Effective diffusivity in partially-saturated carbon-fiber gas diffusion layers: Effect of through-plane saturation distribution

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Abstract

The effective diffusivity of gaseous species in partially-saturated finite-size porous media is a valuable parameter for mathematical modeling of many processes, but it is difficult to measure experimentally. In this work, the effective diffusivity of carbon-fiber gas diffusion layers (GDLs) used in polymer electrolyte fuel cells (PEFCs) was determined by performing lattice Boltzmann (LB) simulations on X-ray tomographic reconstructions of invading water configurations. Calculations on dry GDLs were in close agreement with previous experimental data; the effective diffusivity was reduced by the addition of PTFE due to the loss of pore volume and the higher tortuosity of transport paths. The effect of water saturation was significantly larger. It was found that the resistance of water to gas transport was extremely dependent on the saturation distribution through the porous medium, particularly the peak saturation, and not just the average saturation as is typically considered in the literature. Through-plane diffusion was dramatically limited in materials with high-peak local saturations, even at low average saturation levels. No significant limitations were observed for diffusion in the material plane. The computed results demonstrate the strong sensitivity of finite-size porous media to local conditions, highlighting the difficulties of applying volume-averaged continuum-scale modeling techniques to micro-scale materials.

Keywords: effective diffusivity; gas diffusion layer; water saturation; finite size; X-ray tomography; lattice Boltzmann method

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are a leading candidate to replace internal combustion engines for automotive applications, as they are the only presently available technology that can offer equivalent power density, range and refueling times in a sustainable way. The electrochemical conversion of reactants in PEFCs leads to virtually zero emissions of pollutants (water and heat are the only products generated in the cell), and provides 2-3 times higher efficiency as compared to high-temperature combustion devices [1]. However, engineering factors such as high cost and limited durability remain significant barriers to large-scale commercialization. To reduce cost, it is imperative that the mass of platinum (Pt) catalyst per vehicle be reduced significantly; this can be achieved by lowering the loading of Pt per unit active cell area, or reducing the active area (or both). The latter approach, however, requires an increase of the current density (A/m^2) of the cells, to maintain the output power (W) of the stack. Therefore, thorough understanding of the transport of reactants and products to/from the catalyst sites in PEFCs is needed [2–5].

One key element of a fuel-cell electrode is the gas diffusion layer (GDL), which is a thin highly porous layer composed of carbon fibers. The GDL must fulfill several functions such as providing structural stability to the cell, and transport pathways for gaseous reactants and liquid water through its pore volume and electronic current and heat through its solid structure. A deep knowledge of the effects of liquid water on the gas diffusivity of GDLs is essential to achieving an increased PEFC performance [2–5].

The standard approach for modeling the effective diffusivity in porous materials is to modify the bulk diffusion coefficient, D_{bulk} , to get an effective diffusivity, D^{eff} , through the porous domain [6],

$$D^{\text{eff}} = D_{\text{bulk}} \frac{\varepsilon_V}{\tau} \quad \text{Eq.(1)}$$

where ε_V is the void volume fraction of the porous medium, and τ is the so-called

tortuosity, which accounts for the indirect route that gas molecules must follow to traverse the ‘tortuous’ pore space. In porous media whose pore structure is partially filled with liquid water, gas diffusion is further blocked since liquid offers essentially no gas flux. The configuration, distribution, and extent of water within the pore space have major impacts on the diffusion rates, above and beyond the pore-structure effects [7]. To differentiate the impacts of the pore/throat structure of the dry material from those of the invading liquid, Eq.(1) can be decomposed into two independent functions, one accounting for the effect of the unsaturated medium, $f(\varepsilon)$, and another for the relative effect of liquid in the pore space, $g(s)$:

$$\frac{D^{\text{eff,wet}}}{D_{\text{bulk}}} = \frac{D^{\text{eff,dry}}}{D_{\text{bulk}}} \frac{D^{\text{eff,wet}}}{D^{\text{eff,dry}}} = f(\varepsilon)g(s) \quad \text{Eq.(2)}$$

where ε is the porosity, s is the liquid saturation (defined as the ratio of liquid volume to pore volume), and $D^{\text{eff,dry}}$ and $D^{\text{eff,wet}}$ are the effective diffusivities of the porous medium under dry, and partially-saturated (or wet) conditions, respectively. A review of previous studies attempting to determine $f(\varepsilon)$ and $g(s)$ for fuel-cell GDL materials is presented below.

Multiple experimental [8–19], numerical [20–22] and semi-analytical [23–28] works on the dry effective diffusivity function, $f(\varepsilon)$, for carbon-paper GDLs can be found in the literature. These investigations provide fundamental information about the effects of compression, the fabrics of the substrate, the addition of wet-proofing agents, and the incorporation of micro-porous layers (MPLs) on the effective gas diffusivity of GDLs. Good agreement is observed among different authors. All of them show that the effective diffusivity of many carbon-fiber papers is anisotropic, with higher values in the in-plane direction due to preferential alignment of the GDL fiber structure in the material plane [8]. Moreover, it has been generally found that the effective diffusivity is notably lower than predicted by most established and widely used models, such as Bruggeman's effective medium theory [29], or the random fiber model by Tomadakis & Sotirchos [30]. The deviations from these idealized models are explained by the complex

structure formed by fibers, binder, and PTFE in carbon-paper materials. For instance, the sintering processes of carbon-fiber GDLs typically results in a webbed region at fiber intersection points that offers little porosity but dramatically increases tortuosity.

In contrast, very few experimental measurements on the relative effective diffusivity, $g(s)$, of GDLs have been reported in the literature [10,31,32]. This is due to the difficulty of measuring species concentration and flux in GDLs with thicknesses between 100 and 400 μm , while simultaneously controlling the amount of water. For instance, Utaka et al. [31] used custom GDLs, which were 10-20 times thicker than those actually used in fuel cells, in order to achieve a detectable concentration gradient. Hence, a wide variety of numerical strategies have been adopted to determine ‘experimentally inaccessible’ properties such as the effective diffusivity. This includes pore network modeling [7,33–36]; pore-scale CFD models using reconstructions of either artificial or tomographic images of partially-saturated GDLs [21,22,37]; inverse modeling techniques in which macroscopic CFD models are combined with experiments to determine the free parameters of prescribed laws for the effective diffusivity [38,39]; and semi-analytical fractal models [23]. In general, the results reported in all these works show a large disparity, particularly for the through-plane direction. A power law of the form:

$$g(s) = (1 - s)^n, \quad \text{Eq.(3)}$$

was used by most of the authors to describe their results, with n ranging from about 2 to more than 5 for the through-plane direction, and $n \approx 2$ for the in-plane direction.

The above literature review shows that additional effort is still needed to shed further light on the influence of water saturation on the effective diffusivity of carbon-paper GDLs. In particular, better understanding of the effects of the water distribution through the GDL on diffusive transport is of paramount importance for the proper operation of PEFCs. A better knowledge of the transport properties of partially-saturated GDLs will also help to improve the predictive capabilities of macroscopic continuum models which are extensively used in fuel cell design [40–42]. One way to accomplish this goal is by the

combination of tomographic reconstructions of GDLs and numerical models that explore transport processes at the pore-scale level ($\sim 10\text{-}100\ \mu\text{m}$). For this purpose, the lattice Boltzmann method (LBM) is an excellent option due to its ability to use 3D image stacks directly as a mesh, rather than sophisticated meshing tools as in traditional finite element (FEM) or finite volume (FVM) methods [43]. An increasing number of LBM studies exploring the properties of woven and nonwoven fabrics can be found in the fuel cell literature (see, e.g., [44–49]).

