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Analysis of representative elementary volume and through-plane regional characteristics of carbon-fiber papers: diffusivity, permeability and electrical/thermal conductivity

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Highlights

- The applicability of the continuum hypothesis to transport in carbon-fiber papers is analyzed
- The LBM is combined with X-ray tomograms to simulate diffusion, convection and conduction
- A representative elementary volume cannot be defined due to the thin nature of these materials
- The heterogeneous fibrous microstructure strongly reduces through-plane transport
- The reduction is particularly critical for solid-phase conductivity due to the bottleneck effect of the surface region

Abstract

Understanding the transport processes that occur in carbon-fiber papers (CFPs) used in fuel cells, electrolyzers, and metal-air/redox flow batteries is necessary to help predict cell performance and durability, optimize materials and diagnose problems. The most common technique used to model these thin, heterogeneous, anisotropic porous media is the volume-averaged approximation based on the existence of a representative elementary volume (REV). However, the applicability of the continuum hypothesis to these materials has been questioned many times, and the error introduced in the predictions is yet to be quantified. In this work, the existence of a REV in CFPs is assessed in terms of dry effective transport properties: mass diffusivity, permeability and electrical/thermal conductivity. Multiple sub-domains with different widths and thicknesses are examined by combining the lattice Boltzmann method with X-ray tomography images of four uncompressed CFPs. The results show that a representative length scale can be defined in the material plane in the order of 1–2 mm, which is comparable to the rib/channel width used in the aforementioned devices. As for the through-plane direction, no distinctive length scale smaller than the thickness can be identified due to the lack of a well-defined separation between pore and volume-averaged scales in these inherently thin heterogeneous materials. The results also show that the highly porous surface region (amounting up to 20% of the thickness) significantly reduces the through-plane electrical/thermal conductivity. Overall, good agreement is found with previous experimental data of virtually uncompressed CFPs when approximately the full thickness is considered.

Keywords: carbon-fiber paper; effective properties; representative elementary volume; modeling; X-ray tomography; lattice Boltzmann method

1. Introduction

Carbon-fiber papers (CFPs) are an integral component of numerous energy conversion and storage technologies, including gas diffusion layers (GDLs) in polymer electrolyte membrane fuel cells (PEM fuel cells) [1–10], cathode GDLs in PEM electrolyzers [11,12] and metal-air batteries (MABs) [13,14], and electrodes in redox flow batteries (RFBs) [15–17]. CFPs must fulfill several critical functions such as providing adequate mechanical support to the membrane electrode assembly (MEA), a transport pathway for reactants/products through its pore volume, and electrical and thermal conductivity through its solid fibrous structure [10,18–20]. In RFBs, they have the added functionality of providing a reactive surface area [17,21–23]. On the way to broad commercialization, a thorough understanding of the mass, charge and heat transport properties of these materials is crucial to achieving improved performance and durability [2,18,19].

CFPs are thin, highly porous composite materials made of polyacrylonitrile (PAN)-based carbon fibers (diameter $\sim 6 - 12 \mu\text{m}$), usually connected by a carbonaceous binder. If necessary, a hydrophobic polytetrafluoroethylene (PTFE) coating can also be added to enhance removal of product liquid water [10,20]. A variety of manufacturers produce CFPs, including Toray® Industries, SIGRACET® SGL Carbon Group, Freudenberg® and Mitsubishi Rayon Corporation® [24]. The porosities and thicknesses of commercial CFPs are in the range of 0.6-0.9 and 100-400 μm , with a mean pore radius in the order of tens of micrometers [19,20]. CFPs typically show high anisotropy between the in-plane (IP) and through-plane (TP) directions due to the predominant arrangement of carbon fibers in the material plane. Moreover, properties can vary within the material plane, where the machine and cross-machine directions can be distinguished due to the preferential orientation of fibers that arise from the manufacturing process [10,25,26].

Modeling the various coupled transport processes that occur in CFPs is one of the key tools used to design novel materials and optimize operation of the above-mentioned devices [2,27,28]. However, there are several approaches to achieve this modeling. The

traditional technique is to use the macro-homogeneous continuum approximation, which treats the porous medium as a homogeneous domain with effective transport properties [2,29]. Examples of effective properties are the permeability used in Darcy's law, the tortuosity factor used to correct Fick's law of diffusion, or the effective electrical and thermal conductivities used in Ohm's and Fourier's laws [2,18,19,30,31]. Continuum formulations are derived upon the assumption of a representative elementary volume (REV) [32,33]. A REV is defined as the smallest subset of a material that shows similar volume-averaged properties as larger subsets. A REV must therefore satisfy two requirements: (i) it has to be large enough to be a representative volumetric average of the discrete microstructure; and (ii) it has to be small enough to not be affected by any large-scale heterogeneity of the porous medium. Additionally, a REV should be significantly smaller than any characteristic length of the problem at hand to ensure that its boundary region is small compared to the size of the modeled domain. The above requisites should be satisfied for all volume-averaged quantities (e.g., porosity, saturation and effective properties) to be confident that the scenario under study can be rigorously described using the continuum approach.

The continuum hypothesis is generally valid for geological applications in pseudo-infinite domains, such as flow in rocks and soils [32,33]. Researchers in these disciplines are concerned that sub-samples used for testing are not too small, being several orders of magnitude smaller than the geologic formation, and that they represent meaningful volumetric averages. If necessary, spatially-varying transport properties can also be incorporated to account for any macroscopic heterogeneity above the REV scale. However, CFPs represent the opposite limit: being so thin allows one to test and model the entire domain (at least in the TP direction), but the question then arises whether the microstructural randomness of the material allows for a definition of a REV within such thin materials, which barely spans 10-20 times its mean pore size across the thickness [18–20,34]. In other words, if the characteristic sizes of the pore-scale features are of the same order of the sample, then there will be a jagged distribution of local quantities and

fluxes that can impact the accuracy of continuum models. This means that a highly spatially-resolved solution of a macro-homogeneous model is not realistic at all since, for example, the concentration of a gas species cannot exist in the solid phase, yet the model would predict a smooth and continuous distribution. Furthermore, the arrangement of the surface region or the presence of defects can affect the overall flux and distribution in layered assemblies. In fact, the relative intrusion between the CFP substrate and the neighboring micro-porous layer (MPL) in PEM fuel cell electrodes, or the presence of layer-layer gaps are challenging to incorporate into continuum models although those are extremely important [2,19,35–42].

The issue of the existence of a REV in CFPs has been considered and evaluated to some extent in previous work, but a rigorous, quantitative error analysis has been lacking, including effects of various REV sizes and morphologies. One of the first works to present an open discussion on the topic was presented by Rebai and Prat [43]. They compared the water saturation profiles predicted by a Darcian continuum two-phase model with those of a pore-network model (PNM), and found that conventional continuum models offer poor predictions of water distribution. The main reasons for this are: (i) the lack of scale separation between the system size (i.e., the thickness) and the REV size over which effective properties are supposed to be defined in the continuum approach, and (ii) the fact that the invasion regime is dominated by capillary effects. Roth et al. [44] examined the water distributions in a running PEFC using X-ray computed tomography (X-CT) to determine the in-plane representative elementary area (REA) of a CFP. They observed that the water distribution pattern is highly impacted by the microstructure of the material, and that the REA can be different under dry and wet conditions depending on the saturation level, s (0.5 mm^2 (dry, $s = 0\%$) vs. $0.35\text{-}0.6 \text{ mm}^2$ ($s = 42 - 49\%$) and $1.35\text{-}1.6 \text{ mm}^2$ ($s = 22 - 25\%$)). Accordingly, they stated that the structural REV (i.e., determined based on geometric quantities) is not enough to fully derive the water distribution, and emphasised the need to determine the REA in terms of transport properties. More recently, Qin and Hassanizadeh [45,46] presented a formulation to

model two-phase flow and solute transport through a stack of thin porous layers. In their approach, porous media were treated as a stack of 2D interacting continua using macroscale conservation equations expressed as a function of thickness-averaged properties. However, no further developments of this model have been reported so far due to some limitations of the method, such as the impossibility to determine TP gradients or the considerable number of unknown parameters. García-Salaberri et al. [18,19] examined the interplay between diffusive transport and water saturation by combining the lattice Boltzmann method (LBM) with X-CT images of partially-saturated CFPs. They showed that CFPs are prone to suffer from finite-size effects, so the blockage of water on gas diffusion cannot be characterized as a function of only average saturation, as it is typically done. The distribution and arrangement of water across thin CFPs have major effects on its diffusive transport properties. Zenyuk et al. [20] used X-CT images to determine the REA of various dry commercial CFPs by examining their pore size distributions. They concluded that domains of around $1 \times 1 \text{ mm}^2$ in the material plane accurately represent the pore space.

