Accepted Manuscript

Title: Microstructure-property relationships in a gas diffusion layer (GDL) for Polymer Electrolyte Fuel Cells, Part II: pressure-induced water injection and liquid permeability

Authors: L. Holzer, O. Pecho, J. Schumacher, Ph. Marmet, F.N. Büchi, A. Lamibrac, B. Münch

PII: S0013-4686(17)30922-2
DOI: <http://dx.doi.org/doi:10.1016/j.electacta.2017.04.141>
Reference: EA 29399

To appear in: *Electrochimica Acta*

Received date: 27-10-2016
Revised date: 18-4-2017
Accepted date: 21-4-2017

Please cite this article as: L.Holzer, O.Pecho, J.Schumacher, Ph.Marmet, F.N.Büchi, A.Lamibrac, B.Münch, Microstructure-property relationships in a gas diffusion layer (GDL) for Polymer Electrolyte Fuel Cells, Part II: pressure-induced water injection and liquid permeability, *Electrochimica Acta*<http://dx.doi.org/10.1016/j.electacta.2017.04.141>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>

Microstructure-property relationships in a gas diffusion layer (GDL) for Polymer Electrolyte Fuel Cells,**Part II: pressure-induced water injection and liquid permeability**

L. Holzer^{1,*}, O. Pecho¹, J. Schumacher¹, Ph. Marmet¹, F. N. Büchi², A. Lamibrac² and B. Münch³

Affiliations:

¹ Zurich University of Applied Sciences (ZHAW), School of Engineering, Institute of Computational Physics (ICP), 8400 Winterthur, Switzerland

² Paul Scherrer Institute (PSI), Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

³ Empa, Materials Science and Technology, Laboratory for Concrete and Construction Chemistry, CH-8600 Duebendorf, Switzerland

* Corresponding author: e-mail holz@zhaw.ch

Highlights:

- Liquid distribution in GDL is investigated with injection tomography experiments
- Anisotropy of liquid breakthrough is triggered by short-range effect in through-plane
- Quantitative 3D analysis reveals microstructure limitations for liquid permeability
- Relative permeability (κ_{rel})-curves are 'S-shaped' due to distinct microstructure effects
- Macroscopic descriptions for κ_{rel} from literature are not capable to capture the 'S-shape'

Abstract

The performance of polymer electrolyte fuel cells (PEFC) strongly depends on a controlled water management within the porous layers. For this purpose we investigate liquid water transport in a commercial gas diffusion layer (SGL 25BA) on the pore scale. X-ray tomography experiments combined with pressure-induced water injection provide 3D images of the liquid water distribution inside the GDL at incremental pressure steps between 0 and 100 mbar.

The breakthrough behavior of the liquid phase is highly anisotropic. In through-plane (tp) direction first bubble points appear at the outlet plane already at 5 mbar and the 'breakthrough' then evolves continuously over an extended pressure range up to > 30 mbar. For in-plane (ip) direction the breakthrough

is discontinuous and takes place at 27 mbar. Simulations of the intrusion process reveal that the different breakthrough behaviors are mainly triggered by different ip- and tp-transport distances. Short tp-transport distances through the thin gas diffusion layer (ca. 100 μm) are responsible for the characteristic continuous tp-breakthrough behavior, which is thus attributed to a so-called short-range effect.

Dedicated methods for 3D-image analysis adapted to fibrous GDL microstructures were presented in part I. With these methods we quantify all microstructure characteristics that are relevant for liquid permeability. These characteristics of pore and liquid phases include size distributions of bulges and bottlenecks, connectivity, effective volume fractions, geodesic tortuosity, constrictivity and hydraulic radius. Quantitative relationships are established between these microstructure characteristics and the liquid permeability, which provide a better understanding of the underlying microstructure limitations for injection and liquid transport.

For the in-plane direction the liquid permeability is limited to roughly a similar extent by tortuosity, constrictivity and effective volume fraction. In contrast, for through-plane direction relatively low volume fractions of the liquid phase put stronger limitations to the liquid permeability than tortuosity, constrictivity and hydraulic radius.