In the present work, the effective gas diffusivity of dry and partially-saturated carbon-paper GDLs is examined by performing LB simulations on X-ray computed tomography (XCT) images of water-invasion experiments. The structure of the paper is as follows. In Section 2, the methodology used for the invasion experiments and the reconstruction of the image stacks is presented. In Section 3, the algorithm adopted for the segmentation of the three phases composing the porous media (solid, air and water) is described. This also includes a comprehensive analysis of the morphological properties of the GDLs, and the amount and distribution of water in the invasion experiments. In Section 4, the LBM model and the case studies examined in the work are presented. The computed results are discussed in Section 5, which also incorporates a detailed comparison with previous data. The effective diffusivity in both the through- and in-plane directions of the material are investigated due to the anisotropic nature of carbon-paper GDLs. Finally, the concluding remarks are given in Section 6.

2. Experimental

2.1. Materials

Experiments were performed on Toray® TGP-H-120 carbon-paper GDLs (Fuel Cell Earth LLC, USA). Uncompressed samples with 0 and 10% by weight PTFE loading were investigated. This material is somewhat thicker than GDLs typically used in modern fuel cells (375 vs. 250 μm) but the thicker domain allowed more space for the invading water fingers to evolve before percolation. In subsequent LBM simulations, the effective diffusivities of both the untreated and PTFE-treated dry GDLs were examined, while only the PTFE-treated GDL was analyzed under partially-saturated conditions. The untreated sample was excluded from the calculations due to the difficulty to prevent leakage of water between the sample and the holder in the experiments.

2.2. Collection of Tomographic Data

Data were collected at Lawrence Berkeley National Lab's Advanced Light Source (ALS) synchrotron (Beamline 8.3.2). Tomographic images were produced by collecting a series of radiographs of a sample as it was rotated 180° on an axis normal to the X-ray beam. Radiographs were obtained every 0.15° for a total of 1080 images. The exposure time for each image was 100 ms, leading to a scan time of less than 2 minutes. An X-ray energy of 35 keV was used so that images could be reconstructed using the phase contrast information, rather than absorption contrast. This approach requires filtering the radiographs to enhance the phase contrast information and this was accomplished using the modified Bronnikov algorithm [50]. All image filtering and reconstructions were performed using the commercial software Octopus® 8.3. Very clear images with low noise and consistent greyscale values across the reconstructed images were obtained, which was essential for the subsequent segmentation of the image stacks as outlined below in Section 3. The resolution of the camera combined with optical magnification allowed for a $1.33\ \mu\text{m}$ voxel size.

2.3. Water-Invasion Experiments

Tomographic data sets of GDLs were taken at various levels of water saturation. The experimental set-up used for the water-invasion experiments is shown in Figure 1 with the assorted parts labeled. The neck of the holder where the GDL sample of 3.2 mm in diameter was located was reduced as small as possible to limit X-ray attenuation by the holder walls (≈ 0.5 mm thick). Water invaded into the GDL from the bottom face through a PTFE pipe with a 1.5 mm inner diameter, while air was allowed to escape out the top face through a PTFE membrane. The hydrophobic membrane prevented liquid water from leaving the system, thereby enabling saturations above the breakthrough point to be reached. The saturation level was controlled by increasing the static head of water in the injection pipe, which was arranged in a u-tube configuration. Because air was always at atmospheric pressure, the capillary pressure was equal to $p_c = p_l - p_g = \rho_w g h$. Liquid pressure was raised by 10 cm increments (≈ 1 kPa), with a full tomographic data set collected at each capillary pressure level. Experiments were finished between 7 and 8 kPa when the sample was almost fully saturated above the breakthrough pressure ($p_c \approx 3 - 4$ kPa) [33,51,52].

3. Image Processing

The reconstructed 3D stacks were segmented in order to differentiate the three phases composing the system, i.e., GDL solid structure (fibers, binder and PTFE), water and air. The segmentation of the images was performed using custom-made code in MATLAB[®], as well as relying heavily on the image processing software Fiji for more common operations. The data exchange between MATLAB[®] and Fiji was done through the public-domain Java package MIJL [53]. A representative square domain of 2×2 mm centered on the injection pipe was extracted from the collected circular samples of 3.2 mm in diameter. Some slices at the top and bottom edges of the GDL were removed due to local interferences of the membrane and the pipe with the rough surface of the GDL. The full thickness of the GDL domains considered for segmentation was $L_z = 0.32$ mm and $L_z = 0.28$ mm for the untreated and PTFE-treated samples, respectively. This resulted in about a 15% and a 25% loss of material as compared with the manufacturer's datasheet ($L_{z,GDL} = 0.37$ mm) [54]. In order to explore the effect of the surface region lost in the above domains on the dry effective diffusivity, an extra subsample of 0.8×0.8×0.37 mm, free of interference artifacts, was carefully selected for each of the GDLs from the dry sample stacks.

3.1. Segmentation Algorithm

The main steps followed for the segmentation of the images are presented below. Further details on the segmentation algorithm, including information on the intensity histograms and several sensitivity analyses, can be found in the supplementary material to this paper. The segmentation of the stacks into the three respective phases was performed sequentially due to the low contrast between solid- and water-phase voxels in the reconstructed images (see Figure 2(a)). First, a base segmentation of the solid structure was performed by global thresholding the bimodal dry sample stack using Otsu's method [55]. The resulting binary mask was then multiplied by the grayscale wet

sample stack, so that solid-phase voxels were identified as zero-intensity black voxels; the result is shown in Figure 2(b). Next, a 3D morphological dilation/contraction operation with a spherical element of 3 voxels was applied to correct the imperfect matching of the solid structure around that previously determined with Otsu's method [55]. Note that this operation could be applied on the dry or on any of the wet sample stacks leading to similar results (see supplementary material for results obtained on a dry sample). As shown in Figure 2(c), the 3D morphological operation resulted in a slight perturbation of the void volume, while including most of the interfacial solid-phase voxels not identified by Otsu's method [55]. The above two steps, Otsu's method [55] and the dilation/contraction operation, led to the final segmentation of the solid phase, so that the next problem became differentiating water from air. To this end, an edge-preserving bilateral filter was applied to remove the overlap of some darkened regions in water fingers with the low-intensity air phase. The high time and memory requirements of this filter were reduced using an in-house version of the fast downsampling/upsampling algorithm by Paris & Durand [56]. As shown in Figure 2(d), the bilateral filtering step gave excellent results, significantly enhancing the contrast between water and air phases, and reducing intensity fluctuations within each phase. Finally, water-phase voxels were identified by manual thresholding of the now non-overlapping wet sample histogram. The partial results from the segmentation of the solid structure of the GDL and water were combined, and the final segmented stack was obtained (see Figure 2(e)).

3.2. Morphological Properties and Water Distribution

Several analyses were performed to confirm the proper segmentation of the dry and wet samples, involving both global and local characteristics of the porous media. The properties examined in the dry samples were the pore size distribution, 1D through-plane porosity profiles and average porosity, whereas the variables studied in the wet samples were the capillary pressure curve and 1D saturation distributions along the

through- and in-plane directions.