The above review clearly illustrates the long-term debate posed about the validity of the continuum assumption to model CFPs, which still remains the most extensively used approach found in the literature [29]. This is understandable given the low computational cost and widespread utilization of continuum models in engineering software, along with the complexities introduced by the development of hybrid models (continuum-PNM or continuum-LBM) in a standardized and versatile way [47–52]. Nevertheless, the source of error incurred in the predictions of continuum models is largely unknown, and a quantification of the consequences is yet to be addressed. The vast body of work presented in the modeling literature has shown that macro-homogeneous models can be conveniently configured to describe overall performance and trends; however, guiding the construction of MEAs, predicting localized effects such as degradation, and diagnosing performance problems demands the development of more advanced multiphysics, multiphase and multiscale models; something that may not be achievable from an

exclusively macro-homogeneous perspective [27].

To the authors' knowledge, no work has rigorously analyzed the definition of a REV in thin CFPs considering several effective transport properties simultaneously. In recent years, it has become increasingly common to model transport in porous media at the pore scale. This has been spurred by the simultaneous proliferation of benchtop X-CT devices and relentless growth of desktop computing power. Such simulations are conducted by solving the transport equations on the voxel image of the porous medium as the computational mesh. This approach provides direct insight into the impact of the microstructure on transport processes, reducing the dependence of the model on parameters that are difficult to measure experimentally (see, e.g., [8,18–20,30,53] and references therein). In this paper, relevant dry transport properties of four commercial CFPs, namely mass diffusivity, permeability and electrical/thermal conductivity, are examined by performing LBM simulations on X-CT images of CFPs of different types. The effective properties in both the TP and IP directions are analyzed due to the anisotropic nature of CFPs. In particular, the aim of the work is three-fold: (i) to compare the results computed on full-size samples with previous experimental data; (ii) to assess the application of the REV concept to CFPs; and (iii) to examine the effect of TP regional characteristics (core vs. surface region) on transport phenomena.

2. Methods

2.1. Materials

Four CFPs from two different manufacturers were examined: untreated and 10 wt% PTFE-treated Toray® TGP-H-120, SIGRACET® SGL 35 AA and SIGRACET® 25 AA (i.e., untreated and without a coated MPL). This set of widely used CFPs include samples with different fabric, thickness and PTFE treatment (see Table 1).

2.2. X-Ray Tomography

X-ray tomography images were acquired at beamline 8.3.2, Advance Light Source (ALS), Lawrence Berkeley National Lab. Details on the experimental set-up, the reconstruction of the image stacks and the algorithm used to segment the images can be found elsewhere [19,20], here we describe only important experimental procedure for this study. X-ray tomograms of dry, uncompressed, circular-shaped CFPs were acquired with a 3.5 mm field of view using a spatial resolution of 1.3 $\mu\text{m}/\text{voxel}$. Domains were then cropped from the center of the image stacks to remove any edge effect present in the region adjacent to the sample holder. The resulting TGP-H-120 CFPs used for simulation had an in-plane extent of 1.56×1.56 mm², including a thickness of 276 μm to eliminate interferences with adjacent elements present in the set-up. In addition, two full-thickness samples ($\delta_{\text{ft}} = 367 \mu\text{m}$) were selected with an extent of 0.975×0.975 mm² and 0.78×0.78 mm² for untreated and PTFE-treated TGP-H-120, respectively. As for SGL CFPs, full-thickness samples with an extent of 2×2 mm² were straightforwardly extracted since no artifacts were found in the surface region (SGL 35 AA: $\delta_{\text{ft}} = 350 \mu\text{m}$, SGL 25 AA: $\delta_{\text{ft}} = 195 \mu\text{m}$).

In general, it is challenging to differentiate PTFE from carbon fibers and binder due to their similar X-ray absorption characteristics [54]. Hence, fibers, binder and PTFE were treated as a single solid phase here, except for the SGL samples where an improved segmentation process enabled differentiation of binder from fibers. The additional information provided by the binder segmentation was used to discuss results qualitatively, but no quantitative differentiation was introduced in the simulation campaign. A small overlap between the threshold values for binder and fibers was considered to capture more of the desired phase in the SGL samples. The threshold values for binder and fibers respectively, as determined by visual comparison to the gray-scale images, where 90–130 and 120–255 for SGL 35 AA; and 85–140 and 130–255 for SGL 25 AA. The open binary operation in Fiji [55] was then used to remove small clusters of pixels (presumed to be

the undesired phase). Lastly, Fiji's close binary operation was used to fill small gaps of pixels (presumed to be the desired phase). Both binary operations were performed with five iterations and a neighbor count of four. These values were determined by trial-and-error and visually comparing the results to the gray-scale images. Figures S1 and S2 in Supplementary Material show the segmentation examples for SGL 35 AA and SGL 25 AA CFPs, respectively.

Table 1: Comparison of the thickness (δ_{ft}), porosity (ε) and mean pore diameter (d_p) of the four CFPs under study with previous data reported in the literature. The structural properties were extracted from the widest full-thickness samples.

CFP	Thickness, δ_{ft} [μm]	Reported [μm]	Porosity, ε [-]	Reported [-]	Mean pore diameter, d_p [μm]	Reported [μm]
TGP-H-120 (0 wt%)	367	370 [56]	0.75	0.76 [56]	30.3	≈ 30 [19]
TGP-H-120 (10 wt%)	367	362 [56]	0.7	0.73 [56]	27.5	≈ 30 [19]
SGL 35 AA	350	300 [56], 333 [20]	0.84	0.88 [56], 0.82 [20]	60.4	60 [20]
SGL 25 AA	195	191 [56], 192 [20]	0.81	0.88 [56], 0.81 [20]	60.9	64 [20]

Table 1 compares the thickness, porosity and mean pore diameter obtained from the X-CT images with previous data reported for virtually uncompressed samples [19,20,56]. Porosity was determined as the ratio of void voxels to total voxels, while the pore diameter was determined using the local thickness plugin in Fiji. For every void voxel, this tool computes the largest spherical kernel that fits inside the void space and encompasses the voxel; an appropriate approach for CFPs where pore bodies are not easy to identify [54,57]. The properties are in good agreement with the data of García-Salaberri et al. [19], Zenyuk et al. [20] and Rashapov et al. [56]. The porosity of SGL 35/25 AA ($\varepsilon_{sgl} = 0.84/0.81$) is around 10% higher than that of untreated TGP-H-120 ($\varepsilon_{tgp} = 0.75$), while the mean pore diameter is nearly double ($d_{p,sgl} = 60.4/60.9 \mu\text{m}$ vs. $d_{p,tgp} = 30.3 \mu\text{m}$). The addition of PTFE reduces the porosity of TGP-H-120 by 7% ($\varepsilon_{tgp} = 0.75$ vs. $\varepsilon_{tgp, ptfe}$

$= 0.7$) and the mean pore diameter by 9% ($d_{p, \text{tgp}} = 30.3 \mu\text{m}$ vs $d_{p, \text{tgp}, \text{ptfe}} = 27.5 \mu\text{m}$). The higher porosity of SGL CFPs can be visualized in Figure 1. A bimodal pore size distribution composed of intra-binder (small) and inter-fiber (large) pores is found in SGL CFPs, resulting in a more irregular and heterogenous microstructure [20]. This is particularly clear for SGL 25 AA due to its higher volume fraction of binder ($\approx 13\%$) compared to SGL 35 AA ($\approx 7\%$). In contrast, TGP-H CFPs show a more regular microstructure with an unimodal pore size distribution, given that the binder is relatively smooth and practically non-porous [58].

Figure 1: (upper plot) 3D segmented images of the full-thickness CFPs. The binder distribution is shown in red for the SGL samples. (lower plot) Area-averaged porosity profiles in the TP and IP directions, ε_z and ε_x , respectively. Sample dimensions: untreated TGP-H-120 ($0.975 \times 0.975 \times 0.367 \text{ mm}^3$), PTFE-treated TGP-H-120 ($0.78 \times 0.78 \times 0.367 \text{ mm}^3$), SGL 35 AA ($1.04 \times 1.04 \times 0.35 \text{ mm}^3$), SGL 25 AA ($1.04 \times 1.04 \times 0.195 \text{ mm}^3$).