The curves for relative permeability vs. saturation (and vs. capillary pressure, respectively) achieved from 3D-analysis reveal complex but characteristic (reproducible) shapes with concave, linear and convex segments. The shape of these segments can be attributed to distinct microstructure effects. In contrast, the conventional macroscopic descriptions from literature cannot capture these complex shapes and the underlying microstructure effects. Future investigations with different GDL materials are necessary in order to understand whether these complex shapes for the relative permeability represent a general feature of gas diffusion layers or if they are specific to the investigated SGL material.

Keywords: Gas diffusion layer (GDL); X-ray tomographic microscopy; anisotropy; liquid permeability; short-range effect (SRE)

1. Introduction

In this work we focus on the investigation of capillary properties and liquid permeability of the gas diffusion layer (GDL) in polymer electrolyte fuel cells (PEFC). We are aiming for a quantitative understanding of the relationships between microstructure characteristics and effective flow properties in GDL. This understanding is the basis for a purposeful optimization of the GDL materials and for low loss operation of the cell. Gas diffusion layers consist of carbon fibers that are often mechanically stabilized with a carbonaceous binder. The fibers typically have diameters of 6 to 8 μm . In many GDL materials the preferred horizontal fiber orientation leads to a distinct anisotropy. The thickness of gas diffusion layers is typically in the range of 100 to 300 μm . The porosity is relatively high (i.e. 60-85%) and it varies with compression and binder content. Furthermore, the capillary properties strongly depend on the surface properties of fibers and binder. In this study we investigate a commercial GDL (25 BA from SGL Carbon). It is hydrophobized with 5% polytetrafluoroethylen (PTFE).

For the dry GDL material (SGL 25BA) the microstructure-property relationships were investigated in great detail in a previous study (part I) [1]. However, under operating conditions the GDL on the cathode side is usually not dry. The electrochemical reaction in the cathode catalyst layer produces water, which must be removed through the GDL. The water transport can take place in liquid or in vapor phase depending on the operating conditions (current density, gas humidity, thermal regime). At high current densities the liquid saturation (S) in the GDL can raise to a critical value, so that gas transport in the pore space is hindered by the presence of liquid water. This may lead to significant transport losses and to an elevated concentration polarization.

The complex mechanisms of water production and liquid transport in PEM fuel cells are extensively discussed in literature [2–6]. In order to minimize losses due to transport resistances, the GDL microstructure as well as the operating conditions have to be optimized for various transport properties, including liquid permeability, gas diffusivity (H_2 , O_2 , H_2O) as well as electrical and heat conductivities. A review of GDL properties in the presence of liquid water was recently given by Zamel et al [7]. However, a quantitative understanding of microstructure effects (e.g. limitations from constrictions and tortuous pathways) in wet GDL is still lacking.

Multi-physics modeling can be used to investigate the complex couplings between different transport processes and phase change reactions (including condensation-evaporation) in the PEM fuel cell [3,4,8–11]. In order to simulate the cell behavior in a reliable and accurate way, a proper description of the relationship between the microstructure (including the morphology of the liquid water phase) and macro-homogeneous properties is urgently requested.

In the subsequent sections of the introduction we first review conventional macroscopic descriptions from literature for the liquid permeability (κ) in the GDL and then we summarize our own methodic approach to quantify micro-macro relationships based on tomography data. These methods were introduced in previous studies mainly for sintered, isotropic materials [13–17], but they were recently adapted specifically for the fibrous, anisotropic GDL materials in part I [1]. In the present study we apply these adapted methods for the study of microstructure effects in wet GDL, using 3D data from in-situ tomography experiments.

