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Flow properties of an intact MPL from nano-tomography and pore network modelling

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Abstract

Adding a hydrophobic micro-porous layer (MPL) between a gas diffusion layer (GDL) and a catalyst layer (CL) at the cathode of a PEM fuel cell was found capable of improving cell performance. However, how an MPL does this is not well-understood because current techniques are limited in measuring, observing and simulating multiphase pore fluid flow across the full range of pores that vary to a great extent in geometry, topology, surface morphology. In this work, we focused our investigation on estimating flow properties of an MPL volume to assess the limiting effect of strongly hydrophobic sub-micron pores on water transports. We adopted a nano-tomography and pore network flow modelling approach. A pore-structure model, purposely reconstructed from an intact MPL sample using Focused Ion Beam milling and Scanning Electron Microscope (FIB/SEM) previously, was used to extract a realistic pore network. A two-phase pore network flow model, developed recently for simulating the flow of gas, liquid or their mixture in both micrometre and nanometre pores, was applied to the pore network. We firstly tested the validity of the constructed pore network, and then calculated the properties: permeability for both water and selected gases, water entry pressure, and relative permeability. Knudsen diffusion was taken into consideration in calculations when appropriate. Our calculations showed that the water permeability was three orders of magnitude smaller than experimentally measured results reported in the literature, and when the water contact angle increased from 95° to 150° , the water-entry pressure increased from 2.5 MPa to 28 MPa. Thus our results revealed that for a strongly hydrophobic MPL that contains nanometre pores only it would behave like a buffer to water, and therefore the structural preferential paths in an MPL, such as cracks, are likely to be responsible for significant liquid water transport from the CL to the GDL that has been observed experimentally recently. We highlighted the needs for multi-scale modelling of the interplays of liquid water and gas transfer in MPLs that contain variable pores.

Key words: PEM fuel cells; micro-porous layer; FIB/SEM tomography; pore network flow modelling; liquid water flow.

54 **1. Introduction**

55 The polymer exchange membrane (PEM) fuel cell has been touted as a promising alternative to
56 combustion engine due to its high efficiency, low emission and sustainable availability of hydrogen.
57 Since the PEM fuel cell operates at a low temperature, the water vapour it produces at the cathode
58 could condense when working at high current density. Managing the condensed water is hence a
59 critical issue. On the one hand, the electrolyte membrane needs to be hydrated in order to facilitate
60 proton movement, and this is commonly done by humidifying the hydrogen at the anode. On the
61 other hand, the condensed water at the cathode needs to be removed from the cell to avoid flooding.
62 Humidifying hydrogen at the anode and removing water from the cathode are self-defeating, and an
63 improved design is hence required to effectively manage the water [1].

64 Recent research found that adding a micro-porous layer (MPL) between a gas diffusion layer
65 (GDL) and a catalyst layer (CL) at the cathode can enhance fuel cell performance [2, 3] because of
66 the improvement in water management. The MPL is highly hydrophobic and functions as a
67 capillary barrier, forcing the condensed water in the CL to build up a sufficiently high pressure
68 before it can move into it [4]. On the other hand, the CL is less hydrophobic than the MPL and the
69 increased pressure in it can drive the water moving backwards into the membrane so as to keep it
70 hydrated [5]. Apart from improving water management, the MPL also increases the CL and GDL
71 contact and reduces the damage caused to the CL by the clamping force applied to the fuel cell
72 assembly. However, the MPL has some detrimental impacts: 1) it makes oxygen difficult to move
73 into the CL because it is less permeable than the GDL; and 2) the increased water pressure in the
74 CL could block the pathways of gaseous oxygen. These conflicting effects reveal that the MPL
75 needs to be optimally designed [6], and this, in turn, calls for a better understanding how different
76 pores in an MPL influence fluid transports.

77 Markedly different pore systems may be formed in MPLs depending on methods used to
78 fabricate them and to assemble them into fuel cells. Fabrication methods may differ in the selection

79 of forming agents and their composition, MPL forming process (e.g. composites mixing, drying and
80 sintering) and techniques for applying an MPL to a GDL (see [7-9] and references therein). Both
81 imaging and laboratory measuring techniques have been used to characterise the pore systems of
82 MPLs and results reported in the literature suggest that an MPL contains three classes of pores:
83 pores at nanometre scales, pores at micrometre scales and cracks, while their proportion can vary
84 from one MPL to another greatly [7, 10, 11]. SEM images of MPLs, which are commonly
85 fabricated using carbon black and polytetrafluoroethylene (PTFE), show that they typically contain
86 a larger number of nanometre pores than micrometre pores, and cracks of variable apertures up to
87 tens of microns [11-13]. The fabrication can induce cracks whose geometrical characters and spatial
88 patterns may be influenced by many factors including the hydrophobicity and thickness of an MPL
89 and drying and sintering conditions [14]. For other MPLs fabricated from carbon black and
90 poly(vinylidene fluoride) (PVDF) for example, they may contain much more micrometre pores than
91 their PTFE counterparts do but none or very few of cracks [7]. Besides those formed during
92 fabrication, cracks are known to be induced during the assembly of fuel cell components under
93 mechanical loads and operations of wet-dry cycles [15, 16].