3.2.1 Dry Samples: Pore Size Distribution, Porosity Profiles and Average Porosity

The pore size distribution of the dry sample stacks was scanned using the heuristic morphological image opening (MIO) algorithm described by Gostick [33]. As shown in Figure 3(a), good agreement is found between the cumulative pore size distributions (average mercury saturation vs. pore diameter) computed by the MIO algorithm and previous experimental data [14,57,58]. This result confirms that pore/throat sizes, as well as connectivity of the pore space, were well represented in the segmented GDL stacks. The characteristic pore diameter, d_p^{char} , of Toray[®] TGP-H-120 is between 20–35 μm , and does not vary significantly with the PTFE loading [52]. The somewhat lower pore diameters predicted by the MIO simulations are explained by the inability of this simple algorithm to account for some key physical phenomena, such as coalescence of menisci and non-spherical invasion fronts [33]. Given that the range of pore diameters in the examined porous media is between 10–60 μm , the 1.33 μm /voxel resolution of the image stacks provided a sufficiently fine mesh for subsequent LBM simulations.

Figure 3(b) shows the xy -averaged porosity profiles along the through-plane direction, $\bar{\epsilon}_z$, of the complete set of dry GDL domains analyzed in this work (see case studies in Section 4.1). As can be seen, the computed porosity profiles are in good agreement with previous studies for Toray[®] carbon-paper GDLs [59–61]. A central core region (CR) can be identified with rather strong fluctuations of the porosity due to the arrangement of the solid structure of the GDL, surrounded by two highly porous surface regions (SR) in which the solid structure progressively vanishes. The addition of PTFE leads to a net decrease of the porosity in the core region, yet the undulations in porosity are similar to the untreated case [51,59]. The similar porosity distributions observed in all the domains indicate that no anomalous features were present in the segmented samples. The porosities of the untreated/PTFE-treated domains mostly excluding the surface region of the material are $\epsilon_{\text{avg}} = 0.69/0.66$, while the porosities of the domains including the

core and surface regions (CR+SR) are notably higher, $\varepsilon_{\text{avg}} = 0.75/0.7$. Similar values were previously reported for uncompressed and compressed Toray® TGP-H-120 GDLs with and without PTFE loading (see [9,10,51,52,57,59,62] among others).

3.2.2 Wet Samples: Capillary Pressure Curve and Saturation Distribution

Figure 4 shows the capillary pressure curve (average water saturation vs. capillary pressure) obtained in the present invasion experiments for the 10% PTFE-treated sample, along with the experimental data reported by Gostick et al. [52]. Even though the water-invasion experiments conducted here were not specifically designed to measure this property, the results are in reasonable agreement with Gostick et al. [52]. The somewhat lower breakthrough pressures (3–4 kPa vs. 5 kPa), and the larger saturations reached in the present experiments at capillary pressures higher than 2 kPa are ascribed to (i) the small size of the samples used for the X-ray visualizations as compared to [52] ($d_{\text{GDL}} = 3.2$ mm vs. $d_{\text{GDL}} = 19$ mm), and (ii) the different injection conditions used in this work (pipe smaller than GDL sample) as compared to [52] (full-face invasion). The non-representativeness of small samples to characterize the water retention properties of GDLs was previously observed in the ex-situ experiments of Flückiger et al. [61]. Note also that an accurate comparison with experimental capillary pressure curves on GDL samples of similar dimensions was not feasible as evaporation would significantly affect the exceedingly small volumes of liquid water injected at each step.

The xy - and yz -averaged saturation profiles obtained along the through-, $\bar{s}_z$, and in-plane, $\bar{s}_x$, directions for a 0.8×0.8 mm 10% PTFE-treated GDL domain extracted from the large segmented sample of 2×2 mm are shown in Figure 5. Only one representative direction is shown in the material plane, since the profiles in other in-plane directions are similar. As can be seen, strong changes in the local saturation level are observed across the GDL, while no significant variations are found in the material plane. The high-gradient saturation profiles through the GDL arise due to the capillary-dominated percolation

process of water. Given that in the experiments the GDL region located on the injection pipe is invaded homogenously, very high saturation levels are reached in the open surface region of low capillary resistance close to the invasion face. The amount of water gradually decreases towards the opposite face as water fingers percolates through the pore/throat structure of the core region of the GDL. As shown in Figure 5(a), the through-plane saturation distribution at the breakthrough point ($p_c \approx 3 - 4$ kPa) varies from almost fully-saturated conditions, $\bar{s}_z \approx 1$, near the inlet surface region to $\bar{s}_z \approx 0.2$ on the face adjacent to the PTFE membrane. Similar results were presented in previous pore network and ex-situ experimental studies (see [33,61,63] among others). The high saturation profiles in the present invasion experiments may then resemble those in an operational fuel cell under severe flooding conditions due, e.g., to a poor water removal rate from the catalyst layer and/or the existence of interfacial gaps between the GDL and the catalyst layer. Besides, these high-gradient saturation profiles provided an opportunity to examine the impact that lower saturation variations through the GDL has on the effective diffusivity. This analysis was accomplished by progressively removing larger portions of the GDL adjacent to the injection pipe in the LBM simulations (see details in Section 4.1).

4. Lattice Boltzmann Method

Gas diffusive transport at the sub-pore scale level in the GDLs was simulated by means of the lattice Boltzmann method [64,65]. The model was implemented using the built-in capabilities of the parallel open-source LB solver Palabos [66]. A 3D seven-speed D3Q7 lattice with the standard Bhatnagar-Gross-Krook (BGK) approximation for the collision operator [67] was adopted for the calculations. The governing equation of the model in index notation is given by:

$$f_{\alpha}(\mathbf{x}_i + \mathbf{c}_{\alpha}\Delta t, t + \Delta t) - f_{\alpha}(\mathbf{x}_i, t) = -\frac{f_{\alpha}(\mathbf{x}_i, t) - f_{\alpha}^{\text{eq}}(\mathbf{x}_i, t)}{\tau}; \alpha = 0, \dots, 6 \quad \text{Eq.(4)}$$

where $f_{\alpha}(\mathbf{x}_i, t)$ are the particle distribution functions at location $\mathbf{x}_i$ and time t , Δt is the time step, τ is the dimensionless relaxation time, and $\mathbf{c}_{\alpha}$ and f_{α}^{eq} are the velocities and equilibrium populations of the distribution functions f_{α} . The time increment, Δt , and lattice spacing, $\Delta \mathbf{x}_i = \mathbf{c}_{\alpha}\Delta t$, were set to 1, as was the relaxation time τ . This value ensured the stability and accuracy of the numerical scheme [68]. The lattice velocities and equilibrium distributions for the D3Q7 model are:

$$\mathbf{c}_{\alpha} = \begin{cases} (0,0,0) & \alpha = 0 \\ (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1) & \alpha \neq 0 \end{cases} \quad f_{\alpha}^{\text{eq}} = \begin{cases} (1 - 3c_s^2)C & \alpha = 0 \\ (c_s^2/2)C & \alpha \neq 0 \end{cases} \quad \text{Eq.(5)}$$

where C is the macroscopic concentration, and $c_s = 1/2$ is the lattice ‘speed of sound’.