1.1 Conventional description of liquid permeability

Fluid flow (Q) driven by a pressure gradient ($\Delta P/L$) is usually described with Darcy's law:

$$\text{Eq. 1:} \quad Q = v A = \frac{\kappa A}{\mu} \frac{\Delta P}{L}$$

where v denotes the average flow velocity, A is the materials cross-section and μ is the dynamic viscosity.

All microstructure effects are lumped together in a single parameter, which is called permeability (κ). The Carman-Kozeny equation describes the influence of microstructure on the permeability [18,19]. It is however derived for flow in granular media (packed beads) and therefore it is not suitable to characterize the properties of fibrous GDL materials. In contrast the so-called Tomadakis-Sotirchos (T-S) model is dedicated specifically for fibrous materials [20,21]:

$$\text{Eq. 2:} \quad \kappa = \frac{\varepsilon}{8(\ln \varepsilon)^2} \frac{(\varepsilon - \varepsilon_p)^{(\alpha+2)} d_f^2}{(1 - \varepsilon_p)^\alpha [(\alpha+1)\varepsilon - \varepsilon_p]^2}$$

Thereby, ε is the porosity, ε_p is the percolation threshold, d_f is the fiber diameter and α is a constant that depends on the microstructure. α is usually determined by fitting with experimental data from a specific

material type. For GDL materials with horizontal fiber orientation Tomadakis et al have determined the following standard values: the percolation threshold (ε_p) is 0.11 and α is 0.521 for in-plane (ip) and 0.785 for through-plane (tp) direction. In part I (Fig. 12b) it was shown that with these standard values the T-S model predicts the intrinsic permeability (κ_{dry}) of our dry GDL material (SGL 25 BA) reasonably well. For the case of single-phase flow, the T-S model also works well for liquid permeability, because the influence of the pore structure on the liquid permeability under fully saturated conditions ($\kappa_{wet_S=1}$) is equal to the influence of the pore structure on the intrinsic gas permeability in a dry material ($\kappa_{dry_S=0}$). However, at partial saturation (S) the description of microstructure limitations for liquid permeability (κ_s) becomes more complicated and therefore it is usually split into separate terms for intrinsic (κ_{dry}) and relative (κ_{rel}) permeability:

$$\text{Eq. 3:} \quad \kappa_S = \kappa_{dry} \kappa_{rel}$$

The relative permeability of the liquid phase can be substituted into the generalized Darcy equation, in order to describe the liquid flow as a function of water saturation and liquid pressure:

$$\text{Eq. 4:} \quad Q_{liq} = v_{liq} A = \frac{\kappa_{dry} \kappa_{rel} A}{\mu} \frac{\Delta P_{liq}}{L}$$

In contrast to the intrinsic permeability (κ_{dry} , which was described in part I), the relative permeability (κ_{rel}) is not just a materials property but it also depends on the liquid saturation and on the spatial distribution of liquid water (for example it may be influenced by gradients of S). The relative permeability is often predicted with either of two following expressions, which were deduced from capillary flow models. These two widely used expressions are the Burdine-function [22]:

$$\text{Eq. 5:} \quad \kappa_{rel_wp} = S_{wp}^2 \left[\frac{\int_0^{S_{wp}} \frac{dS_{wp}}{P_c^2}}{\int_0^1 \frac{dS_{wp}}{P_c^2}} \right] \quad \kappa_{rel_nwp} = (1 - S_{wp})^2 \left[\frac{\int_{S_{wp}}^1 \frac{dS_{wp}}{P_c^2}}{\int_0^1 \frac{dS_{wp}}{P_c^2}} \right]$$

and the Mualem-function [23]:

$$\text{Eq. 6:} \quad \kappa_{rel_wp} = S_{wp}^n \left[\frac{\int_0^{S_{wp}} \frac{dS_{wp}}{P_c}}{\int_0^1 \frac{dS_{wp}}{P_c}} \right]^2 \quad \kappa_{rel_nwp} = (1 - S_{wp})^n \left[\frac{\int_{S_{wp}}^1 \frac{dS_{wp}}{P_c}}{\int_0^1 \frac{dS_{wp}}{P_c}} \right]^2$$

Note that in a hydrophobized GDL the wetting phase (wp) is gas (humid air or fuel) and the non-wetting phase (nwp) is liquid water. A difficulty for practical application of these expressions is the fact that they require a quantitative knowledge of the relation between saturation (S) and capillary pressure (P_c).