94 Over the past few years, advances in imaging technology such as X-ray computed tomography
95 (XCT) and FIB/SEM enable one to visualise the interior structures of a GDL, an MPL, a CL or an
96 assembly of them at a resolution ranging from a few tens of microns down to a few tens of
97 nanometres [17-19]. Therefore these techniques allow one to characterise MPL pore geometry,
98 topology and surface morphology quantitatively and to develop pore-space models on which to
99 simulate multi-phase flow and to estimate flow properties. Because MPL pores are diverse in size
100 and shape, and every imaging technique has a limited field view, it is not possible to obtain ‘a
101 representative element pore volume’ of the sample by any technique alone. For example, FIB/SEM
102 and nano-XCT are ideal for imaging MPL nanometre pores on a small sample of a few tens of
103 microns in dimension [20]. On the other hand, a micro-XCT is ideal for imaging a larger volume of

104 a fuel cell assembly up to a few centimetres in dimension at a resolution adequate for revealing
105 micrometre pores and cracks [17, 18].

106 In conjunction with imaging-based pore characterisation, X-ray and neutron radiography
107 imaging techniques have been used to observe multiphase fluid displacements in a single or
108 multiple fuel cell units to examine qualitatively gas and liquid water transports [10, 21, 22]. Due to
109 their limiting spatial resolutions, these techniques have been exploited to the most effective for
110 visualising water movement in large pores or along cracks and the build-up of water saturation
111 along an MPL. Using soft X-ray radiography, Deevanhxay et al. [10, 23] observed water movement
112 preferential along cracks of an MPL and concluded that the MPL plays a crucial role in water
113 management.

114 Many laboratory tests have been designed to characterise pore structures and transport
115 properties of individual fuel cell components or an assembly of them. By measuring injection
116 pressure and injected fluid volume, a gas or mercury intrusion test on a unit can measure the pore
117 volume, surface area, size distribution and connectivity as well as capillary pressure of it [11].
118 Multi-phase flow experiments may be extended to measure liquid and gas permeability and the
119 relative permeability of gas and liquid for MPLs [24, 25]. These tests have their limitations too.
120 Fluid intrusion tests are often insufficient to discriminate normal pores from cracks. In flow
121 experiments, the permeability and relative permeability characterise the overall flow of a measured
122 sample but cannot be attributed to different types of pores. Consequently, the experimental results
123 have limited use for designing optimal MPLs. It should be noted that all laboratory tests are difficult
124 to apply to an individual MPL because it is too small. As a result, the effect of an MPL has to be
125 inferred from multiple tests carried out on samples with and without it.

126 Numerical modelling techniques have been developed and applied to study fluid flow
127 behaviours in MPLs and GDLs. Pasaogullari and Wang [26] developed a multi-phase mixture
128 model. Unlike other continuum models based on the unsaturated flow theory, their model considers

129 the gas-phase flow countering capillarity-induced liquid water motion, and, therefore, enables those
130 authors to elucidate the effects of porosity, thickness and wettability of an MPL on the two-phase
131 flow more appropriately. They found that the optimal thickness of an MPL is 30 to 45 microns for
132 water management. However, the validity of the continuum models is questionable. Rebai and Prat
133 [27] argued that even a GDL is too small to be considered as a representative elementary volume
134 (REV) and showed that the two-phase flow properties become size-dependent rather than size-
135 independent that would be expected for a REV and also assumed in the continuum models. They
136 concluded that pore-scale modelling, in particular pore-network flow modelling, is the most
137 appropriate approach.

138 In conjunction with image-based pore characterisation and the pore-scale reconstruction of
139 MPL volumes, some recent work adopted pore-scale flow models to estimate fluid flow properties.
140 Ostadi et al. [17] reconstructed a model from a small intact MPL volume using FIB/SEM, and they
141 then estimated its phase volume fractions, pore connectivity, tortuosity and pore size distribution,
142 and calculated its fluid flow properties including the diffusivity coefficient and permeability. Wargo
143 et al. [18] took a similar approach and reconstructed models for an intact MPL volume to, in
144 addition, characterise capillary pressure–saturation relationship; it shows that a strongly
145 hydrophobic MPL forms a good capillary barrier to water. Both groups estimated permeability
146 values for their respective MPL models using a lattice Boltzmann method and their results are in a
147 good agreement with each other. As a lattice Boltzmann method is applied to a voxel-based binary
148 image model directly, it can account for the full geometric complicity of that model. However, two-
149 phase simulation on a binary image is not only much more time consuming than a single-phase
150 simulation but also prone to numerical instability for high-density contrasted phases like gas and
151 liquid water. Although latest modifications have improved the stability of the two-phase lattice
152 Boltzmann models, they require time-consuming calculations of second-order derivatives [28, 29].

153 In addition, the standard lattice Boltzmann models could not account for the Knudsen diffusion
154 appropriately in small pores [30].