The lower plots of Figure 1 show the area-averaged porosity profiles of the different CFPs. Strong regional changes of the porosity are observed in the TP direction, whereas in the IP direction it varies stochastically around the mean [19,59,60]. The wider fluctuations of the porosity observed for SGL 25 AA in the in-plane direction can be attributed to the larger volumetric fraction of binder present in this thin CFP. Two regions can be identified in the TP direction: a central core region (CR) where the porosity varies due to the random arrangement of the fibers, sandwiched between two highly porous surface regions (SR) where the solid phase gradually vanishes. The contrast between the core and surface regions is sharper in thick CFPs, such as TGP-H-120 and SGL 35 AA, where the preferential accumulation of binder and PTFE in the transition region leads to a local minimum in the porosity profile [59,60]. However, for thin CFPs, such as SGL 25 AA, the transition region cannot be recognised. In this case, the surface region is roughly identified as the highly porous region external to the denser core region. The surface region can amount up to 20% of the material thickness and is particularly sensitive to compression owing to its lower stiffness [61–64]. The ratios between the average porosities of the surface and core regions labeled in Figure 1 are: 1.17 for untreated and PTFE-treated TGP-H-120, 1.04 for SGL 35 AA, and 1.22 for SGL 25 AA. Among them, SGL 35 AA shows the lowest ratio due to the elevated porosity of the internal core region.

2.3. Lattice Boltzmann Method

Effective transport properties (mass diffusivity, permeability and electrical/thermal conductivity) were computed using the LBM on the $1.3 \mu\text{m}$ voxel-sized images. Further details of the model set-up can be found elsewhere [18,19]. The computational models were implemented using the built-in capabilities of the parallel open-source LBM solver Palabos [65]. D3Q7 and D3Q19 lattices were used to solve the macroscopic Laplace's and Navier-Stokes equations, respectively, considering a single relaxation time Bhatnagar-Gross-Krook (BGK) collision operator [66]. The evolution equation in index notation of the particle distribution functions $f_\alpha(\mathbf{x}_i, t)$ at location $\mathbf{x}_i$ and time t can be written as:

$$f_{\alpha}(\mathbf{x}_i + \mathbf{c}_{\alpha}\Delta t, t + \Delta t) - f_{\alpha}(\mathbf{x}_i, t) = -\frac{f_{\alpha}(\mathbf{x}_i, t) - f_{\alpha}^{\text{eq}}(\mathbf{x}_i, t)}{\tau} \quad (1)$$

where 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; $\alpha = 0, \dots, 6$ and $\alpha = 0, \dots, 18$ for the D3Q7 and D3Q19 lattices, respectively. The time step, lattice spacing ($\Delta \mathbf{x}_i = \mathbf{c}_{\alpha}\Delta t$) and the relaxation time were fixed to 1 to ensure the stability and accuracy of the numerical scheme [67,68]. The lattice velocities and equilibrium distributions for the D3Q7 and D3Q19 models are given by:

$$\begin{aligned} \mathbf{c}_{\alpha} &= \begin{cases} (0,0,0) & \alpha = 0 \\ (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1) & \alpha = 1, \dots, 6 \end{cases} & f_{\alpha}^{\text{eq}} &= \begin{cases} (1 - 3c_s^2)C & \alpha = 0 \\ (c_s^2/2)C & \alpha = 1, \dots, 6 \end{cases} \\ \mathbf{c}_{\alpha} &= \begin{cases} (0,0,0) & \alpha = 0 \\ (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1) & \alpha = 1, \dots, 6 \\ (\pm 1, \pm 1, 0), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1) & \alpha = 7, \dots, 18 \end{cases} & f_{\alpha}^{\text{eq}} &= \begin{cases} c_s^2 \rho h_{\alpha}^{\text{eq}} & \alpha = 0 \\ (c_s^2/6) \rho h_{\alpha}^{\text{eq}} & \alpha = 1, \dots, 6 \\ (c_s^2/12) \rho h_{\alpha}^{\text{eq}} & \alpha = 7, \dots, 18 \end{cases} \end{aligned} \quad (2)$$

where $h_{\alpha}^{\text{eq}} = [(1 + \mathbf{c}_{\alpha} \cdot \mathbf{u})/c_s^2 - (\mathbf{u} \cdot \mathbf{u})/(2c_s^2) + (\mathbf{c}_{\alpha} \cdot \mathbf{u})/(2c_s^4)]$, C , ρ and $\mathbf{u}$ are the macroscopic concentration, density and velocity, respectively, and c_s is the lattice speed of sound ($c_s^2 = 1/4$ for D3Q7 and $c_s^2 = 1/3$ for D3Q19).

The macroscopic concentration, bulk diffusivity (D^{bulk}) and diffusion flux ($\mathbf{j}$) are related to the mesoscopic variables f_{α} , $\mathbf{c}_{\alpha}$ and τ by [68,69]:

$$C = \sum_{\alpha=0}^6 f_{\alpha}, \quad D^{\text{bulk}} = c_s^2 \Delta t \left(\tau - \frac{1}{2} \right), \quad \mathbf{j} = \left(1 - \frac{1}{2\tau} \right) \sum_{\alpha=0}^6 f_{\alpha} \mathbf{c}_{\alpha} \quad (3)$$

Similarly, the expressions for the macroscopic density, kinematic viscosity (ν) and velocity are [70]:

$$\rho = \sum_{\alpha=0}^{18} f_{\alpha} \quad v = c_s^2 \Delta t \left(\tau - \frac{1}{2} \right), \quad \mathbf{u} = \frac{1}{\rho} \sum_{\alpha=0}^{18} f_{\alpha} \mathbf{c}_{\alpha} \quad (4)$$

Transport properties were determined in the TP direction (z-axis) and one representative IP direction (x-axis). A concentration/pressure differential was prescribed and then the average flux/velocity was computed in the direction of interest i ($i = z$ or $i = x$); Dirichlet boundary conditions were implemented using the formulation of Zou & He [71]. The concentration differential in diffusivity/conductivity calculations was arbitrarily set to 1, while the pressure differential in permeability calculations was set small enough so as to ensure that the flow was in the creeping regime ($R_e = u^{\text{avg}} L_i / \nu \ll 1$). At the remaining boundaries of the domain and at the void-solid interfaces, a non-conducting wall boundary condition was imposed using a half-way bounce-back scheme [68].

Simulations were run on the void voxels for transport properties that rely on the gas phase (diffusivity and permeability), while the solid voxels were used in the computations of the electrical and thermal conductivity. The latter assumption was made based on the low electrical and thermal conductivities of air ($k_{\text{air}} \sim 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$, $\sigma_{\text{air}} \sim 10^{-15} \text{ S m}^{-1}$ [72,73]) compared to those of high-modulus PAN-based carbon fibers ($k_f \sim 10 - 10^2 \text{ W m}^{-1} \text{ K}^{-1}$, $\sigma_f \sim 10^4 - 10^5 \text{ S m}^{-1}$ [74]) and graphite ($k_{\text{gr}} \sim 1 - 10^3 \text{ W m}^{-1} \text{ K}^{-1}$, $\sigma_{\text{gr}} \sim 10^2 - 10^5 \text{ S m}^{-1}$ [75]). The worst case is found when comparing the thermal conductivity of air and graphite, but there are still two orders of magnitude of difference. For instance, no significant variations in the thermal conductivity of CFPs between experiments conducted in vacuum and air have been reported in the literature [76]. The values adopted for the bulk electrical and thermal conductivities of the solid phase were: $\sigma^{\text{bulk}} = 10^5 \text{ S m}^{-1}$ and $k^{\text{bulk}} = 100 \text{ W m}^{-1} \text{ K}^{-1}$ for TGP-H-120, and $\sigma^{\text{bulk}} = 6 \times 10^4 \text{ S m}^{-1}$ and $k^{\text{bulk}} = 80 \text{ W m}^{-1} \text{ K}^{-1}$ for SGL CFPs. These properties are similar to those considered in previous works: $\sigma^{\text{bulk}} = 9.5 \times 10^4 \text{ S m}^{-1}$ and $k^{\text{bulk}} = 70 - 120 \text{ W m}^{-1} \text{ K}^{-1}$ [31,76–85]. Note that an exact determination of the bulk properties of the solid phase is challenged by the possible anisotropy of carbon fibers, as well as the differences

that may exist between fibers and binder [80,82]. Nevertheless, the bulk properties used here are considered a good estimation since the main goal of this work is to explore the applicability of the REV rather than a precise determination of transport properties. The effect of PTFE on electrical/thermal conductivity was also not examined due to the inability to distinguish the PTFE coating in the images. Therefore, the results reported here for PTFE-treated TGP-H-120 are only representative of the entire bulk solid phase.