Thereby, the capillary pressure (P_c) is defined as the pressure difference between the non-wetting and the wetting phase. According to the Washburn equation (also called 'Young-Laplace'), the capillary pressure scales inversely with the capillary pore radius (r):

$$\text{Eq. 7:} \quad P_c = \frac{2\sigma \cos\theta}{r}$$

Hence, capillary pressure and associated saturation are both linked with the pore size distribution (PSD) and the pore structure. However, the Washburn equation assumes cylindrical pore shapes, which is not the case in GDL materials. In order to describe S - P_c relationships for realistic, disordered microstructures, specific models were introduced, which also take into account the breakthrough pressure (P_{cb}). Two widely used expressions for S - P_c relationships are the Van Genuchten-model [24]:

$$\text{Eq. 8:} \quad S_{wp} = \left(1 + \left(\frac{P_c}{P_{cb}}\right)^n\right)^{-m}$$

and the Brooks-Corey model [25]:

$$\text{Eq. 9:} \quad S_{wp} = \left(\frac{P_c}{P_{cb}}\right)^{-\lambda}$$

These S - P_c relationships (Eqs. 8 and 9) can then be merged with the previous expressions for relative permeability (Eqs. 6 and 7) [6]. This approach leads to combined expressions for κ_{rel} , such as the one combining the van Genuchten- and Mualem-functions:

$$\text{Eq. 10:} \quad \kappa_{rel_wp} = S_{wp}^n \left[1 - \left(1 - (S_{wp}^{1/m})^m\right)^2\right] \quad \kappa_{rel_nwp} = (1 - S_{wp})^n \left(1 - S_{wp}^{1/m}\right)^{2m}$$

and the one combining the Brooks-Corey- and Burdine-functions:

$$\text{Eq. 11:} \quad \kappa_{rel_wp} = S_{wp}^{3+2/\lambda} \quad \kappa_{rel_nwp} = (1 - S_{wp})^2 \left(1 - S_{wp}^{1+2/\lambda}\right)$$

As an alternative to these combined expressions, the relative permeability is often also described with a much simpler power-law expression:

$$\text{Eq. 12:} \quad \kappa_{rel_wp} = S_{wp}^n \quad \kappa_{rel_nwp} = (1 - S_{wp})^n$$

In order to describe the relationships κ_{rel} - S (Eqs. 10-12) and S - P_c (Eqs. 8, 9) for a specific GDL material, the parameters n , m , λ and P_{cb} have to be fitted with experimental data. Zamel et al [6] for example used the full morphology approach including 3D numerical simulations of water injection and flow in combination with experimental data in order to fit the above mentioned expressions for a commercial GDL material from Toray. The resulting fitting parameters are given in Table 1. In the results part (section 3.3.3) we will compare the relative permeability obtained with our 3D methods with these expressions from literature.

It must be emphasized that for relative permeability (κ_{rel}) in GDL only very limited amount of experimental data is available to validate the above mentioned expressions. In addition, there is quite some uncertainty in the available experimental data from literature (i.e. large variation of κ_{rel}). As a consequence, the fitted exponents for the power law expression (Eq. 12) reported in literature show a very large variation from 2 to 8 [26]. Therefore, there is also much debate, which function and which fitting parameters best describe the liquid permeability in GDLs. Since these parameters and associated κ_{rel} - S relationships are used as input for macro-homogeneous modeling, the mentioned uncertainties are also inherited into the modeling results. It was shown that the mentioned expressions (Eqs 8 -12) have a strong impact on the modeling results [8,9]. Thereby, already a small variation of the input parameters may lead to a large variation in the calculated water saturations, associated transport losses and cell performances. Hence, more reliable descriptions of liquid permeability are required.