The relationship of the macroscopic concentration, C , the bulk diffusivity, D_{bulk} , and the Fickian diffusion flux, $\mathbf{j}$, with the mesoscopic variables (f_{α} , $\mathbf{c}_{\alpha}$ and τ) is obtained through the Chapman-Enskog asymptotic analysis of Eq.(4) [68,69]:

$$C = \sum_{\alpha=0}^6 f_{\alpha}; \quad D_{\text{bulk}} = c_s^2 \left(\tau - \frac{1}{2} \right); \quad \mathbf{j} = \left(1 - \frac{1}{2\tau} \right) \sum_{\alpha=0}^6 f_{\alpha} \mathbf{c}_{\alpha} \quad \text{Eq.(6)}$$

A sketch of the computational domain used for the LBM simulations is shown in Figure 6(a). In addition to the GDL domain, a block of 5 gas-phase voxels was padded at both sides of the GDL in the direction of interest to mimic the inlet/outlet conditions in an experimental setup. The effective diffusivities in both the through-plane direction and

one (representative) in-plane direction were examined in this work. The system was excited by imposing a concentration difference between 1 and 0 at the outermost faces in the direction under study according to the formulation of Zou & He [70]. On the remaining faces, the geometry was padded with solid walls. The set-up of the numerical domain for the LBM simulations was performed in MATLAB®. The segmented GDL samples (with air labeled 0, solid 1, and water 2), were conveniently padded with the exterior walls (labeled 1) and inlet/outlet gas zones (labeled 0). Then, an in-house search algorithm was used to identify the interfacial computational nodes (voxels) delimiting the pore space, so that all the nodes in the multiphase system were classified in three groups: gas (0), water/gas and solid/gas interfacial nodes (1), and internal water and solid nodes (2). In the LBM simulations, diffusive dynamics were assigned to nodes labeled 0, a standard half-way bounce back scheme [68] to nodes labeled 1, and no dynamics to nodes labeled 2. In this way, solid and water phases were both treated as impermeable phases to gas transport.

According to Fick's law, the normalized effective diffusivity, $D_j^{\text{eff}}/D_{\text{bulk}}$, was calculated as the ratio between the (constant) overall diffusive flux in the j -direction of interest and the overall bulk flux in that direction:

$$\frac{D_j^{\text{eff}}}{D_{\text{bulk}}} = \frac{\iint_A j_j \, dA}{A(D_{\text{bulk}} \Delta C_j / L_{\text{CD},j})} \quad \text{Eq.(7)}$$

where A is the cross-sectional area of the examined GDL domain to the j -direction under study, and j_j , $\Delta C_j = 1$, and $L_{\text{CD},j}$ are the local diffusive flux in a computational node, the prescribed concentration difference, and the length of the computational domain (CD) in j -direction, respectively; note that $L_{\text{CD},j} = L_j + L_{\text{in}} + L_{\text{out}}$, with L_j the length of the GDL domain in j -direction, and $L_{\text{in}}/L_{\text{out}}$ the lengths of the inlet/outlet gas zones padded to the GDL domain.

Simulations were started from a linear concentration profile and run until steady state, that is, when the relative variation of the volume-averaged concentration over a fixed

time window of 10^4 steps was below 10^{-6} . This stop criterion assured negligible variations of the effective diffusivity. To exploit the parallel capabilities of the Palabos [66] implementation of LBM, computations were performed on the supercomputers Gullimin and Colosse; both managed by Calcul Québec and Compute Canada [71]. The number of processors was varied between 64 and 180, depending on the extent of the domain under study. Details on the validation campaign performed before the calculations on the GDL samples are provided as supplementary material. The computed concentration fields both in the in- and through-plane directions for the largest GDL wet sample ($1.3 \times 1.3 \times 0.28$ mm) are shown in Figure 6(b) and (c), respectively.

4.1. Case Studies

The segmented stacks were divided into numerous domains to study the impact of sample size and saturation distribution across the GDL. The domains explored in the simulation campaign are described below.

4.1.1. Dry Conditions

Four different cases were examined under dry conditions for both the untreated and PTFE-treated GDLs. Three domains including the full thickness of the segmented samples of 2×2 mm ($L_z = 0.32/0.28$ mm for the 0/10% PTFE by weight GDLs), but different xy -sections were used to test the influence of sample size. These domains, as previously discussed in Section 3, do not incorporate the complete surface region of the GDL due to interferences of the membrane and the pipe with the irregular surface of the GDL. Additionally, an extra domain of $0.8 \times 0.8 \times 0.37$ mm, free of interfacial artifacts, was meticulously selected for each of the GDLs from the dry sample stacks. These additional GDL domains allowed us to explore the effect of the surface region excluded in the three previous cases.

4.1.2. Wet Conditions

Under wet conditions, only the PTFE-treated GDL was investigated due to the better control of water in the invasion experiments. The same domains of 0.8×0.8 , 1×1 , and $1.3 \times 1.3 \times 0.28$ mm used for dry diffusivity calculations were also examined under wet conditions. In addition, an extensive analysis was carried out on the smaller sample of $0.8 \times 0.8 \times 0.28$ mm to investigate the impact of water distribution through the GDL on gas diffusive transport. As depicted in Figure 7, starting from the face next to the PTFE membrane, different cases were considered by gradually reducing the through-plane window length of the GDL included in the simulations, $\delta_z \approx 0.056 - 0.28$ mm, with respect to the full thickness (FT) of the sample, $L_z = 0.28$ mm. In other words, a larger portion of the highly-saturated region near the injection pipe was progressively removed, so that the saturation variation in the numerical domain was decreased. The computed relative effective diffusivities, $g = D^{\text{eff,wet}}/D^{\text{eff,dry}}$, in all these thinner subdomains is aimed to provide fundamental information on the effect that the saturation distribution in finite-thickness GDLs has on diffusive transport.

5. Results and Discussion

The following discussion of results is divided in two parts. First, in Section 5.1, the dry effective diffusivity of the untreated and PTFE-treated GDLs is examined. Then, the effective diffusivity of the PTFE-treated GDL under partially-saturated conditions is explored in Section 5.2. The diffusive properties in both the through- and in-plane directions of the material are investigated. Further details on the case studies can be consulted in Section 4.1.

5.1. Dry Effective Diffusivity

The computed results for the dry effective diffusivity in terms of the normalized function, $f = D^{\text{eff,dry}}/D_{\text{bulk}}$, along with the average porosity, ε_{avg} , of the analyzed GDL domains are listed in Table 1. Small changes in the dry effective diffusivity and porosity are observed for different domain sizes. The effective diffusivity is significantly higher in the in-plane direction due to the preferential alignment of fibers in the material plane. On average, the addition of PTFE decreases the effective diffusivity in the through-/in-plane directions ($f_{\text{TP}}/f_{\text{IP}}$) from 0.25/0.41 to 0.2/0.37 due to the reduction of the porosity and the increase of the tortuosity of the material [8]. Besides, a notable increase of the effective diffusivity and the porosity is found in the samples fully including the core (CR) and the surface regions (SR) of the GDL (0.31/0.54 and 0.24/0.47 for the untreated and PTFE-treated GDLs, respectively). The increase of the dry effective diffusivity in these domains can be explained by the lower transport resistance offered by the highly porous surface region as compared to the internal core region of the GDL [72]. In fact, this result suggests that the strong nonlinear effect of compression on the effective diffusivity of carbon-paper GDLs [8,73] may be attributed to a large extent to the densification and depletion of the low-stiffness surface region [72,74]. The thin heterogeneous nature of GDL materials means that the surface region is a significant fraction of the material, which is an ever-present issue when dealing with finite-thickness porous media.