The normalized effective diffusivity (electrical/thermal conductivity) and permeability in the direction of interest i were determined as

$$f_i = \frac{D_i^{\text{eff}}}{D^{\text{bulk}}} = \frac{\left(\iint_A j_i \, dA \right) / A}{D^{\text{bulk}} \Delta C_i / L_i} \quad (5)$$

$$K_i = \frac{\rho v \left(\iint_A u_i \, dA \right) / A}{\Delta p_{g,i} / L_i}$$

where A is the cross-sectional area of the inspected CFP normal to the direction under study, ΔC_i and $\Delta p_{g,i}$ are the prescribed concentration (electronic potential/temperature) and pressure differential, L_i is the length of the CFP in the i -direction, and $j_i = -D^{\text{bulk}} \partial_i C$ and u_i are the i -component of the diffusion flux (electrical current/conduction flux) and the velocity, respectively.

Note that in Eq. (5) D_i^{eff} and D^{bulk} can be simply interchanged by σ_i^{eff} and σ^{bulk} , or k_i^{eff} and k^{bulk} , since mass diffusion and electron/heat conduction are all described by Laplace's equation (either, Fick's, Ohm's or Fourier's law), the only difference being the domain (void or solid) used for the computations. Using the normalized quotient f_i , calculations for the electrical/thermal conductivity were performed only once, and the results were then scaled by the corresponding bulk value; diffusivity was always kept in dimensionless

form for presentation purposes. Simulations were run until steady state was achieved on several of the supercomputing clusters managed by Calcul Québec and Compute Canada (Briarée, Colosse, Guillimin and Mp2) [86], varying the number of processor between 48 and 160. Details on the testing and validation of the models implemented in Palabos can be found in Supplementary Material and Refs. [19,65,70]. Figure 2 shows an illustrative example of the computed concentration, velocity and electronic potential/temperature fields corresponding to 10 wt% PTFE-treated TGP-H-120.

Figure 2: Example of concentration, average velocity and electronic potential/temperature fields, corresponding to calculations of the TP and IP effective diffusivity, permeability and effective electrical/thermal conductivity on a $1.2 \times 1.2 \times 0.28 \text{ mm}^3$ sample of 10 wt% PTFE-treated TGP-H-120.

3. Discussion of Results

3.1. Comparison with Experimental Data: Full-Sample Results

The effective transport properties computed on the widest full-thickness samples are compared to published experimental data in Figures 3 and 4 [10,23,25,26,58,76,85,87–122]. The results considering mostly the core region of the material are also included to indicate the extent of the variations that may exist between simulated and tested samples. Figure 3 shows the results for the diffusivity and permeability, while Figure 4 shows the results for the electrical and thermal conductivity. In all cases, the transport properties are represented with bar graphs against average data of nearly uncompressed CFPs from several literature sources. The only exception is the mass diffusivity, where the results are plotted as a function of porosity due to the larger availability of data of compressed samples. The corresponding quantitative comparison is listed in Table 3, along with the collected references (see Appendix A).

As expected, overall good agreement is found between the numerical and experimental data since the simulations conducted on the full sample are equivalent to experimental protocols. The deviations with respect to the collected data can be attributed to the assumptions made in the model and/or imprecisions in the measurements, as well as dissimilarities between the examined samples. For example, differences can arise due to the compression ratio, the extent of the domain in the material plane or the batch-to-batch manufacturing process. As a matter of fact, considerable variations are found in some cases among the data presented by different authors (e.g., thermal conductivities ranging from 0.5 to $1.8 \text{ W m}^{-1} \text{ K}^{-1}$ were reported for TGP-H CFPs [76,107,110,111,115]). For the purpose of this work, the good agreement found in average terms was considered fair enough so as to validate the methodology employed. An explicit description of the samples and conditions used for testing should be considered for a one-to-one comparison, but this was out of the scope of the present study.

As found in previous studies (see [18,19] and references therein), the effective diffusivity of the four CFPs is lower than that predicted by random fiber models, such as the one by Tomadakis and Sotirchos [123]. The differences are larger in the TP direction due to the stronger impact of the complex fibrous structure across the finite thickness, leading to correlations of the form $f_{tp} = \varepsilon^{3.8}$ and $f_{ip} = \varepsilon^{2.5}$ for the TP and IP directions, respectively. The diffusivity and permeability of SGL CFPs are higher compared to TGP-H CFPs owing to their higher porosity and larger mean pore size ($f_{sgl}/f_{tgp} \sim 1.4$, $K_{sgl}/K_{tgp} \sim 4.7$). Besides, the PTFE treatment reduces the diffusivity and permeability of TGP-H-120 because of the loss of pore volume and the increased tortuosity of transport pathways ($f_{tgp,ptfe}/f_{tgp} \sim 0.8$, $K_{ptfe}/K \sim 0.8$). The gas-phase transport properties of the different CFPs are sorted in decreasing order as follows: SGL 35 AA > SGL 25 AA > untreated TGP-H-120 > PTFE-treated TGP-H-120. All of them show higher gas-phase properties in the IP direction due to the predominant orientation of fibers and pores in this direction. The degree of anisotropy of diffusivity and permeability is between 1.3 and 3 ($f_{ip}^{eff}/f_{tp}^{eff} \sim 1.5 - 2$, $K_{ip}/K_{tp} \sim 1.3 - 3$), being the anisotropy of SGL CFPs somewhat lower than that of TGP-H CFPs [120].

Figure 3: TP and IP normalized effective diffusivity ($f_{tp/ip}$) and permeability ($K_{tp/ip}$) of the widest full-thickness samples compared to previous experimental data reported in the literature (L). The results including (FT) and mainly excluding (mostly CR) the surface region are shown by white and black bars, respectively. The error bars indicate the range of variation of the collected experimental data (see Table 3). The extent and porosity of the samples incorporating the full thickness/mainly the core region are as follows: untreated TGP-H-120 ($0.975 \times 0.975 \times 0.365/0.321 \text{ mm}^3$, 0.75/0.72), PTFE-treated TGP-H-120 ($0.78 \times 0.78 \times 0.365/0.321 \text{ mm}^3$, 0.7/0.67), SGL 35 AA ($2 \times 2 \times 0.348/0.287 \text{ mm}^3$, 0.84/0.83), SGL 25 AA ($2 \times 2 \times 0.194/0.163 \text{ mm}^3$, 0.81/0.78).

Unlike gas-phase transport, Figure 4 shows that the electrical and thermal conductivities of SGL CFPs are significantly lower than that of TGP-H CFPs ($\sigma_{sgl}^{\text{eff}}/\sigma_{tgp}^{\text{eff}} \sim 0.2$, $k_{sgl}^{\text{eff}}/k_{tgp}^{\text{eff}} \sim 0.3$). Comparing the two SGL CFPs, SGL 25 AA has a larger electrical and thermal conductivity due to its lower porosity and higher volume fraction of binder. The electron and heat transport of the CFPs is sorted in decreasing order as follows: untreated TGP-H-120 > SGL 25 AA > SGL 35 AA. Both fabrics display a strong anisotropy to current and heat conduction, being the electrical/thermal conductivity one order of magnitude larger in the IP direction ($\sigma_{ip}^{\text{eff}}/\sigma_{tp}^{\text{eff}}, k_{ip}^{\text{eff}}/k_{tp}^{\text{eff}} \sim 10 - 50$). The large anisotropy of solid-phase properties arises from

the preferential arrangement of carbon fibers in the material plane, so that the mesh-like fibrous structure approximately behaves as a parallel-resistor network in the IP direction. In contrast, TP conduction is closer to a series-resistor network, in which transport is restrained by the infrequent contacts through the fiber and binder structure [31,82].

Figure 4: TP and IP effective electrical conductivity ($\sigma_{tp/ip}^{eff}$) and thermal conductivity ($k_{tp/ip}^{eff}$) of the widest full-thickness samples compared to previous experimental data reported in the literature (L). PTFE-treated TGP-H-120 was excluded from the analysis due to the impossibility to distinguish the PTFE coating. See caption to Figure 3 for further details.