155 Pore network flow modelling is another approach to study the multiphase fluid flow at the pore
156 scales. There the pore space is simplified into connected network of node and bond elements on
157 which multiphase flow can be simulated efficiently. High contrasts in fluid density and viscosity do
158 not cause numerical stability while the slip flow and Knudsen diffusion can be modelled too. This
159 approach has been applied to study gas and water flow in PEM fuel cell, where void space is
160 simplified as spherical or cubic pores connected by cylinders with circular or rectangular cross-
161 sections on a regular lattice [31, 32] and to model the interactions of complex coupled processes
162 [33]. On the other hand, this approach underwent a substantial development over past two decades
163 in the fields of soil sciences and petroleum engineering. In recent years, the techniques have been
164 developed for extracting a pore network from a 3D binary image [34] and simulating multiphase
165 displacements on that network efficiently [35]. One of the emphases of the recent improvements has
166 been to capture the effect of complex geometry and topology of pore structures on multi-phase fluid
167 flow processes. This approach has been shown to be predictive in estimating multi-phase flow
168 properties when applied to natural soil and carbonate rocks, and can therefore be used to gain
169 accurate predictions of fluid flow properties for MPLs.

170 It is, however, difficult to quantify fluid flow of an MPL sample using any type of the
171 techniques alone if its pore structure is composed of multi-scale pores varying greatly in space. For
172 example, cracks have been postulated to offer preferential pathways for water, but laboratory tests
173 have not been able to confirm this unambiguously and to explain the precise mechanisms that an
174 MPL improves the cell performance. Imaging-based experimental observations may reveal the
175 existence of crack networks in an MPL and liquid water flowing through its cracks into a GDL, but
176 are insufficient to explain the emergent water saturations away from cracks [10]. Therefore, a better
177 understanding of the role of MPLs in water management may be gained by pore network modelling

178 to quantify the contributions of different pore types (e.g. nanometre, micrometre or crack pores) to
179 gas and water transports, respectively and collaboratively.

180 This paper reports a pore network modelling study of an intact MPL to estimate the likely
181 contribution of nanometre pores alone to gas and water transports. It is organised as follows.
182 Section 2 describes the methodology this work took, namely FIB/SEM imaging, pore-network
183 construction and a pore-network flow modelling. Section 3 presents the results and analyses,
184 followed by a section of discussion and remarks. It argues that MPL cracks contribute mainly to the
185 water flow if an MPL contains cracks and pre-dominantly nano-scale pores and that it is important
186 to take a multi-scale approach when coming to model fluid flow interactions within an MPL that
187 contains cracks, micrometre and nanometre pores. Section 5 concludes this work.

188 **2. Methodology**

189 **2.1 FIB/SEM imaging**

190 The details of the FIB/SEM tomography used to acquire the microstructure of an MPL were
191 given in our previous work [17]. We briefly describe it below for completeness.

192 A thin slice of approximately 14 nanometres wide on the side-wall of a trench inside an MPL
193 (provided by Johnson Matthey Fuel Cells Ltd., UK) was milled away using FIM (Ca^+) first. The
194 exposed structure was then captured using SEM. Repeating this procedure produced a number of
195 2D slices. To protect the soft surface of the MPL from ion bombardment and pollution caused by
196 FIB-induced re-decomposition of the precursor gases, the surface was coated by 100 nm-thick layer
197 of platinum prior to the side-wall milling. Each 2D image was processed by choosing a threshold to
198 digitize it into a binary image with 0 for pore and 1 for solid. A procedure was employed to ensure
199 the segmentation of pores and solids as accurate as possible. Stacking all these binary 2D images
200 yields a 3D structure as shown in Figure 1.

201 For this sample, all pores are well-resolved by FIB/SEM at the acquisition resolution. In fact
202 the pores are over-resolved as pore diameters are greater than 9nm and 18nm for more than 99.99%

203 and 99.8% of all pores. For the purpose of reconstructing an image-based model with as many as
204 cubic voxels in each direction, which is needed for accurately estimating pore geometry for a pore
205 network, we re-sampled the segmented image at the voxel resolution of 8nm in all 3 directions.
206 From that re-sampled image, a volume of 149^3 voxels was obtained and used in this work.

207 To ensure the selected volume large enough to be representative, we examined the variability
208 of the porosity across sub-volumes. We randomly drew over 100 unique cubic sub-volumes at
209 dimensions, ranging from 30 to 140 voxels with multiple volumes for each dimension. For each
210 volume we calculated its porosity. The mean of the porosity values at each selected dimension is
211 plotted against the dimension with one standard deviation being drawn as errors around the mean as
212 shown in Figure 3. The figure shows that when the dimension increases above 100 voxels the mean
213 porosity converges to that of the full volume (just below 34%) with a fast decreasing error. It can
214 also be shown that when the dimension is greater than 120, the relative difference of the mean
215 porosity is smaller than 2%. Based on these results, we consider the selected volume to be large
216 enough and representative.

