flooded and the performance dropped below 0.3 V. The initial performance was 0.51 V. GDL 3 flooded first with the performance falling to 0.3 V at  $100 \text{ ml min}^{-1}$ , followed by GDL 2 at  $95 \text{ ml min}^{-1}$  and finally GDL 1 at  $91 \text{ ml min}^{-1}$ . Fig. 11 shows the imbibition curves for three GDLs. It would therefore appear that a high modal imbibition pressure gives better resistance to flooding, the higher the modal imbibition pressure the lower the air flow rate at which the GDL can perform. Qualitatively this seems reasonable: the harder it is to force water into the structure the less likely it is to fill under operating conditions. Interestingly, whilst it is more difficult to force water into GDL 1, it is also more difficult to remove it. This is further evidence for the hysteresis being due to structural entrapment in hydrophobic pores.

A refinement of the ranking on the basis of imbibition pressure is the realisation that the water pressure present in the cell will differ for each GDL. This is because the water flux passing through the GDL is fixed by the rate of water generation in the cell, which

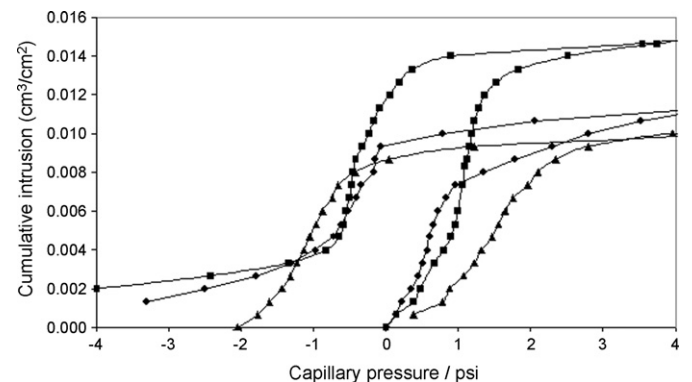
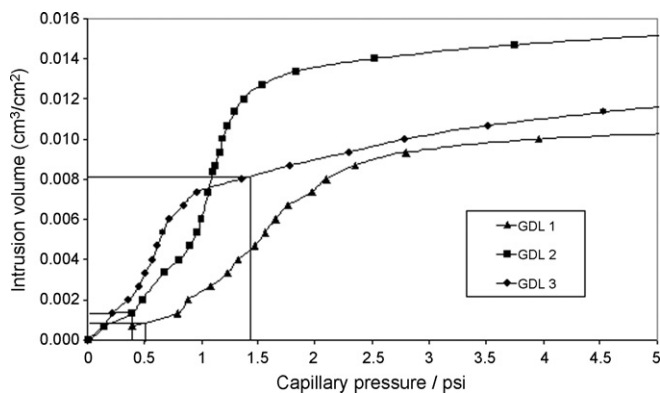
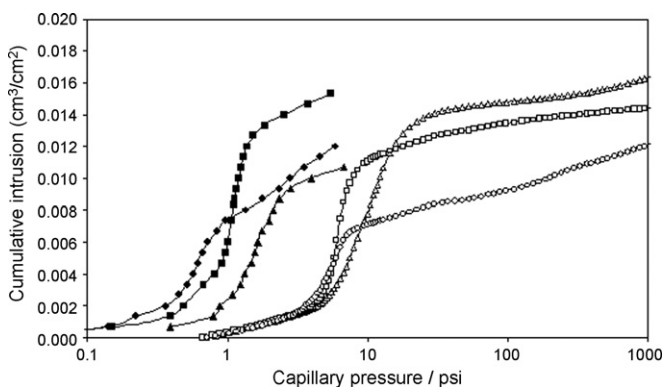


Fig. 11. Capillary pressure curves for three GDLs with differing in-cell performance. GDL 1 (▲) has good resistance to water build up, GDL 2 (■), average resistance and GDL 3 (●) poor.



**Fig. 12.** Imbibition curves for three GDLs with differing in-cell performance, the vertical lines mark the pressure required to flow a water flux equivalent to  $1.5 \text{ A cm}^{-2}$  operating current. The horizontal lines show the pore volume which would be filled under those conditions. GDL 1 ( $\blacktriangle$ ) has good resistance to water build up, GDL 2 ( $\blacksquare$ ), average resistance and GDL 3 ( $\bullet$ ) poor.