3.2. Representative Elementary Volume (REV)

A massive computational campaign, consisting of over 2500 simulations, was performed to evaluate the existence of a REV. Multiple sub-domains with different widths ($L_x = L_y \approx 0.15 - 2$ mm) and thicknesses ($L_z/\delta_{ft} \approx 0.1 - 0.99$) were analyzed for each transport property. Figures 5 and 6 show the results of the REV analysis corresponding to untreated TGP-H-120, including the four properties in both the TP and IP directions. The results for the remaining CFPs are presented in Appendix A using a similar representation. For a

given thickness, L_z , the property of interest is plotted as a function of the sub-sample width, L_x . This representation results more appropriate for finite-thickness CFPs, allowing one to observe independently the effect of heterogeneities in the material plane (varying width, indicated by the x-axis) and across the material (varying thickness, indicated by each set of markers). The sub-samples were taken concentrically to the main sample, so that thin sub-samples lie in the core region and eventually include the surface region when the thickness is increased ($L_z/\delta_{ft} \geq 0.8$).

The domain width necessary to obtain virtually invariable transport properties is in the order of 1-2 mm. This result is in agreement with the microstructural analysis conducted by Zenyuk et al. [20], as well as the studies carried out under two-phase conditions by Roth et al. [44] and Santamaria et al. [124]. The IP representative size is larger for SGL CFPs (~ 1.75 mm) compared to TGP-H CFPs (~ 1.25 mm) owing to their more irregular microstructure. For instance, effective properties of SGL CFPs do not completely stabilize in the examined width range, including sub-samples of up to 2 mm width. This length scale is comparable to the rib/channel width used in PEM fuel cells, RFBs and other devices, which is usually around 1 mm. Hence, the boundary condition imposed by the rib/channel pattern on transport processes can be below or at the same scale of the representative length of CFPs in the material plane. Consequently, a continuum model including more than, say, a couple of REV for each rib-channel unit cell would be spatially over-resolved.

Figure 5: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity ($\sigma_{tp}^{\text{eff}}, k_{tp}^{\text{eff}}$) on varying-size sub-samples of untreated TGP-H-120. The x-axis shows the sub-domain width ($L_x = L_y$), while the colored markers show the sub-domain thickness (L_z). The relative thickness (L_z/δ_{ft}) is indicated in brackets. The green-colored region indicates the width range for which transport properties are virtually invariable for a given thickness. The extrapolated data that were not computed in the full-size sample are shown by gray-colored markers. The inset shows the variation of the property of interest for the widest sample as a function of the thickness.

As for the TP direction, no representative length scale can be clearly identified. It is impossible to find a piece of material across the thickness for which the complete set of transport properties settles around a single value. Substantial variations are observed for properties that rely on either the gas phase, diffusivity and permeability, or the solid phase, electrical and thermal conductivity. As shown in Section 3.1, the set of transport properties only approaches previous experimental data when almost the full thickness of the material is taken into account. This holds for thin CFPs as SGL 25 AA ($\delta_{ft} \approx 200 \mu\text{m}$) but also for thicker CFPs as TGP-H-120 and SGL 35 AA ($\delta_{ft} \approx 300 - 400 \mu\text{m}$). Similar

results were obtained in the numerical work of Gao et al. [125] when examining the impact of sample size on the permeability of a carbon-fiber paper and cloth.

Figure 6: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity ($\sigma_{ip}^{\text{eff}}, k_{ip}^{\text{eff}}$) on varying-size sub-samples of untreated TGP-H-120. See caption to Figure 5 for further details.

Putting all together, it can be stated that a REV cannot be defined in CFPs, since the basic tenets of volume-averaging are not met in these inherently thin heterogeneous materials [18,19]. No distinctive length scale significantly smaller than the thickness can be established for which transport properties are fully representative of the microstructure. That is, there is not a well-defined separation between pore and macroscopic/volume-averaged scales. This has important implications on modeling of CFPs since it also applies in the reverse direction: effective properties measured from a

full sample cannot be assumed to prevail in each sub-region of the examined domain. Discretizing the domain and applying a globally measured property to all elements will produce erroneous results in the spatial distributions. This situation is further challenged by the arrangement of the surface region and defects in layered assemblies, since they play an important role on interfacial phenomena. The coupling between interfacial finite-size effects and the lack of separation of scales undermines the definition of a REV even further. Therefore, the continuum and smooth solution offered by macro-homogeneous models is not realistic, even if the model is conveniently tuned to predict suitable overall fluxes across the porous medium.

On the experimental side, diagnostic and visualization tools have repeatedly shown an intimate relationship between spatial distributions and microstructural heterogeneities of CFPs. This fact has been mainly stressed under two-phase conditions in the fuel cell community (see, e.g., [18,19,126–133]), and under single-phase conditions in the context of RFBs [21,134]. However, the correct modeling of CFPs is still a source of debate and further work is required. In particular, effort is needed (1) to quantify and assess the error introduced in the calculations of macro-homogeneous models, and (2) to develop proper modeling strategies for CFPs that are computationally efficient, such as including spatially-varying properties within the modeled mesh. Inverse modeling techniques like global upscaling [135] might be used to determine the pseudo-effective transport properties at the local block level, thus providing a direct connection between pore-scale and volume-averaged simulations. Alternatively, an efficient combination of volume-averaged and pore-network models is another option to improve the modeling capabilities within a CFD framework [51].

The TP variations of the transport properties are further examined in Figure 7, where the normalized properties of the four CFPs under study are plotted as a function of porosity. Only data corresponding to sub-samples thicker than $90\text{ }\mu\text{m}$ from the widest full-thickness samples were taken into account in order to get meaningful relationships [18,125].

Permeability was normalized with the cross-sectional area of the pores, measured perpendicular to the direction of interest. That is, the average pore cross-section in the material plane for TP transport ($A_{p,tp} = l_{ip}^2$) and the average pore cross-section in the across-the-thickness plane for IP transport ($A_{p,ip} = l_{ip}l_{tp}$). The pore sizes were determined from the average chord lengths l_{tp} and l_{ip} using the algorithm described in [18], leading to the following values: $A_{p,tp} = 3.2 \times 10^3 \mu\text{m}^2$ and $A_{p,ip} = 1.8 \times 10^3 \mu\text{m}^2$ for untreated TGP-H-120 ($l_{tp} = 31.5 \mu\text{m}$, $l_{ip} = 56.8 \mu\text{m}$), $A_{p,tp} = 3 \times 10^3 \mu\text{m}^2$ and $A_{p,ip} = 1.7 \times 10^3 \mu\text{m}^2$ for PTFE-treated TGP-H-120 ($l_{tp} = 31.3 \mu\text{m}$, $l_{ip} = 54.8 \mu\text{m}$), $A_{p,tp} = 1.2 \times 10^4 \mu\text{m}^2$ and $A_{p,ip} = 5.2 \times 10^3 \mu\text{m}^2$ for SGL 35 AA ($l_{tp} = 46.4 \mu\text{m}$, $l_{ip} = 112.1 \mu\text{m}$), $A_{p,tp} = 1.1 \times 10^4 \mu\text{m}^2$ and $A_{p,ip} = 3.3 \times 10^3 \mu\text{m}^2$ for SGL 25 AA ($l_{tp} = 30.8 \mu\text{m}$, $l_{ip} = 107.6 \mu\text{m}$). As can be seen, the normalized properties correlate quite well in the porosity range $\varepsilon = 0.65 - 0.9$ despite the microstructural differences among the CFPs. The trends are similar to experimental data reported for compressed samples [20,58,76,93,94,102,103,111,118,122,136], showing a net increase of gas-phase properties (diffusivity and permeability) and a decrease of solid-phase properties (electrical and thermal conductivity) with porosity. Similar findings were observed by García-Salaberri et al. [18] when analyzing the effective diffusivity of meaningful pieces of TGP-H-120. The normalized transport property with the largest relative variation is the TP electrical/thermal conductivity, for which it was necessary to introduce a percolation threshold at $\varepsilon \approx 0.95$ to capture the low conductivities present there. Excluding this fact, transport properties in both the TP and IP directions vary almost linearly in the porosity range considered here. This result is in agreement with Holzer et al. [120], who showed that the change of the transport properties of SGL 25 BA is practically linear in the range $\varepsilon = 0.58 - 0.74$.

Figure 7: Predicted correlations for (upper plot) normalized effective diffusivity, $f_{tp/ip}$, (middle plot) normalized permeability, $K_{tp/ip} A_p^{-1}$, and (lower plot) normalized effective electrical/thermal conductivity, $f_{solid, tp/ip}$, as a function of porosity, ε . Only sub-samples thicker than 90 μm extracted from the widest full-thickness samples were included in the analysis. See text for details.