217 **2.2 Pore network extraction and pore network flow modelling**

218 A set of techniques developed by Jiang et al [34] was applied to extract a pore network from
219 the selected volume. Here a Euclidean distance map for every pore voxel is calculated first,
220 followed by a medial axial transformation to identify the skeletons of the pore space; then both the
221 distance map and the skeletons are used to partition pore space into node space, while the remaining
222 pore space, between each pair of nodes, into bond space; geometrical properties are calculated for
223 every node and bond, including volume, hydraulic radius and shape factor. A shape factor is defined
224 as the ratio of the area and the squared perimeter of the cross-section for an element; it indicates that
225 an element has a cross-section that resembles a triangle, rectangle or circle, if it falls between (0,
226 0.048], (0.048, 0.062] or (0.062, 0.08], respectively. For a more detailed discussion of the
227 construction of a pore network from a 3D binary image, the reader is referred to Appendix A for the

228 a brief description of the extraction procedure and the original publication [34] for a full description.
 229 In this work the pore network was extracted using an in-house software package that implements
 230 those techniques.

231 A pore network constructed as such makes it possible to simulate multiphase fluid flow
 232 efficiently and to capture critical phase displacement behaviours in geometrically and topologically
 233 complex pores. It has been shown that a pore network model can predict the relative permeability of
 234 oil and water for reservoir rocks [35, 36]. In this work, single and two phase fluid flows were
 235 simulated on the extracted pore network using a pore network flow model, extended from the two-
 236 phase pore network flow model of Valvatne and Blunt [36]. The key extensions were made
 237 primarily in calculating the gas-phase conductance in order to deal with slip flow and Knudsen
 238 diffusion as they affect both single- and two-phase flows and, therefore, apparent gas permeability
 239 and relative permeability. Those extensions have been discussed in details in a separate publication
 240 [37] and summarised briefly here. The gas conductance for each network element is defined by
 241 Equation (1) to account for the effects of the slip flow and the Knudsen diffusion in the second and
 242 third terms inside the bracket, respectively. The equation was developed for the element with a
 243 circular cross-section first and then adapted for an element with a non-circular cross-section through
 244 a correction factor C_g . The non-ideal gas effect was expressed using van der Waals's two-parameter
 245 principle of corresponding states in coefficient terms NIG#. Because the gas conductance is
 246 pressure-dependent and the gas pressure equations are no longer linear, an iterative solution
 247 procedure was developed. For a brief explanation of nomenclature in the equation, see Appendix B.
 248 The reader is referred to the original publication for details.

$$249 \quad C_{NIG} = \frac{C_g R_h^2 \rho_2}{\mu_2} \left\{ \frac{\mu_2}{\mu_0} NIG_c + \frac{\mu_2}{\mu_2^{ig}} \frac{8}{3} \left(\frac{2-\alpha}{\alpha} \right) k_{n,2h} + \frac{\mu_2}{\mu_2^{ig}} \frac{64}{9C_g \pi} NIG_k k_{n,2h} \right\} A \quad (1)$$

250 The same phase displacement rules as given in [36] remain. Therefore, the extended model can
 251 simulate capillary-dominated flow with insignificant viscous pressure drops across the model. The

252 order of capillary domination is defined by the capillary number, the ratio between viscous to
 253 capillary forces, and should be around 10^{-4} or less. Under this condition, the phase interfaces
 254 through a connected pore network can be considered to be static and the phase displacement is
 255 defined a sequence of ordered events determined by the capillary pressure. The capillary pressure of
 256 an element, p_c , was calculated from the Young-Laplace equation, $p_c = p_w - p_a = \sigma(1/r_1 + 1/r_2)$,
 257 where p_a and p_w are the air and water pressures, respectively, σ is the water-air interfacial tension,
 258 and r_1 and r_2 are the principal radii of the curvature of water-air interface in the element if it is
 259 invaded by the water. For an element with a circular cross section, its capillary pressure is
 260 $p_c = 2\sigma \cos(\theta)/r$, where r is the radius of the cross section of the element while θ is the contact
 261 angle of the wetting phase measured from the solid to the fluid interface. For each element with a
 262 triangular, rectangular or circular cross-section, its capillary pressure can be determined analytically
 263 (see [36] and the references therein).

264 Note that equation (1) was applied to gas and liquid two-phase flow where the wetting gas
 265 occupies the corners of a pore element, or as gas film, and connects throughout pore volumes from
 266 the inlet to the outlet. Note that gas can be present in corners only when the contact angle is
 267 sufficiently high, and this condition was assumed to hold in this work because only strongly
 268 hydrophobic pores are of concern. When the liquid occupies the centre of an element, each corner
 269 was considered as an independent element with a variable volume that can be empirically
 270 determined [38]. Because each of the corner volumes is smaller than the host whole volume of the
 271 host element, the total Knudsen diffusion effect for that element is expected to be stronger in two-
 272 phase than single-phase cases. In summary, the extended pore network flow model can simulate
 273 single-phase flow of the water or a non-ideal gas, and the two-phase flow for the non-wetting water
 274 phase displacing the wetting gas phase in gas filled pores. The gas slip flow at pore surface and
 275 Knudsen diffusion in pores are taken into consideration when appropriate.