The dry effective diffusivities obtained here are in good agreement with previous experimental data reported for Toray[®] carbon paper [8–11,15]. The computed effective diffusivities for the CR+SR domains are similar to the values presented for uncompressed samples, whereas the computed effective diffusivities in the domains mostly excluding the surface region are in line with data reported for compressed GDLs of similar porosity. The effective diffusivity of Toray[®] TGP-H-120 over the porosity range analyzed here ($\varepsilon_{\text{avg}} = 0.66 - 0.75$) can be well correlated by power laws of the form $f = \varepsilon_{\text{avg}}^n$, with $n_{\text{TP}} \approx 3.8$ and $n_{\text{IP}} \approx 2.3$ for the through- and in-plane directions, respectively [8–11,15]. The agreement between the present results and the available experimental data confirms the representativeness of the sample sizes used in the simulations, as well as the correct segmentation of the GDL samples.

5.2. Wet Effective Diffusivity

5.2.1. Through-Plane Direction

The computed results for the partially-saturated GDL in the through-plane direction are presented in Figure 8(a)-(b). The left panel shows the relative effective diffusivity, $g_{TP} = D_{TP}^{\text{eff,wet}}/D_{TP}^{\text{eff,dry}}$, as a function of average saturation, s_{avg} , while the right panel shows the best-fit exponent n_{TP} to a power-law of the form $g_{TP} = (1 - s_{\text{avg}})^{n_{TP}}$, plotted as a function of the normalized through-plane window length, δ_z/L_z , included in the numerical simulations (see sketch in Figure 7). The markers and colors between these two plots coincide, so it can be seen, for example, that the best-fit exponent n_{TP} for the three window lengths examined between 52% and 61% of the full thickness (FT) in Figure 8(a) corresponds to $n_{TP} \approx 3$ in Figure 8(b).

A striking feature of the results shown in Figure 8(a)-(b) is that the gas transport resistance of water at a given average saturation, as characterized by the exponent n_{TP} , never stabilizes as the *peak* saturation through the GDL decreases (the window length δ_z/L_z is reduced). This essentially shows that a unique power-law exponent n_{TP} relating the relative effective diffusivity of partially-saturated GDLs with average saturation does not exist. The value of n_{TP} fitted to the full-thickness domain data is about 7.5. Such strong resistance, even at low average saturations, is due to the severe bottleneck effect caused by the highly-flooded region close to the invasion face. It can be seen in Figure 8(b) that this region of high diffusive resistance is extended up to about 5% of the full thickness with $n_{TP} > 5$ (note that the high-resistance region would be somewhat thicker and n_{TP} even higher if the complete surface region had been included in the segmented domain). In contrast, when the highly-saturated region near the invasion face is removed, the resistance of water to gas diffusive transport is sharply reduced. As shown in Figure 8(b), the power-law exponent n_{TP} in the GDL domains of low-to-middle diffusive resistance varies from about 4.5 to 1.5, being the average value 3.1.

The inadequacy of the average saturation level to correlate the effective diffusivity fully can be more clearly illustrated qualitatively. Consider the schematic picture of through-plane saturation distributions in the GDL shown in Figure 9(a), corresponding to a linear and a flat saturation profile. In both cases, the average saturation is the same, $s_{\text{avg}} = s_{\text{crit}}/2$, where s_{crit} is the local saturation level slightly below the gas percolation threshold. However, despite having the same average saturation, as shown in Figure 9(b), the effective diffusivity is dramatically reduced in the case of the linear profile due to the strong bottleneck effect caused by the high-saturation region. In contrast, for the flat profile there is no such bottleneck region. Introducing some numbers to this picture, if we assume that $s_{\text{crit}} = 0.8$ ($s_{\text{avg}} = 0.4$), and the relative effective diffusivities in the GDLs with the linear and flat saturation distributions are $g_{\text{TP}}^{\text{lin}} = 0.05$ and $g_{\text{TP}}^{\text{flat}} = 0.5$, the associated power-law exponents turn out to be $n_{\text{TP}}^{\text{lin}} = 5.9$ and $n_{\text{TP}}^{\text{flat}} = 1.4$, respectively. Similar differences can be observed in the numerical results. This simplistic but illustrative explanation shows that any measured effective diffusivity in partially-saturated GDLs must explicitly consider the distribution of water in the sample, and not only the average amount. Such hypersensitivity to the saturation distribution stems from the finite-thickness nature of GDLs, spanning only 10-20 pores in the through-plane direction. The most basic tenets of percolation theory (infinite medium) and volume averaging (representative elementary volume) are not met in such thin materials [75]. Therefore, it should not be surprising that the average saturation alone cannot fully characterize transport phenomena in finite-thickness GDLs.

To further illustrate the impact of the through-plane saturation distribution on the effective diffusivity, the exponent n_{TP} obtained by fitting each data point in Figure 8(a) is represented against different representative functions $\lambda(s)$ in Figure 10(a); $\lambda(s) = s_{\text{avg}}$ corresponds to the hollow blue circles. This plot clearly shows that the diffusive resistance caused by water is highly uncorrelated, e.g., for $\lambda(s) = s_{\text{avg}} = 0.5$, where the exponent n_{TP} ranges randomly from 2 to more than 7. The variations of n_{TP} can be better explained by introducing some metric that captures the basic features of the

saturation distribution through the GDL, specifically the peak saturation. A normalized parameter $\lambda(s) = \psi_{TP}$ (solid green diamonds), can be defined as:

$$\psi_{TP} = \frac{\bar{s}_z^{\max} - \bar{s}_z^{\min}}{1 - \bar{s}_z^{\min}} \quad \text{Eq.(8)}$$

where $\bar{s}_z^{\min}$ and $\bar{s}_z^{\max}$ are the minimum and maximum local saturation level across the GDL, respectively. The parameter ψ_{TP} measures the amplitude of the through-plane saturation distribution in the GDL, as compared to the maximum possible variation for a given value of $\bar{s}_z^{\min}$, that is, when $\bar{s}_z^{\max} = 1$. Accordingly, ψ_{TP} tends to 0 for a fully flat saturation profile ($\bar{s}_z^{\max} = \bar{s}_z^{\min}$), while it approaches 1 when fully-saturated conditions are reached near the invasion face ($\bar{s}_z^{\max} = 1$). As can be seen in Figure 10(a), the exponents n_{TP} collapse onto a single curve when they are expressed in terms of ψ_{TP} rather than s_{avg} , and correlate quite solid over the whole range. The value of n_{TP} varies from about 1.5 when the saturation distribution in the GDL is nearly flat ($\psi_{TP} \rightarrow 0$), sharply increasing to more than 7 when a high-peak saturation distribution exists in the GDL ($\psi_{TP} \rightarrow 1$). These exponents are physically sound. They lie within the range of values for a porous medium composed of straight capillary tubes partially-filled with a water film on their walls ($n_{TP} = 1$), and a partially-saturated porous medium with no connected gas transport pathways ($n_{TP} \rightarrow \infty$). This analysis further demonstrates that the inhomogeneous distribution of water and, in particular, the existence of local bottleneck regions in the GDL has major impacts on diffusive transport not taken into account just considering the average saturation.