3.3. TP Regional Characteristics: Effect of Surface Region

In this section, the effect of the surface region shown in Figures 3 and 4 is further explored. CFPs are not only too thin to be accurately treated as a continuum, but they are also too heterogeneous since the surface region constitutes a significant portion of the total domain. Table 2 summarizes the percentage variations of the thickness, porosity and

transport properties obtained when including or not including the surface region in the calculations. The effect of the surface region is to increase the effective diffusivity and permeability, and to decrease the effective electrical/thermal conductivity. SGL 35 AA shows the lowest relative variation because the high porosity of the core region diminishes the effect of the surface region (see Figure 1). In terms of gas-phase transport, the impact of the surface region is in general higher on IP properties since it acts as a low gas transport resistance region connected in parallel to the denser core region. This is particularly evident for the IP permeability, where changes of up to 35% are observed. For the solid-phase transport properties (electrical/thermal conductivity), the impact of the surface region is much stronger, leading to variations of more than 200% in the TP direction. Such hypersensitivity arises from the serial arrangement of the low-conducting surface region to charge and heat transport in this direction. Consequently, the bottleneck effect created by the surface region dramatically reduces the flux across the material. Similar results were reported by Yablecki and Bazylak [78] using an analytical model for the thermal conductivity of CFPs based on X-CT images.

Table 2: Relative variation of the thickness, porosity and TP/IP effective transport properties (normalized diffusivity, permeability, and electrical/thermal conductivity) when the surface region of the material is included (FT) or mainly excluded (mostly CR). The percentage changes were determined with respect to the domain mostly excluding the surface region. See caption to Figure 3 for further details.

CFP	Thickness [%]	Porosity [%]	Normalized diffusivity TP/IP [%]	Permeability TP/IP [%]	Electrical/thermal conductivity TP/IP [%]
TGP-H-120 (0 wt%)	12%	4%	7.1/9.61	8.6/31.8	-152.9/-10.7
TGP-H-120 (10 wt%)	12%	4%	9.1/15.5	7.3/35.3	-
SGL 35 AA	17%	1%	2.2/2.9	7.0/9.8	-25/-3.3
SGL 25 AA	16%	4%	7.9/4.5	18.9/28.6	-214.3/-11.6

The re-arrangement of the surface region under compression and its effect on transport properties help us to understand the variability in the data reported by different authors and collected in Section 3.1. This effect is especially critical for the TP electrical/thermal

conductivity. Moreover, the impact of the surface region serves to explain some controversial behaviors, such as the counter-intuitive increase of the thermal conductivity of MPL-coated CFPs compared to CFP substrates alone [137–139]. This fact can be attributed to the interplay between compression and intrusion of the MPL ($k_{\text{mpl}}^{\text{eff}} \sim 10^{-1} \text{ W m}^{-1} \text{ K}^{-1}$) into the low-conducting surface region ($k_{\text{air}} \sim 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$), which increases the thermal conductivity of the dual-layered porous media. Nevertheless, additional factors, such as the nano-porosity of the binder and/or nano-scale contact details [76,83,121,122,140], should also be examined before drawing definitive conclusions.

4. Conclusions

Simulations of various transport processes were carried out on micro X-ray computed tomography (X-CT) images using the lattice Boltzmann method to assess the existence of a representative elementary volume (REV) and analyze the regional characteristics (core vs. surface region) of carbon-fiber papers (CFPs). This is relevant information for modelers, designers and experimentalists, who rely on the validity and applicability of macro-homogeneous continuum models to predict cell performance, forecast durability, optimize materials, and diagnose problems. Key transport properties (mass diffusivity, permeability and electrical/thermal conductivity) were examined in both the through- (TP) and in-plane (IP) directions on thousands of sub-samples extracted from four dry, uncompressed CFPs: untreated TGP-H-120, 10 wt% PTFE-treated TGP-H-120, SGL 35 AA and SGL 25 AA.

It was shown that a REV cannot be defined in CFPs due to the lack of a well-defined separation between pore and volume-averaged scales, owing largely to the small thickness of the samples, which is just one order of magnitude or less than the average pore size. The representative length scale in the material plane required to obtain sufficiently invariable volume-averaged transport properties is in the order of 1–2 mm,

which is comparable to the rib/channel width typically used in fuel cells, redox flow batteries and other electrochemical devices. The IP representative size is larger for SGL CFPs compared to TGP-H CFPs (~ 1.75 vs. 1.25 mm) due to their more irregular and heterogeneous microstructure. For instance, effective properties of SGL CFPs did not completely stabilize in domains of up to 2×2 mm². As for the TP direction, it was impossible to identify a length scale for which the complete set of transport properties remains unchanged. The computed effective properties are only similar to reported experimental data if the full thickness of the material is considered. This fact was found to be particularly critical for TP transport properties that rely on the solid phase (electrical and thermal conductivity) due to the bottleneck effect created by the highly porous surface region, which amounts up to 20% of the material thickness. Besides, the interfacial arrangement of the surface region or the presence of defects can affect the overall flux and distribution in layered assemblies, which weakens the definition of a REV even further. The interplay between compression and the surface region also helps to explain the variations found between different authors in previous experimental studies.

In summary, the present work has shown that macro-homogeneous models of CFPs widely used in the literature can lead to non-negligible errors in their predictions. This circumstance may have important consequences in the modeling of electrochemical devices, such as fuel cells and redox flow batteries, either in terms of performance or durability. The development of new self-predictive CFD models adapted to these thin materials warrants further work. Specifically, it is of interest to compare volume-averaged fuel cell model results to direct numerical simulations performed on the actual microstructure of CFPs. This would indicate the magnitude and importance of any error incurred by the macro-homogeneous continuum assumption. On the experimental side, testing protocols suitable for CFPs should be standardized in order to unify the available information. All these considerations will provide a better understanding of the complexities posed by thin, heterogeneous, anisotropic, mixed-wettability CFPs.

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Appendix A

• Comparative table

Table 3: Comparison of computed transport properties (normalized diffusivity ($f_{tp/ip}$), permeability ($K_{tp/ip}$), and electrical and thermal conductivity, ($\sigma_{tp}^{eff}, k_{tp}^{eff}$)) including the full thickness (FT) and mainly excluding the surface region (mostly CR) with previous experimental data reported in the literature.

CFP	Transport property	Value (FT)	Value (mostly CR)	Experimental
TGP-H-120 (0 wt%)	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.28/0.52	0.26/0.47	0.25-0.35 [87-93]/ 0.45-0.6 [58,93]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	0.7/2.2	0.64/1.5	0.5-1.5 [10,94-102]/ 1.0-2.5 [94,98-100,103-106]
	Electrical conductivity, $\sigma_{tp}^{eff} / \sigma_{ip}^{eff} [S\ cm^{-1}]$	8.7/158.6	22.0/175.7	12.5-15.0 [10,85,107,108]/ 124-213 [23,25,26,97,107-109]
	Thermal conductivity, $k_{tp}^{eff} / k_{ip}^{eff} [W\ m^{-1}K^{-1}]$	0.87/15.9	2.2/17.6	0.45-1.8 [76,107,110-113]/ 11.6-21 [107,114,115]
TGP-H-120 (10 wt%)	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.22/0.45	0.2/0.38	0.19-0.3 [87,90,91,93,95,96]/ 0.4-0.55 [58,93]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	0.55/1.7	0.51/1.1	0.7-1.1 [87,95,96,102]/ 0.5-1.5 [104,106]
SGL 35 AA	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.45/0.68	0.44/0.66	0.4-0.6 [92]/ 0.6-0.7 [58]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	4.3/9.2	4/8.3	0.8 ^{a,c} [116], 5.3 ^a [117]/ 4.7-6 ^{a,c} [116]
	Electrical conductivity, $\sigma_{tp}^{eff} / \sigma_{ip}^{eff} [S\ cm^{-1}]$	0.76/44.9	1.0/46.7	0.8-1.2 ^a [118]/ 25-35 ^a [118]
	Thermal conductivity, $k_{tp}^{eff} / k_{ip}^{eff} [W\ m^{-1}K^{-1}]$	0.12/6.0	0.15/6.2	0.14 ^a [119]/ NA
SGL 25 AA	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.38/0.66	0.35/0.63	0.3-0.55 [93]/ 0.4-0.6 [93], 0.6-0.7 [58]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	3.7/5.6	3.0/4.0	3.2 ^b [120], 4.5 ^b [117]/ 3-4 ^{b,c} [120]
	Electrical conductivity, $\sigma_{tp}^{eff} / \sigma_{ip}^{eff} [S\ cm^{-1}]$	1.4/58.2	4.4/64.9	1.5-3.5 [118]/ 25-35 [118], 38.1 [23]
	Thermal conductivity, $k_{tp}^{eff} / k_{ip}^{eff} [W\ m^{-1}K^{-1}]$	0.19/7.7	0.6/8.7	0.2-0.4 [121,122]/ NA
a value reported for SGL 35 BA, b value reported for SGL 25 BA, c computed numerically.				