276 In this work, we simulated single-phase flow for water and three individual gases and two-
277 phase displacement of the air by the water on the extracted pore network. In the single-phase
278 simulations, we first simulated water flow under a pressure gradient in which only the continuum
279 flow was considered and then calculated the water permeability. To show the impact of the
280 Knudsen diffusion on the permeability for different gases, we simulated the gas flow, under applied
281 pressure gradients from 50kPa/m to 350kPa/m with the outlet pressure being fixed at 100kPa, and
282 then calculated the apparent gas permeability for oxygen, helium and hydrogen, respectively. The
283 gas pressures were chosen to be similar to the experimental settings used by Pant et al [24].

284 In the two-phase simulation, the MPL was initially dry and filled with the air. Then the liquid
285 water was driven into the MPL by a pressure imposed at the inlet. The water percolated through a
286 gas filled element from its centre quasi-statically. When the pressure is increased incrementally, the
287 saturation and capillary pressure relationship can be determined. Because of the contrasting density
288 of the air and the water, the impact of air-water friction on water flow was neglected in the
289 simulations.

290 In both single- and two-phase simulations, we considered the Knudsen diffusion effect for any
291 pore whose Knudsen number is greater than 0.1, and set parameter α in Equation (1) to be 1.0 to
292 control gas slippage at pore walls (see comments on choosing values for this parameter in [37]).

293 **3. Result analysis**

294 Figure 2 shows the partitioning of the pore space. Figure 4 shows the distribution of the
295 calculated shape factors for all elements in the extracted pore network. The pore network have 1317
296 pores and 3222 throats, in which 2028 are triangular throats, 1064 rectangular throats and 71
297 cylindrical throats. Note that to simplify the calculation of the capillary pressure for elements with
298 irregular cross-sections, we follow the same approximation convention as in [36]; that is, in all
299 simulations we treated every element as to have equilateral triangular, square or circular cross-
300 section if its shape factor falls between (0, 0.048], (0.048, 0.062] or (0.062, 0.08], respectively. To

301 validate representativeness of this network and the simplification above, we calculated the water
302 permeability in all three directions on the extracted network, and then compared them with the
303 permeability calculated on the corresponding volume of the binary image using the lattice
304 Boltzmann model we developed and validated previously [39, 40]. The comparison is shown in
305 Table 1. The results agree well, indicating that the extracted pore network is accurate enough to
306 hydraulically represent the pore geometry in the MPL.

307 The MPL is highly hydrophobic with a water contact angle higher than 100° [41]. As a result,
308 the water can only enter the MPL from the CL after building up a water pressure so that the
309 pressure difference between the water and air pressures ΔP , i.e. capillary pressure, exceeds the
310 water-entry pressure at each pore. The value of the water-entry pressure depends on the geometry of
311 each pore and its hydrophobicity, which is represented by the water contact angle [41]. The change
312 of the water-entry pressure with the water contact angle is shown in Figure 5. When the contact
313 angle changes from 95° to 150° , the associated water-entry pressure increases from 2.8 MPa to 28
314 MPa. The increase of the water-entry pressure with the water contact angle θ can be fitted to
315 $\Delta P = A \cos \theta$ with $A=32.5\text{MPa}$, which may be regarded as the formula for an effective cylindrical
316 capillary tube.

317 Figure 6 shows the dependence of the water saturation and the capillary pressure for contact
318 angles of 130° and 150° for water, respectively. The accordant curves suggested that for this model
319 there is little noticeable change to both node and bond filling orders at such high contact angles.
320 Therefore, the results simulated from one contact angle can be used to predict the results for other
321 contact angles. Note that the accordance of curves is not expected in general as the order of the
322 filling events for each node cannot be pre-determined and depends on the fluid configurations of all
323 connected bonds (see [36] and references therein). Figure 7 shows the relative permeability for the
324 liquid water versus the capillary pressure where the curve for the contact angle of 130° was
325 calculated from the network model in comparison with the predicted from the capillary data

326 simulated for the contact angle of 150° . Because of the impact of the Knudsen diffusion, the
327 summation of the relative permeability for the air and liquid water is not unity.

328 Form the results above, it is clear that nanometre pores in the non-cracked MPL are capillary
329 barriers to the water but paths to gaseous oxygen in which the Knudsen diffusion is significant [42].
330 Similar to the experimental work of Pant et al [24], we simulated the movement of oxygen,
331 hydrogen and helium in the extracted pore network and calculated the apparent gas permeability for
332 them. Table 2 shows the apparent gas permeability for the three gases as well as their Knudsen
333 diffusion coefficients calculated at the same temperature of 299°K . The mean-free-path between
334 two consecutive collisions for oxygen, helium and hydrogen are $3.61 \times 10^{-10}(\text{m})$, $2.18 \times 10^{-10}(\text{m})$ and
335 $2.74 \times 10^{-10}(\text{m})$, respectively. Because the Knudsen number changes with the molecular properties
336 of the gas, the associated apparent gas permeability increases with a decrease in molecular weight
337 as expected. The oxygen permeability is nine times of the water permeability.