The present data are compared to the available literature sources [10,22,32] in Figure 11, and a wide dispersion can be seen. The experimental data presented by Koresawa & Utaka [32] are in the range of the results computed in the domains suffering from a severe bottleneck effect, which is not surprising given that they reported a high saturation region near their inlet using soft X-ray radiography [32]. In contrast, the works of Rosén et al. [22] and Hwang & Weber [10] tend to agree more with the present results for the cases where the flooded inlet region was removed. The deviations of the

results computed on the full-thickness domains with respect to both works [10,22] could be anticipated. The numerical study by Rosén et al. [22] considered water distributions from an actual fuel cell. Hence, water did not invade into the full face of the GDL, unlike the present invasion experiments, which may resemble more the scenario found in a cell under severe flooding conditions (see discussion in Section 3.2.2). Moreover, Hwang & Weber [10] controlled saturation by allowing water to evaporate from a fully-saturated GDL. Since GDLs are hydrophobic, evaporation of water corresponds to an imbibition of air, meaning that air enters the GDL via cracks and corners along the solid structure which are not filled by water. Therefore, it is likely that the water configurations of Hwang & Weber [10] did not exhibit the large through-plane saturation variations observed in this work, which are characteristic of access-limited percolation processes. From the trends in Figure 11, it can be concluded that a power-law fit of the form $g_{TP} = (1 - s_{avg})^{n_{TP}}$ with an exponent $n_{TP} \approx 3$ falls through the middle of the data, which is in good agreement with the values presented in other numerical works [7,21,23,33,36–39]; all of them in the range from $n_{TP} \approx 2$ to $n_{TP} \approx 4$.

5.2.2. In-Plane Direction

The computed results in the in-plane direction for the same GDL domains analyzed in the previous section are shown in Figure 8(c)-(d). A much lower impact of the saturation distribution through the GDL on the in-plane relative effective diffusivity, $g_{IP} = D_{IP}^{eff,wet}/D_{IP}^{eff,dry}$, is observed. This different behavior arises from the perpendicular arrangement of transport processes in the material plane with respect to the through-plane saturation gradients. Hence, no important bottleneck effects are visible on in-plane gas diffusion, and the power-law exponent n_{IP} remains in all the cases between 2 and 3.

Intriguingly, the results presented in Figure 8(d) show a progressive increase of the exponent n_{IP} as the peak saturation across the GDL is decreased (δ_z/L_z is reduced), opposite to the behavior shown in Figure 8(b) for n_{TP} . This effect can be qualitatively

explained by the nonlinear effect of saturation on local transport processes, so that the diffusive flux in a region of low saturation is disproportionally higher than the diffusive flux in a region of either intermediate or high saturation. As illustrated in Figure 12, for a given average saturation, s_{avg} , the relative effective diffusivity, g_{IP}^{lin} , in a GDL with a linear saturation distribution is expected to be somewhat higher due to the high diffusive flux existing in the low-saturation region. In contrast, an intermediate diffusive resistance acts everywhere in a GDL with a flat saturation distribution, so that g_{IP}^{flat} is lower, i.e., the equivalent diffusive resistance is larger. Even though this phenomenon is less important than that observed for the through-plane direction, this effect again stresses that any transport property in finite-thickness porous media is highly influenced by the actual saturation distribution across the material and not only the average saturation level. A good correlation can be established between the exponent n_{IP} and the parameter ψ_{IP} , defined as:

$$\psi_{IP} = \frac{MAD(\bar{s}_z)}{s_{avg}} \quad \text{Eq.(9)}$$

where $MAD(\bar{s}_z)$ is the mean absolute deviation of the saturation distribution across the GDL. The parameter ψ_{IP} measures the variations of the local saturation level in the GDL from the average saturation, s_{avg} , so that $\psi_{IP} = 0$ for a flat saturation profile. This definition is more suitable to characterize diffusive transport in the perpendicular direction to the saturation gradients unlike the one considered for the through-plane direction, which was based on the closeness of the maximum saturation, $\bar{s}_z^{max}$, towards 1 owing to the series arrangement of transport processes. Figure 10(b) shows the power-law exponent n_{IP} as a function of the normalized parameter $\psi_{IP}^* = \psi_{IP}/\psi_{IP}^{max}$, where ψ_{IP}^{max} is the maximum value in the dataset. As can be seen, the exponent n_{IP} slightly increases as the saturation variation in the porous medium is lower (ψ_{IP}^* decreases), thus in agreement with the qualitative explanation given before in Figure 12. The inadequacy of the average saturation, s_{avg} , to correlate the power-law exponent n_{IP} is also clearly observed, although the spread of the data is lower compared to the through-plane direction due to the small changes of n_{IP} in the numerical results.

Figure 13 shows data previously presented in the literature for partially-saturated carbon-paper GDLs, along with the results computed in this work for the in-plane relative effective diffusivity. The data extracted from the literature correspond to the numerical studies by Zamel et al. [21], Rosén et al. [22], and Becker et al. [37]. No experimental works on the in-plane relative effective diffusivity of partially-saturated GDLs were found. Good agreement is observed between the present work and the results reported by other authors, with a much lower dispersion of the data than seen for the through-plane direction. Despite the slightly higher values of Becker et al. [37] and the lower values computed here for GDL domains with flatter saturation profiles (reduced window length δ_z/L_z), the influence of saturation on in-plane diffusion is well characterized by a power-law of the form $g_{IP} = (1 - s_{avg})^{n_{IP}}$, with $n_{IP} \approx 2$. This value is also consistent with the pore network results of Gostick [33] and Nam & Kaviany [7]. The good agreement of the data among all the authors further shows that the in-plane effective diffusivity is less influenced by the distribution of water across the GDL. Hence, a significant number of connected pathways for in-plane gaseous transport between and around water fingers should be expected for most operating conditions in fuel cells [22,76]. Note that this observation holds only for in-plane diffusion when water invades the GDL in the through-plane direction. This scenario is the most relevant for fuel-cell operation since water is generated at the catalyst layer and must percolate through the GDL to exit the cell. If water had been injected in the in-plane direction, however, one would expect similarly strong resistance to in-plane gas diffusion as in the results presented here for the through-plane direction.

6. Conclusions

In this work, micrometer resolution X-ray computed tomography (XCT) was used to image dry and partially-saturated carbon-paper gas diffusion layers (Toray[®] TGP-H-120) at various levels of applied capillary pressure. The reconstructed image stacks were segmented into solid, air and liquid phases, and then used as computational domains for lattice Boltzmann (LB) simulations aimed to characterize the effective gas diffusivity. Excellent agreement was found between the computed dry effective diffusivity and previous experimental data in both the through- and in-plane directions. Under wet or partially-saturated conditions, diffusive transport in the GDL is strongly influenced by not only the amount of water but its distribution across the GDL. The dependence of the effective gas diffusivity with average saturation, s_{avg} , was well described by power laws of the form $(1 - s_{avg})^n$. However, it was observed that the exponent in the through-plane direction, n_{TP} , decreased systematically as the peak saturation in the GDL was lower. Extremely low effective diffusivities were found due to the bottleneck effect caused by the high-saturation region near the invasion face, leading to values of $n_{TP} > 5$. When this region was removed, the power-law exponent n_{TP} was strongly reduced, eventually reaching values around 2 for GDL domains with nearly flat saturation profiles. The average exponent n_{TP} for saturation distributions with moderate peak values was about 3 in agreement with previous data reported in the literature. On the other hand, diffusive transport in the in-plane direction did not suffer from a bottleneck effect, leading to an exponent n_{IP} about 2 but slightly increasing as the peak saturation was lower. This effect was explained by the nonlinear effect of water saturation on local transport processes, such that a sample with a flat saturation profile has a different equivalent resistance as the same sample with regions of high and low saturation, even if they have equal average saturation levels.