- 10 wt% PTFE-treated TGP-H-120

Figure A.1: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity (σ_{tp}^{eff} , k_{tp}^{eff}) on varying-size sub-samples of 10 wt% PTFE-treated TGP-H-120. The extrapolated data that were not computed in the full-size sample are shown by gray-colored markers. See caption to Figure 5 for details.

TGP-H-120 (10 wt% PTFE)

IP

Figure A.2: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity (σ_{ip}^{eff} , k_{ip}^{eff}) on varying-size sub-samples of 10 wt% PTFE-treated TGP-H-120. The extrapolated data that were not computed in the full-size sample are shown by gray-colored markers. See caption to Figure 5 for details.

- SGL 35 AA

Figure A.3: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity ($\sigma_{tp}^{\text{eff}}, k_{tp}^{\text{eff}}$) on varying-size sub-samples of SGL 35 AA. See caption to Figure 5 for details.

SGL 35 AA

IP

Figure A.4: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity (σ_{ip}^{eff} , k_{ip}^{eff}) on varying-size sub-samples of SGL 35 AA. See caption to Figure 5 for details.

- SGL 25 AA

Figure A.5: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity (σ_{tp}^{eff} , k_{tp}^{eff}) on varying-size sub-samples of SGL 25 AA. See caption to Figure 5 for details.

Figure A.6: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity (σ_{ip}^{eff} , k_{ip}^{eff}) on varying-size sub-samples of SGL 25 AA. See caption to Figure 5 for details.

Nomenclature

Symbols

A	cross-sectional area [m^2]
C	mass concentration [mol m^{-3}], temperature [K], electronic potential [V]
c	lattice velocity [m s^{-1}]
c_s	lattice speed of sound [m s^{-1}]
D	mass diffusivity [$\text{m}^2 \text{s}^{-1}$]
d	diameter [m]
f	particle distribution function, normalized effective gas-phase diffusivity [-]
f_{solid}	normalized effective solid-phase conductivity [-]
h	mute variable
j	diffusion flux [$\text{mol m}^{-2} \text{s}^{-1}$], conduction flux [$\text{J m}^{-2} \text{s}^{-1}$], current density vector [$\text{C m}^{-2} \text{s}^{-1}$]
K	permeability [m^2]
k	thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]
L	length [m]
l	chord length [m]
p	pressure [Pa]
Re	Reynolds number [-]
s	water saturation [-]
t	time [s]
u	velocity [m s^{-1}]
x	in-plane coordinate [m]
x_i	node position [m]
y	secondary in-plane coordinate [m]
z	through-plane coordinate [m]

Greek letters

α	index
Δ	increment
δ_{ft}	full thickness [m]
ε	porosity [-]
ε_i	area-averaged porosity in i-direction [-]
ν	kinematic viscosity [$\text{m}^2 \text{s}^{-1}$]
ρ	density [kg m^{-3}]
σ	electrical conductivity [S m^{-1}]
τ	dimensionless relaxation time [-]

Subscripts

f	carbon fiber
g	gas phase
gr	graphite
i	direction of interest
ip	in-plane direction
p	pore
tp	through-plane direction

Superscripts

avg	average
bulk	bulk property
eff	effective property
eq	equilibrium

Abbreviations & acronyms

CFP	carbon-fiber paper
CR	core region

FT	full thickness
GDL	gas diffusion layer
IP	in-plane
LBM	lattice Boltzmann method
MAB	metal-air battery
MEA	membrane electrode assembly
MPL	micro-porous layer
PEM	polymer electrolyte membrane
PNM	pore-network model
PTFE	polytetrafluoroethylene
REA	representative elementary area
REV	representative elementary volume
RFB	redox flow battery
SR	surface region
TP	through-plane
X-CT	X-ray computed tomography

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Figures and Tables

Figure 1: (upper plot) 3D segmented images of the full-thickness CFPs. The binder distribution is shown in red for the SGL samples. (lower plot) Area-averaged porosity profiles in the TP and IP directions, ε_z and ε_x , respectively. Sample dimensions: untreated TGP-H-120 (0.975×0.975×0.367 mm³), PTFE-treated TGP-H-120 (0.78×0.78×0.367 mm³), SGL 35 AA (1.04×1.04×0.35 mm³), SGL 25 AA (1.04×1.04×0.195 mm³).

Figure 2: Example of concentration, average velocity and electronic potential/temperature fields, corresponding to calculations of the TP and IP effective diffusivity, permeability and effective electrical/thermal conductivity on a 1.2×1.2×0.28 mm³ sample of 10 wt% PTFE-treated TGP-H-120.

Figure 3: TP and IP normalized effective diffusivity ($f_{tp/ip}$) and permeability ($K_{tp/ip}$) of the widest full-thickness samples compared to previous experimental data reported in the literature (L). The results including (FT) and mainly excluding (mostly CR) the surface region are shown by white and black bars, respectively. The error bars indicate the range of variation of the collected experimental data (see Table 3). The extent and porosity of the samples incorporating the full thickness/mostly the core region are as follows: untreated TGP-H-120 (0.975×0.975×0.365/0.321 mm³, 0.75/0.72), PTFE-treated TGP-H-120 (0.78×0.78×0.365/0.321 mm³, 0.7/0.67), SGL 35 AA (2×2×0.348/0.287 mm³, 0.84/0.83), SGL 25 AA (2×2×0.194/0.163 mm³, 0.81/0.78).

Figure 4: TP and IP effective electrical conductivity ($\sigma_{tp/ip}^{eff}$) and thermal conductivity ($k_{tp/ip}^{eff}$) of the widest full-thickness samples compared to previous experimental data reported in the literature (L). PTFE-treated TGP-H-120 was excluded from the analysis due to the impossibility to distinguish the PTFE coating. See caption to Figure 3 for further details.

Figure 5: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity ($\sigma_{tp}^{eff}, k_{tp}^{eff}$) on varying-size sub-samples of untreated TGP-H-120. The x-axis shows the sub-domain width ($L_x = L_y$), while the colored markers show the sub-domain thickness (L_z). The relative thickness (L_z/δ_{ft}) is indicated in brackets. The green-colored region indicates the width range for which transport properties are virtually invariable for a given thickness. The extrapolated data that were not computed in the full-size sample are shown by gray-colored markers. The inset shows the variation of the property of interest for the widest sample as a function of the thickness.

Figure 6: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity ($\sigma_{ip}^{eff}, k_{ip}^{eff}$) on varying-size sub-samples of untreated TGP-H-120. See caption to Figure 5 for further details.

Figure 7: Predicted correlations for (upper plot) normalized effective diffusivity, $f_{tp/ip}$, (middle plot) normalized permeability, $K_{tp/ip} A_{p,tp/ip}^{-1}$, and (lower plot) normalized effective electrical/thermal conductivity, $f_{solid,tp/ip}$, as a function of porosity, ε . Only sub-samples thicker than $90 \mu m$ extracted from the widest full-thickness samples were included in the analysis. See text for details.

Figure A.1: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity ($\sigma_{tp}^{eff}, k_{tp}^{eff}$) on varying-size sub-samples of 10 wt% PTFE-treated TGP-H-120. The extrapolated data that were not computed in the full-size sample are shown by gray-colored markers. See caption to Figure 5 for details.

Figure A.2: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity ($\sigma_{ip}^{eff}, k_{ip}^{eff}$) on varying-size sub-samples of 10 wt% PTFE-treated TGP-H-120. The extrapolated data that were not computed in the full-size sample are shown by gray-colored markers. See caption to Figure 5 for details.

Figure A.3: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity ($\sigma_{tp}^{eff}, k_{tp}^{eff}$) on varying-size sub-samples of SGL 35 AA. See caption to Figure 5 for details.

Figure A.4: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity ($\sigma_{ip}^{eff}, k_{ip}^{eff}$) on varying-size sub-samples of SGL 35 AA. See caption to Figure 5 for details.

Figure A.5: TP normalized effective diffusivity (f_{tp}), permeability (K_{tp}), and electrical and thermal conductivity ($\sigma_{tp}^{eff}, k_{tp}^{eff}$) on varying-size sub-samples of SGL 25 AA. See caption to Figure 5 for details.

Figure A.6: IP normalized effective diffusivity (f_{ip}), permeability (K_{ip}), and electrical and thermal conductivity ($\sigma_{ip}^{eff}, k_{ip}^{eff}$) on varying-size sub-samples of SGL 25 AA. See caption to Figure 5 for details.