338 **4. Discussion and Remarks**

339 The calculated permeability for the liquid water in the MPL without cracks is in the order of
340 10^{-17} m^2 , smaller than the permeability reported in Pant et al [24], which was in the order of 10^{-13}
341 m^2 , for their MPL which was also made from black carbon and PTFE. Their MPL permeability was
342 measured indirectly by comparing the permeability of two GDLs with and without an MPL. The
343 permeability of GDLs reported in the literature is in the order of 10^{-11} m^2 , and the GDL
344 permeability measured by Pant et al. was also in this range. It is well-known that for a cylindrical
345 pore throat with a radius of r its permeability is proportional to r^2 . Pant et al. did not present the
346 pore sizes of their MPL, but from their estimated Knudsen numbers for their GDL and MPL, it can
347 be estimated that the average pore size in their MPL should be three orders of magnitude smaller
348 than that in the GDL; these were also consistent with the MPL we investigated in this paper and the
349 GDL we studied previously [43, 44]. The average pore size in our GDL and MPL were 13 microns
350 and 30 nanometres, respectively, and the permeability of the GDL in both in-plane and through-

plane directions is in the order of 10^{-11} m^2 . Given the effect of the Knudsen diffusion on the liquid water being negligible, the permeability of the MPL for the liquid water should be in the order of 10^{-17} m^2 rather than 10^{-13} m^2 as reported in Pant et al.. One reason for such a large discrepancy is that the MPL permeability measured by Pant et al. could be for a gas, and the associated Knudsen numbers were approximately 2. In this case, the gas permeability is not a constant but depends on the gas pressure and Knudsen number, and it is higher than the liquid water permeability. However, the difference in the Knudsen number for the water and gases alone still cannot explain that large difference in their permeability. The most likely reason is that there might be cracks in the MPL used by Pant et al. As mentioned previously crack development is a common phenomenon in MPLs. Martinez-Rodriguez et al. [13] showed that the aperture of the cracks was in the range of 4.4 to 32 microns estimated on the SEM images of MPLs. Furthermore, the density and aperture of the cracks appear to increase as the hydrophobicity increases [14]. In a hydrophobic media, big pores have less water-entry pressure and are much easier for the water to move through. The cracks hence provide preferential pathways for the liquid water to flow and substantially increase the permeability of MPLs. The impact of a set of cracks on the permeability of a low-permeability intact MPL can easily be illustrated analytically. For an MPL let the area-fraction of cracks be ε and the area-fraction of the remaining non-cracked be $(1 - \varepsilon)$. When a fluid flows in the through-plane direction in a saturated matrix, there is little interference between the fluid in different cracks and the fluid in the MPL nanometre pores. Hence the averaged absolute permeability of a cracked MPL in the through-plane direction, k , consists of a permeability for cracks, k_{crack} , and a permeability for nano-scale pores, k_{MPL} , that is, $k = \varepsilon k_{crack} + (1 - \varepsilon) k_{MPL}$. For the simplicity of this analysis, we assume that the aperture of all cracks is h , and therefore the permeability of a single crack is $h^2 / 12$. Take the low bound of crack apertures reported in Martinez-Rodriguez, which was 4.5 microns, and the permeability of a cracked MPL is $k = 1.7 \times 10^{-12} \varepsilon + (1 - \varepsilon) k_{MPL} (\text{m}^2)$. So even with 1% of the MPL area being cracked, its contribution to the MPL permeability is in the order of 10^{-13} m^2 , much higher

376 than the permeability of the nanometre pores in the MPL, which is in order of 10^{-17} m^2 . Taking the
377 cracks into account could bring our results in consistency with the measurement of Pant et al. [24].
378 This reveals that the cracks developed in the strongly hydrophobic MPL would be the dominant
379 pathways for the liquid water from the CL to the GDL, and the water fingering in the GDL
380 observed in [45] is likely to be related to the cracks.

381 Figure 8 illustrates the possible water movement induced by the hydrophobic MPL. The MPL
382 functions as a barrier to the water and the water condensed in the CL underneath the non-cracked
383 MPL builds up a pressure first. Instead of pushing the water into the MPL, this increased pressure
384 forces water moving backwards into the membrane as the CL is less hydrophobic; in the meantime,
385 it also pushes the condensed water flowing laterally along the MPL-CL interface into the adjacent
386 cracks, through which it migrates into the GDL. The nanometre pores in the MPL play only a minor
387 role in the liquid water flow, but are the main pathways for oxygen to diffuse from the GDL to the
388 CL. This is consistent with recent experimental observations that liquid water indeed moves through
389 the cracks in the MPL rather than the nanometre pores [10, 46]. This implies that although the
390 cracks might accelerate MPL degradation, they appear to be beneficial to the water management.

391 Given the importance of pore structures and surface properties of an MPL on controlling gas
392 and water flow behaviours, and the performance and durability of a PEM fuel cell, such
393 relationships need to be better understood quantitatively than have ever been in order to improve the
394 design of MPLs for better water management. As pointed out in a previous section, the size-
395 dependent pore distribution in an MPL excludes scale and resolution limited techniques for
396 investigating pore scale fluid transport directly. It is envisaged that multi-scale numerical modelling
397 has a great potential to address ‘what-if’ questions concerning the water management in a cost-
398 efficient manner. We, therefore, make the following remarks on developing multi-scale numerical
399 models.