Two important consequences arise from the present findings. First, any determination of the effective diffusivity in finite-size GDLs should not only report the average saturation,

but also an explicit description of the water configuration under which the measurements/calculations were made. This can take the form of ensuring well controlled water placement, or visualizations of the actual water distribution as was done here. Second, any realistic PEFC volume-averaged continuum model incorporating an ex-situ effective diffusivity vs. saturation relationship must be mindful of the particular conditions under which the correlation was determined to ensure its applicability to the modeled scenario.

In fact, the present findings suggest that volume-averaged multiphase models explicitly solving local diffusion processes within GDLs must incorporate constitutive relations obtained under conditions of *no* saturation gradient. This is because volume-averaged models predict their own saturation distributions, over which they evaluate the effective diffusivity at each computational node, implicitly assuming that all transport properties are locally homogeneous in every computational node. Hence, the application of any correlation determined globally in an inhomogeneous medium (i.e. with saturation gradients) to the virtually homogeneous computational nodes composing the effective medium is inconsistent. The development of a methodology for determining an ‘intrinsic effective diffusivity’ relationship suitable for volume-averaged continuum models remains an important challenge to be explored in future work.

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Nomenclature

Symbols

A	GDL cross-sectional area [LB units]-[m ²]
C	mass concentration [LB units]-[mol/m ³]
c	lattice velocity [LB units]-[m/s]
c_s	lattice 'speed of sound' [LB units]-[m/s]
D	mass diffusivity [LB units]-[m ² /s]
d	diameter [m]
d_p	pore diameter [m]
f	particle distribution function [LB units]
$f(\varepsilon)$	normalized dry effective diffusivity function; see Eq. (3)
g	gravitational acceleration [m/s ²]
$g(s)$	relative effective diffusivity; see Eq. (3)
h	height [m]
I	grayscale intensity
j	Fickian diffusion flux [LB units]-[mol/m ² s]
L_i	GDL sample length in i-direction [LB units]-[m]
n	best-fit power-law exponent
p	pressure [Pa]
p_c	capillary pressure [Pa]
R	radius [m]
s	liquid saturation
$\bar{s}_x(x_i)$	yz-averaged liquid saturation at slice $x = x_i$
$\bar{s}_z(z_i)$	xy-averaged liquid saturation at slice $z = z_i$
t	time [LB units]-[s]
Δt	time step [LB units]-[s]
V	volume [LB units]-[m ³]
x	in-plane coordinate [LB units]-[m]

x_i	node position [LB units]-[m]
Δx	spatial increment [LB units]-[m]
y	secondary in-plane coordinate [LB units]-[m]
z	through-plane coordinate [LB units]-[m]

Greek letters

α	index
δ_z	thickness window length of the GDL in the LBM simulations [m]; see Figure 7
ε	porosity
$\bar{\varepsilon}_z(z_i)$	xy -averaged porosity at slice $z = z_i$
ε_v	void volume fraction
$\lambda(s)$	saturation-dependent function; see Figure 10
ρ	density [kg/m ³]
τ	tortuosity/dimensionless relaxation time
ϕ_v	solid volume fraction
ψ	parameter defined in Eqs. (8) and (9)

Subscripts

avg	volume-averaged quantity in the whole sample
bulk	bulk conditions
CD	computational domain
crit	critical local transport conditions; see Figures 9 and 12
D/C	dilation/contraction
F	fiber
FT	full thickness
g	gas phase
IP	in-plane direction
in	inlet/ inner
j	direction of interest or under study

l	liquid phase
out	outlet
T	total
TP	through-plane direction
th	threshold
w	water

Superscripts

char	characteristic
eff	effective
eq	equilibrium
flat	flat saturation distribution
dry	dry conditions
lin	linear saturation distribution
max	maximum
min	minimum
wet	wet or partially-saturated conditions
*	dimensionless or normalized value

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List of Tables and Figures

Table 1: Computed through-plane (TP) and in-plane (IP) normalized dry effective diffusivities, $f = D^{\text{eff,dry}}/D_{\text{bulk}}$, for the untreated and 10% PTFE-treated GDLs corresponding to domains with different xy -sections but mostly excluding the surface region of the material, and comparison with domains including both the core and the surface region (CR+SR) of the GDLs; see Figure 3(b) for details. The average porosity, ε_{avg} , of each GDL domain, and the average exponents $n_{\text{TP}}/n_{\text{IP}}$ from a fit of the numerical results to a power law of the form $f = \varepsilon_{\text{avg}}^n$ are also included.

Figure 1: (a) Schematic of the capillary pressure cell used in the water-invasion experiments, illustrating sample position and X-ray path, and (b) micron resolution reconstructed cross-section of the GDL, showing the direction of the x - z coordinate axis. The pipes above and below the GDL are visible, as is the PTFE membrane on the sample.

Figure 2: Cross-sectional view of the $2 \times 2 \times 0.28$ mm segmented sample of 10% PTFE-treated carbon paper (capillary pressure $p_c = 4$ kPa) at different steps of the segmentation process: (a) original grayscale image; (b) a base segmentation of the solid phase is extracted from the dry sample stack applying Otsu's method [55]; (c) the imperfect matching of the solid structure is corrected using a 3D dilation/contraction morphological operation; (d) darkened regions in water fingers are removed applying a 3D bilateral filter; (e) water is differentiated by manual thresholding, and the final segmented stack is obtained by combining the results of the solid phase and water (see supplementary material for further details).

Figure 3: (a) Average mercury saturation, s_{avg} , as a function of pore diameter, d_p , computed by the MIO algorithm of Gostick [33] on the untreated and 10% PTFE-treated segmented dry samples of $2 \times 2 \times 0.32$ and $2 \times 2 \times 0.28$ mm, as compared to previous experimental data [14,57,58]. The characteristic pore diameter, d_p^{char} , of Toray® TGP-H-120 is between 20-35 μm . (b) xy -averaged local porosity distribution, $\bar{\epsilon}_z$, across the GDL (z -direction) corresponding to the complete set of domains used for dry diffusivity calculations. The case studies are composed of three domains with different xy -sections (0.8×0.8 , 1×1 and 1.3×1.3 mm) extracted from the large segmented samples of 2×2 mm mostly excluding the surface region (SR) of the GDL, and two additional domains of $0.8 \times 0.8 \times 0.37$ mm carefully selected from the dry sample stacks to include both the core and surface regions (CR+SR).

Figure 4: Variation of the average water saturation level, s_{avg} , with capillary pressure, p_c , in the present water-invasion experiments for the 10% PTFE-treated GDL, as compared to the experimental data of Gostick et al. [52]. The average saturation level was calculated on the large segmented sample of $2 \times 2 \times 0.28$ mm. The ± 0.5 kPa error bars accounts for the resolution of the ruler (± 0.5 mm) used to measure the static head of water in the invasion experiments.