Table 1: Comparison of the thickness (δ_{ft}), porosity (ε) and mean pore diameter (d_p) of the four CFPs under study with previous data reported in the literature. The structural properties were extracted from the widest full-thickness samples.

Table 2: Relative variation of the thickness, porosity and TP/IP effective transport properties (normalized diffusivity, permeability, and electrical/thermal conductivity) when the surface region of the material is included (FT) or mainly excluded (mostly CR). The percentage changes were determined with respect to the domain mostly excluding the surface region. See caption to Figure 3 for further details.

Table 3: Comparison of computed transport properties (normalized diffusivity ($f_{\text{tp/ip}}$), permeability ($K_{\text{tp/ip}}$), and electrical and thermal conductivity, ($\sigma_{\text{tp}}^{\text{eff}}, k_{\text{tp}}^{\text{eff}}$)) including the full thickness (FT) and mainly excluding the surface region (mostly CR) with previous experimental data reported in the literature.

Figure 1:

TGP-H-120 (0 wt% PTFE)

TP

Figure 2:

TGP-H-120 (0 wt% PTFE)

IP

Figure 3:

TGP-H-120 (10 wt% PTFE)

TP

Figure 4:

TGP-H-120 (10 wt% PTFE)

IP

Figure 5:

SGL 35 AA

TP

Figure 6:

SGL 35 AA

IP

Figure 7:

SGL 25 AA

TP

Figure 8:

SGL 25 AA

IP

Figure 9:

CFP	Thickness, δ_{ft} [μm]	Reported [μm]	Porosity, ε [-]	Reported [-]	Mean pore diameter, d_p [μm]	Reported [μm]
TGP-H-120 (0 wt%)	367	370 [56]	0.75	0.76 [56]	30.3	≈ 30 [19]
TGP-H-120 (10 wt%)	367	362 [56]	0.7	0.73 [56]	27.5	≈ 30 [19]
SGL 35 AA	350	300 [56], 333 [20]	0.84	0.88 [56], 0.82 [20]	60.4	60 [20]
SGL 25 AA	195	191 [56], 192 [20]	0.81	0.88 [56], 0.81 [20]	60.9	64 [20]

CFP	Thickness [%]	Porosity [%]	Normalized diffusivity TP/IP [%]	Permeability TP/IP [%]	Electrical/thermal conductivity TP/IP [%]
TGP-H-120 (0 wt%)	12%	4%	7.1/9.61	8.6/31.8	-152.9/-10.7
TGP-H-120 (10 wt%)	12%	4%	9.1/15.5	7.3/35.3	-
SGL 35 AA	17%	1%	2.2/2.9	7.0/9.8	-25/-3.3
SGL 25 AA	16%	4%	7.9/4.5	18.9/28.6	-214.3/-11.6

CFP	Transport property	Value (FT)	Value (mostly CR)	Experimental
TGP-H-120 (0 wt%)	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.28/0.52	0.26/0.47	0.25-0.35 [87-93]/ 0.45-0.6 [58,93]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	0.7/2.2	0.64/1.5	0.5-1.5 [10,94-102]/ 1.0-2.5 [94,98-100,103-106]
	Electrical conductivity, $\sigma_{tp}^{eff} / \sigma_{ip}^{eff} [S cm^{-1}]$	8.7/158.6	22.0/175.7	12.5-15.0 [10,85,107,108]/ 124-213 [23,25,26,97,107-109]
	Thermal conductivity, $k_{tp}^{eff} / k_{ip}^{eff} [W m^{-1}K^{-1}]$	0.87/15.9	2.2/17.6	0.45-1.8 [76,107,110-113]/ 11.6-21 [107,114,115]
TGP-H-120 (10 wt%)	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.22/0.45	0.2/0.38	0.19-0.3 [87,90,91,93,95,96]/ 0.4-0.55 [58,93]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	0.55/1.7	0.51/1.1	0.7-1.1 [87,95,96,102]/ 0.5-1.5 [104,106]
SGL 35 AA	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.45/0.68	0.44/0.66	0.4-0.6 [92]/ 0.6-0.7 [58]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	4.3/9.2	4/8.3	0.8 ^{a,c} [116], 5.3 ^a [117]/ 4.7-6 ^{a,c} [116]
	Electrical conductivity, $\sigma_{tp}^{eff} / \sigma_{ip}^{eff} [S cm^{-1}]$	0.76/44.9	1.0/46.7	0.8-1.2 ^a [118]/ 25-35 ^a [118]
	Thermal conductivity, $k_{tp}^{eff} / k_{ip}^{eff} [W m^{-1}K^{-1}]$	0.12/6.0	0.15/6.2	0.14 ^a [119]/ NA
SGL 25 AA	Normalized diffusivity, $f_{tp} / f_{ip} [-]$	0.38/0.66	0.35/0.63	0.3-0.55 [93]/ 0.4-0.6 [93], 0.6-0.7 [58]
	Permeability, $K_{tp} / K_{ip} [m^2] (\times 10^{11})$	3.7/5.6	3.0/4.0	3.2 ^b [120], 4.5 ^b [117]/ 3-4 ^{b,c} [120]
	Electrical conductivity, $\sigma_{tp}^{eff} / \sigma_{ip}^{eff} [S cm^{-1}]$	1.4/58.2	4.4/64.9	1.5-3.5 [118]/ 25-35 [118], 38.1 [23]
	Thermal conductivity, $k_{tp}^{eff} / k_{ip}^{eff} [W m^{-1}K^{-1}]$	0.19/7.7	0.6/8.7	0.2-0.4 [121,122]/ NA
a value reported for SGL 35 BA, b value reported for SGL 25 BA, c computed numerically.				

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We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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Supplementary material to

Analysis of representative elementary volume and through-plane regional characteristics of carbon-fiber papers: diffusivity, permeability and electrical/thermal conductivity

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1. Binder segmentation

S1: (a) Gray-scale cross-section tomography of SGL 35 AA, (b) thresholded image with fibers and binder shown in blue and red colors, respectively, (c) histogram of gray-scale values, where selected thresholds are shown, (d) gray-scale profile along the line shown in plot (a), where fiber and binder regions are identified.

S2: (a) Gray-scale cross-section tomography of SGL 25 AA, (b) thresholded image with fiber and binder shown in blue and red colors, respectively, (c) histogram of gray-scale values, where selected thresholds are shown, (d) gray-scale profile along the line shown in plot (a), where fiber and binder regions are identified.

2. Validation of the permeability model

Before proceeding with the simulation campaign, the permeability model implemented in Palabos [1] was validated against a well-known analytical solution; details on the validation of the diffusivity model can be found elsewhere [2]. Specifically, the predictive capabilities of the model were compared to the hydraulic permeability, K , of a fully-developed laminar flow in a square-shaped channel [3]:

$$K_{an} = \frac{h^2}{12} \left[1 - 192 \sum_{n=1}^{\infty} \frac{1}{u_n^5} \tanh\left(\frac{u_n}{2}\right) \right] \quad (1)$$

where h^2 is the cross-sectional area and $u_n = (2n - 1)\pi$.

Figure 3 shows the relative error of the numerical results as a function of the collision frequency, $\omega = \tau^{-1}$, for different cross-sectional grid resolutions (25×25 , 50×50 and 100×100 cells) in a channel of side $h = 32.5 \mu\text{m}$. These cell densities are in the order of those present in the “channels” of the $1.3 \mu\text{m}$ voxel-sized images of the carbon-fiber papers, whose mean pore chord lengths are between $30 - 100 \mu\text{m}$. In all cases, a very small pressure drop was prescribed to ensure that the flow was in the creeping regime ($Re = u^{\text{avg}}h/\nu \sim 10^{-6}$) and the secondary pressure drop at the entrance was negligible. Good agreement is found with the analytical solution when $\omega \gtrsim 1$, being the relative error lower than 0.25%. In subsequent simulations, $\omega = \tau = 1$ was chosen to preserve the accuracy and stability of the numerical scheme, while reducing the number of iterations for convergence (see, e.g., [4, 5]).

S3: (a) Computed laminar velocity profile in a square cross-section channel, corresponding to a grid resolution of $25 \times 25 \times 100$ cells and a collision frequency $\omega = 1$, (b) relative error of the hydraulic permeability (K) as a function of ω for different cross-sectional grid resolutions: 25×25 , 50×50 and 100×100 cells. Channel dimensions: height ($h = 32.5 \mu\text{m}$), length ($L = 130 \mu\text{m}$); $K_{\text{an}} = 3.712 \times 10^{-11} \text{ m}^2$.

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