400 **Remark 1: modelling multi-modal flow behaviours**

401 Hydrophobic MPL pore systems may lead to bi-/tri-modal fluid flow behaviours balanced by
402 viscous, capillary and gravity forces at different locations in time. Water mainly flows preferably
403 through wide cracks. This may be driven mainly by the viscous force when the water pressure is
404 above the capillary entry pressure and the pressure gradient is not negligible. The gas flows
405 preferably in nanometre pores as their strong hydrophobicity and small diameters make it difficult
406 for the water to overcome the capillary entry pressure if the water can be removed through the
407 cracks. The water and gas flow behaviours could be more complex in micrometre pores as the water
408 and gas may flow through them simultaneously, and the fractions of both phases may be equally
409 significant at places in time. Micrometre pores, if connected to cracks, may function as a tributary;
410 during water pressure build-up the water may be driven into those pores, pushing the gas back and
411 aside, while during water pressure draw-down, the gas may be imbibed into those water-filled pores,
412 along gas boundary layer, pushing back invading water or even ‘swelling’ at narrower throats to
413 snip off and trap the water phase.

414 Numerical modelling work on MPLs reported in the literature, however, ignores the complex
415 nature of multi-phase fluid dynamics, instead, deals with one aspect of the dynamics at a time, and
416 therefore neglects important multi-modal flow interactions. Because of aforementioned difficulties
417 in capturing diverse pore structures of an MPL sample, this problem is unlikely to be addressed by
418 any technique in use alone. Nevertheless, multi-scale imaging may offer a way to reconstruct a
419 multi-scale model of an MPL sample on which coupled crack flow, and micrometre and nanometre
420 pores network flow would be appropriate and may be modelled using similar techniques [47-49].
421 Note that quasi-static pore-network models may not be sufficient to capture fluid dynamics when
422 the viscous force is not negligible. In this case dynamic pore network models would be required
423 (see [50, 51]).

424 **Remark 2: multi-scale reconstruction of MPL pore structure**

Multi-scale imaging can be taken at selected sampling points at different resolutions to aid the reconstruction of an MPL. For example, one can use SEM to capture pore features on the surface of an MPL including cracks and large micro-pores and FIB/SEM, nano-XCT and micro-XCT to capture nanometre and micrometre pores. By registering multi-scale images together, aided by stochastic modelling to fill missing data, one could in principle generate a range of high-resolution models that capture a full range of pore types, sizes and distributions for an MPL [52]. When crack patterns can be treated as global features independently from local micro-/nano-scale pore structures and crack surface structures, we can extract pore networks from local volumes that do not contain cracks and populated over the non-cracked regions in a crack-pattern model.

For cracks that occur during drying and sintering processes of the MPL fabrication, the formations of crack patterns may depend on many factors as mentioned in a previous section. However, those patterns, in terms of crack intersecting angles and the area of partitioning, may closely resemble those of soils which undergo constrained desiccation. Therefore, it would be possible to model crack patterns stochastically as for soils [53]. An integrated pore network and crack model will enable investigations into the effects of crack patterns and composition of different pores on gas and water transports.

5. Conclusions

This paper presented a method to calculate fluid flow properties of an intact MPL. A three-dimensional microstructure of the MPL was acquired using the FIB/SEM tomography and the pore network was then extracted from a volume of 149^3 voxels from a segmented image after being re-sampled at a resolution of 8nm in voxel dimension. Water permeability values, which were calculated from the extracted pore network using our pore network flow model and from the corresponding volume of the binary image using our lattice Boltzmann model, respectively, are shown to be in a good agreement, and this suggests that the extracted pore network is accurate

449 enough to represent the MPL. We then calculated other flow properties on the extracted pore
450 network.

451 The calculated absolute permeability for the liquid water is several orders of magnitude smaller
452 than that reported in the literature. Further analysis indicated that such a discrepancy is likely due to
453 the cracks developed in the MPL, as observed by many researchers. Such cracks did not appear in
454 the volume of our MPL sample. Primary calculation shows that with only 1% of an MPL being
455 cracked, its permeability could increase by two to five orders of magnitude, depending on the crack
456 apertures. Given that the water entry pressure into the nanometre pores in the MPL is in the order of
457 10MPa, it is very likely that the crack networks developed in an MPL are the dominant pathways
458 for the liquid water to move from the CL to the GDL, and the nanometre pores in the MPL the
459 pathways for oxygen diffusion from the GDL to the CL.

460 There has been an exponential growth in research on PEM fuel cells over the past decade. Most
461 physical and electrochemical processes occurring in the cells are difficult to measure, and numerical
462 modelling is therefore expected to play an important role in fuel cell design [54]. Success of these
463 numerical models, however, relies on a detailed characterisation of the multi-scale MPL pore
464 system and an accurate description of each and all of important fluid flow processes. Since most
465 components in the PEM fuel cells are opaque and only a few microns in size, experimentally
466 identifying mechanisms that control each transport process is difficult. The development in
467 tomography and pore-scale modelling has potential to bridge this gap as they have become
468 increasingly accessible and more accurate. This work is an attempt to use these technologies to
469 improve our understanding how an MPL may improve the water management in a PEM fuel cell,
470 and to suggest ways of modelling the multi-modal fluid flow effects in an MPL using an integrated
471 pore network and crack-pattern model.