**Fig. 13.** Comparison of water and mercury porosimetry imbibition curves for three GDLs. GDL 1 ( $\blacktriangle$ , water;  $\triangle$ , mercury) has good resistance to water build up, GDL 2 ( $\blacksquare$ , water;  $\square$ , mercury), average resistance and GDL 3 ( $\bullet$ , water;  $\circ$ , mercury) poor.

is proportional to the current density. Therefore at any given current, a fixed flux must flow and the pressure required will build up in the GDL to ensure that it does. Measurements of this pressure were made for each GDL by sealing a part in a fuel cell fixture and pumping water from one flow field plate to the other. The pressure required for a current density of  $1.5 \text{ A cm}^{-2}$  are shown on the imbibition curves shown in Fig. 12. This also seems to predict the performance ranking of the GDLs correctly, in that GDL 1 would only fill a very small portion of its porosity at the required pressure, whereas GDL 3 would be almost completely full.

As discussed above the imbibition pressure is a complex convolution of the pore size, shape and fluid–surface interaction energetics, therefore a comparison of the behaviour with water and with mercury is instructive, since the pore size and shape contributions are the same for the two fluids, whilst the fluid–surface interactions will be very different. Fig. 13 shows a comparison of water porosimetry and mercury porosimetry for the same three materials. The agreement of the intruded volumes is poor, but there is sufficient similarity in the shapes of the curves to make comparison possible. The mercury imbibition pressures for GDLs 2 and 3 agree to a much greater extent than for water, which imbibes into GDL 3 significantly more easily than into GDL 2. This suggests that the affinity of water for the surface of GDL 3 is greater than that for the surface of GDL 2. For GDL 1, although the mercury results clearly show it has the smallest pores, the difference is not as marked as for the water results. This implies that the interaction of water with the surface of GDL 1 is demonstrably different to that of the other two GDLs. To put these observations on a more quantitative footing, the

Washburn equation was used to calculate a water contact angle for each GDL. This was done by accounting for the difference in surface tension between water and mercury and then varying the water contact angle to get agreement between the modal imbibition pressures for water and mercury, assuming the mercury contact angle was  $130^\circ$ . The water contact angles thus calculated are  $147^\circ$ ,  $133^\circ$  and  $117^\circ$  for GDLs 1, 2 and 3, respectively. This ranking of apparent hydrophobicity is therefore also in agreement with the in-cell performance. However, the calculated contact angles appear unrealistically high. In particular it is hard to see how even the most hydrophobic GDL has a water contact angle in excess of the mercury contact angle. As has been seen above, surface porosity, roughness and pore shape can all contribute to apparent Washburn contact angles that are higher than the intrinsic surface contact angle, but these effects will also be present in mercury. Why the apparent contact angle of water should be affected more is unclear.

Using this limited dataset of three GDLs it does appear that the capillary pressure curves measured in this work are capable of qualitatively predicting the behaviour of the GDL under operating conditions. Of the three measures used, the degree of filling at a given water flux is the most theoretically rigorous, however it appears to offer no benefit over simply ranking the materials in order of modal imbibition pressure. It appears that this is a suitable *ex situ* screening test to determine the suitability of GDLs for fuel operation under well-humidified conditions.

#### 4. Conclusions

It has been demonstrated that the apparatus described in this work is capable of determining the capillary pressure properties of gas diffusion media. The ability to control the compression of the sample is an improvement on the existing instruments.

It has been shown that water porosimetry is a more suitable technique for the characterisation of GDLs than the more conventional mercury porosimetry. Comparison of mercury and water porosimetry has shown that extrapolation from one fluid to another is not straightforward and thus to determine the water handling properties of gas diffusion media, water should be used. The use of fluids that wet the media along with extrapolation based on contact angles will also be prone to error.

The data obtained are of a form that can be directly input to fuel cell models and would reasonably be expected to give a more accurate, robust model than the existing literature based largely on correlations derived for systems with quite different porous architectures.

It has been shown that water is not spontaneously expelled from hydrophobic gas diffusion media, even at zero capillary pressure. Application of negative pressure is required to draw the water out of the structure.

Detailed measurements of the effect of surface properties on the capillary pressure have shown that the imbibition is controlled by surface contact angle and is approximately proportional to the cosine of the contact angle. The drainage of water from the gas diffusion medium is shown to be independent of surface contact angle. This cannot be explained quantitatively by any existing model or correlation, the value of directly measuring the interaction of water is therefore demonstrated.

It is demonstrated that the capillary pressure curve of a gas diffusion medium can be used empirically to predict the likelihood that the gas diffusion medium would cause flooding in an operating fuel cell.

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