Figure 5: Local distributions of water saturation along (a) the through-plane direction ($\bar{s}_z$, locally averaged in each xy -slice), and (b) the in-plane direction ($\bar{s}_x$, locally averaged in each yz -slice) at different applied capillary pressures, p_c , for a 10% PTFE-treated GDL domain of $0.8 \times 0.8 \times 0.28$ mm centered on the injection pipe. The average saturation level, s_{avg} , in the whole domain is indicated in brackets. The breakthrough point in the invasion experiments was reached around $p_c \approx 3 - 4$ kPa.

Figure 6: (a) Computational domain used for effective gas diffusivity calculations with the LBM, showing the different elements of the system. (b) and (c) Computed concentration fields corresponding to simulations in the in- and through-plane directions, respectively. The resolution of the $1.3 \times 1.3 \times 0.28$ mm 10% PTFE-treated GDL domain was downscaled by a factor $3 \times 3 \times 1$ to avoid memory limitations of the 48 GB rendering workstation.

Figure 7: Sketch of the study performed to examine the impact of the saturation distribution across the GDL, $\bar{s}_z$, on the relative effective diffusivity, $g = D^{\text{eff,wet}}/D^{\text{eff,dry}}$, in a 0.8×0.8×0.28 mm 10% PTFE-treated domain centered on the injection pipe. Starting from the face adjacent to the PTFE membrane, multiple thinner subdomains are examined by varying the through-plane window length of the GDL, δ_z , with respect to the full thickness (FT). That is, larger portions of the GDL near the invasion face are gradually removed. The extent of the thinner subdomains in the xy -plane remains unaltered. See Figure 5 for the saturation profiles in the entire range of applied capillary pressures.

Figure 8: Left panel: computed relative effective diffusivity, $g = D^{\text{eff,wet}}/D^{\text{eff,dry}}$, in (a) the through-plane (TP), and (c) the in-plane (IP) directions, as a function of average saturation, s_{avg} , corresponding to the full-thickness (FT) 10% PTFE-treated domains with different xy -sections (1.3×1.3, 1×1, 0.8×0.8×0.28 mm), and thinner subdomains with different through-plane window lengths, δ_z/L_z , belonging to the 0.8×0.8×0.28 mm GDL domain (colored markers); see Section 4.1 for details. Right panel: variation of the best-fit exponent n to a power-law of the form $g = (1 - s_{\text{avg}})^n$, as a function of the normalized window length, δ_z/L_z , for the computed results in (b) the through-plane, and (d) the in-plane directions on the 0.8×0.8×0.28 mm domain.

Figure 9: Schematic of the effect of water distribution across the GDL on through-plane (TP) diffusive transport: (a) qualitative differences between two GDLs partially-saturated with the same average saturation, $s_{\text{avg}} = s_{\text{crit}}/2$, but with a linear and a flat saturation profile, $\bar{s}_z$, across the porous medium (z -direction), and (b) consequences of the above differences on the through-plane relative effective diffusivity, $g_{\text{TP}} = D_{\text{TP}}^{\text{eff,wet}}/D_{\text{TP}}^{\text{eff,dry}}$; s_{crit} is the local saturation level slightly below the gas percolation threshold. The high-saturation region strongly limiting the through-plane gas diffusive flux in the linear profile is indicated in orange.

Figure 10: Variation of the power-law exponent, $n = \log(g)/\log(1 - s_{\text{avg}})$, associated to each data point (s_{avg}, g) presented in Figure 8(a) and (c) with two different saturation-dependent functions $\lambda(s)$ for (a) the through-plane (TP), and (b) the in-plane (IP) directions: $\lambda(s) = s_{\text{avg}}$ (average saturation) corresponds to the hollow blue circles, and $\lambda(s) = \psi$ to the solid green diamonds (see Eqs. (8) and (9)); $\psi_{\text{IP}}^{\text{max}}$ is the maximum value in the dataset. Only the results computed at capillary pressures above the breakthrough point are included ($p_c \geq 3$ kPa).

Figure 11: Through-plane (TP) relative effective diffusivity, $g_{\text{TP}} = D_{\text{TP}}^{\text{eff,wet}}/D_{\text{TP}}^{\text{eff,dry}}$, as a function of average saturation, s_{avg} , reported in previous works for carbon-paper GDLs [10,22,32], as compared to the present numerical results. The data computed on the GDL domains including the flooded inlet region of high diffusive resistance (solid black diamonds) are differentiated from the remaining results (hollow black diamonds). See Figure 8(a)–(b) for further details.

Figure 12: Schematic of the effect of water distribution across the GDL on the in-plane (IP) relative effective diffusivity, $g_{\text{IP}} = D_{\text{IP}}^{\text{eff,wet}}/D_{\text{IP}}^{\text{eff,dry}}$. See caption to Figure 9 for details. The yellow/orange color map indicating the local resistance to in-plane gas diffusion is non-linearly scaled according to the expression: $[(s_{\text{crit}} - \bar{s}_z)/s_{\text{crit}}]^2$.

Figure 13: In-plane (IP) relative effective diffusivity, $g_{\text{IP}} = D_{\text{IP}}^{\text{eff,wet}}/D_{\text{IP}}^{\text{eff,dry}}$, as a function of average saturation, s_{avg} , reported in previous studies for carbon-paper GDLs [21,22,37], as compared to the present numerical results (hollow black diamonds). See Figure 8(c)–(d) for further details.

	Domains mostly excluding SR (different xy -section)			CR + SR	
	$f_{\text{TP}} / f_{\text{IP}} (\epsilon_{\text{avg}})$			$f_{\text{TP}} / f_{\text{IP}} (\epsilon_{\text{avg}})$	
PTFE	$0.8 \times 0.8 \text{ mm}$	$1.0 \times 1.0 \text{ mm}$	$1.3 \times 1.3 \text{ mm}$	$0.8 \times 0.8 \text{ mm}$	$n_{\text{TP}} / n_{\text{IP}}$ (average)
0%	0.26 / 0.42 (0.69)	0.24 / 0.41 (0.69)	0.25 / 0.40 (0.69)	0.31 / 0.54 (0.75)	3.85 / 2.32
10%	0.20 / 0.37 (0.66)	0.20 / 0.38 (0.66)	0.21 / 0.37 (0.66)	0.24 / 0.47 (0.70)	

(a)

(b)

—▼ $p_c = 1$ kPa ($s_{\text{avg}} = 0.01$) —■ 2 (0.12) —● 3 (0.52) —▶ 4 (0.53) —◀ 5 (0.61) —★ 6 (0.62) —◆ 7 (0.76) —▲ 8 (0.9)

(a)

(b)

In-Plane Direction

(c)

Through-Plane Direction

Reduce Saturation Variation Across GDL

Reduce GDL Window Length δ_z in Simulations

PTFE Membrane

(a)

(b)

(a)

(b)

(a)

(b)

- Gas diffusion is simulated on X-ray images of partially-saturated carbon-fiber GDLs.
- The dry effective diffusivity is anisotropic and decreases by the addition of PTFE.
- Invading water has a dramatic influence on through-plane diffusive transport.
- The effective diffusivity in finite-thickness GDLs is not uniquely described by average saturation.
- The distribution of water through the GDL has major impacts on the effective diffusivity.