472 **Appendix A: Key facts on the construction of pore network from a 3D binary image**

473 The pore network extraction procedure:

1. Compute a Euclidean distance map for every pore voxel to its nearest solid voxel where this distance is the radius of the maximal inscribed ball centred at that pore voxel;
2. Transform the pore space into the medial axis (skeleton) by an improved thinning algorithm to ensure that: a) the skeleton is topology-preserving; b) the skeleton is central-located; and c) the skeleton is geometrically equivalent to the original pore space. Note that the geometrical equivalence means the major geometry and shape of the original pore space can be recovered from the skeleton by allocating a maximal ball at each skeleton voxel;
3. Identify the location of each node of a pore network; each node is located at a single junction of the skeleton, or a location centred at which a maximal inscribed sphere contains multiple junctions; then label all skeleton voxels within the maximal inscribed ball centred at every node as node backbone and each segment of the remaining skeleton voxels as a bond backbone;
4. Partition the pore space into node volumes and bond volumes by firstly allocating respective backbones to nearest nodes and bonds, respectively, and then pore voxels one by one into the closest node or bond in terms of the geodesic distance.
5. Compute geometrical properties for each network element such as volume, hydraulic radius, bond length, and shape factor, using the information on its partitioning structure, and the skeleton and distance map. For a node, from its centre 13 discrete/digital cross sections can be determined to find one that is the most perpendicular to the tangent line of the skeleton and to use it to estimate the hydraulic (area/perimeter) and the shape factor (area/squared perimeter) for the node. For a bond, a digital cross section is selected at each bond backbone, perpendicular to the skeleton locally, to calculate a hydraulic radius and a shape factor, and then the harmonic average of all hydraulic radii and shape factors is calculated and assigned to that bond.

The reader is referred to [34] for detailed information on associated algorithms and methods.

Appendix B: nomenclature for Equation 1

	Description
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C_g	Correction factor for a circle, square or equilateral triangle and 0.5, 0.5623 and 0.6.
R_h	Hydraulic radius - the perimeter over the area of a cross-section
ρ_2	Density of gas at the outlet of an element
μ_2	Viscosity of non-ideal gas at the outlet of an element
μ_0	Reference viscosity of gas typically taken at 1 atmosphere
μ_2^{ig}	Viscosity of ideal gas at the outlet of an element
NIG_c	The non-ideal gas coefficient for the continuum term
NIG_k	The non-ideal gas coefficient for the Knudsen term
α	Tangential Momentum Accommodation Coefficient (TMAC) at pore wall
$k_{n,2h}$	Knudsen number
A	Area of the cross-section

498

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653 **Table 1** Comparison between the pore-network permeability and the image permeability calculated
 654 using a lattice Boltzmann model.

	Image permeability (10^{-17} m^2)	Network permeability (10^{-17} m^2)
Through-plane direction	5.08	5.82
In-plane direction (1)	1.35	1.51
In-plane direction (2)	1.60	1.87

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657 **Table 2** Apparent gas permeability for the three gases (k_{gas}) in comparison with the permeability for
 658 liquid water (k_s). D_p is the Knudsen diffusion coefficient.

Gas	$k_{gas} (\text{m}^2)$	k_{gas}/k_s	$D_p(\text{m}^2/\text{s})$
Oxygen	1.99×10^{-16}	9.19884	1.46×10^{-11}
Helium	5.05×10^{-16}	23.3573	3.83×10^{-11}
Hydrogen	3.28×10^{-16}	15.1809	5.53×10^{-11}

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665 **Figure 1.** The reconstructed binary 3D volume corresponding to a volume of $1.5\ \mu\text{m} \times 1.5\ \mu\text{m} \times 5$
666 μm acquired from an MPL sample using FIB/SEM tomography (the blue is for solid and the gray
667 for pores).
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Figure 2. The partitioned pore space for the 149^3 volume used in this work. Note that the voxel resolution is 8nm, and the node and bond volumes are in pink and yellow, respectively.

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 679 **Figure 3.** The mean porosity versus the dimension of sub-volume (the solid line) with errors of one
 680 standard deviation drawn at both sides (dotted dash lines). The porosity of the selected volume is
 681 about 34% and plotted as the dotted line for reference.

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685 **Figure 4.** Frequency distribution of the shape factors calculated from the pore network.

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Figure 5. Increase of water-entry pressure with water contact angle. Symbols are simulations and the solid line is the fitting to $\Delta P = A \cos \theta$.

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Figure 6. Impact of the water contact angle on the water saturation and the capillary pressure relationship.

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703 **Figure 7.** Change of relative permeability for liquid water with capillary pressure. Symbols are
704 simulations and the solid line is prediction using the results simulated with another contact angle.

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708 **Figure 8.** Schematic illustration of liquid water movement in a cracked MPL.

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