In order to achieve further progress, it is important to understand the limitations and sources of uncertainty in the above-mentioned descriptions. Some of the problems and uncertainties are related to the spatial distribution of liquid water inside the GDL. In the above expressions it is not considered, that the spatial distribution of water can vary considerably even at a fix degree of saturation. In principle it is well known that the liquid distribution depends on various factors, such as the history and mechanism of water propagation/retraction (e.g. injection-drainage or evaporation-condensation mechanism), the

microstructure (e.g. variation of bottleneck sizes) and also on the length of percolation pathways (e.g. thickness of the GDL). This means that the spatial distribution is an additional degree of freedom and therefore it is not sufficient to consider only the variation of S . Hence, a detailed description of the spatial distribution and associated liquid phase morphology is also of major importance for the understanding of liquid permeability.

Some authors reported strong gradients of the liquid saturation in tp -direction across the GDL. It was shown for example by Garcia-Salaberry [26,27] that in the presence of such gradients the global effective properties are significantly different from the local properties inside the GDL. In this case, the conventional global expressions (such as Eqs 8 - 12) may give misleading results. Therefore alternative approaches are required, which take into account the spatial distribution of the liquid phase and its morphological characteristics on the pore scale.

1.2 Description of liquid permeability based on 3D-analysis

New possibilities to characterize the relationship between saturation, morphology of water clusters, and liquid permeability arise due to the significant progress that was achieved over the last few years in X-ray tomography. Spatial resolution, temporal resolution as well as imaging contrast are now sufficiently high, so that it becomes possible to follow the water migration on the pore scale based on in-situ X-ray tomographic microscopy experiments [28–33]. Using these methods, the mechanisms that lead to a specific water distribution and associated liquid permeability can be investigated. For this purpose it is also necessary to establish suitable methods for 3D image analysis that provide quantitative relationships between the microstructure (including the spatial distribution and morphology of the liquid phase) and the corresponding effective properties (e.g. liquid permeability).

In previous studies, we have introduced a new approach to predict effective transport properties (permeability, diffusivity, conductivity) based on microstructure characteristics from 3D analysis such as effective volume fractions of pores (ϵ_{pore}) or liquid phase (ϕ_{liq}), geodesic tortuosity (τ_{geod}), constrictivity (β) and hydraulic radius (R_h) [13,15,16,]. Thereby, the permeability is calculated from hydraulic radius and from a dimensionless microstructure-factor (M).

$$\text{Eq. 13: } \kappa = (R_h^2 / 8) M$$

In part I, it was shown that the hydraulic radius can be approximated as the average of $r_{\min}$ and $r_{\max}$:

$$\text{Eq. 14: } R_h = (r_{\min} + r_{\max}) / 2$$

where $r_{\max}$ represents the mean size of pore bulges. It is determined with the so-called continuous pore size distribution (cPSD) method (i.e. it corresponds to the r_{50} value from the cumulative cPSD curve). In contrast, $r_{\min}$ represents the mean size of bottlenecks. It is determined with the so-called mercury intrusion porosimetry (MIP) method (i.e. it corresponds to the r_{50} value from cumulative MIP-PSD curve). The cPSD and MIP-PSD methods were both introduced by Münch and Holzer [34], and the two different PSD principles were illustrated in part I [1].

For the above-mentioned M-factor ($0 \leq M \leq 1$) the following relationship was derived statistically based on the analysis of microstructural characteristics and effective properties from more than 8'000 different 3D microstructures [16,17].

$$\text{Eq. 15: } M = (\varepsilon_{eff}, \phi_{eff})^{1.15} \beta^{0.37} / \tau_{geod}^{4.39}$$

The involved dimensionless characteristics are the effective phase volume fraction (pores (ε) or liquid (ϕ)), tortuosity (τ) and constrictivity (β). For more details see description in the methods section below.

All these methods were introduced and validated in earlier studies, which were dealing mainly with effective properties of sintered ceramic materials with isotropic structures [13–17]. In part I [1] this approach was then adapted specifically for the fibrous microstructure of GDL in PEFC, including special treatment of anisotropic features such as the elliptical shape of bottleneck cross-sections (specific case for transport in ip direction). In part I, the methods were then also applied for the study of effective properties in a dry GDL, including gas diffusivity (D_{eff}) and intrinsic permeability (κ_{dry}) of the pores as well as electric conductivity (σ_{eff}) of the solids. By comparison with numerical transport simulations it was shown that the proposed 3D methods are well capable to predict the effective properties of dry GDL. The results in part I also document that this 3D-approach is capable to explain the complex pattern of different anisotropic transport properties in the dry material (SGL 25BA). It was observed that the intrinsic permeability is

slightly higher in the tp direction ($\kappa_{dry_tp} > \kappa_{dry_ip}$), which can be attributed to larger hydraulic radii for tp direction ($R_{h_tp} > R_{h_ip}$). In contrast, for the intrinsic gas diffusivity higher values are observed for the ip-direction ($D_{dry_ip} > D_{dry_tp}$), which can be explained by lower geodesic tortuosity (i.e. less limiting) in ip-direction ($\tau_{geod_ip} < \tau_{geod_tp}$). Overall, the results from part I show that the proposed quantitative relationships provide new insight to microstructure effects, which help to improve the understanding of the dry GDL properties. In the present work (part II) the same methods are now used to investigate the properties of a wet GDL. The following tasks and questions are addressed specifically:

X-ray tomography experiments are performed in order to characterize the spatial distribution of the liquid water inside the GDL. The evolution of water migration is dynamically captured by tomography. Thereby the liquid water is injected into the GDL from one side with a homogeneous liquid pressure boundary condition. It must be emphasized that saturation and water distribution from operando conditions can be very different, especially when phase change transport is involved (i.e. evaporation and condensation). Such operando experiments will be performed in the near future. For the present study simplified conditions of pressure injection are chosen because they can be well controlled and the process can be easily simulated. The observations from the injection experiment are thus compared with the results from simulation of liquid intrusion into the same fibrous 3D microstructure. The aim is to understand the different breakthrough behaviors for in-plane and through-plane directions and the corresponding evolution of the spatial distribution and connectivity in the water phase. The question is, how the evolution of the wetting process and the breakthrough behavior can be related to distinct features of the pore microstructure (e.g. limiting bottlenecks).

Furthermore, the aim is also to understand the evolution of liquid permeability upon pressure-induced injection of water. For each pressure step the above-proposed 3D methods are applied to characterize quantitatively the relationship between microstructure characteristics (ε , β , τ , R_h) with the liquid permeability. In this way, the limiting microstructure effects (e.g. from narrow bottlenecks or from small hydraulic radii) can be identified. In this context it is also important to note that the relevant characteristics for liquid permeability have to be extracted from the connected portion of the water clusters for each step

of the pressure injection. If the water is distributed heterogeneously, this puts additional challenges for the elaboration of quantitative micro-macro relationships. The problems caused by possible gradients in the water distribution are given particular attention in the methods section below.

Finally, the relative permeability obtained from 3D analysis is compared with conventional descriptions from literature (Eq. 10-12). A major question for the present investigation is how the trends of liquid permeability (upon change of water saturation) obtained from 3D analysis compare with the conventional descriptions from literature (Eqs 8-12) and how eventual deviations from conventional trends can be explained using the detailed 3D microstructure information.

2. Materials and Methods

2.1 Materials

In this study we investigate the properties of a commercial GDL (SGL 25BA, SGL Carbon, Meitingen, D) at a fixed state of compression (23 %). It consists of carbon fibers (diameter 6 - 8 μm), carbonaceous binder and 5% PTFE. The porosity deduced from tomography images is 72.7 %. The relationship between porosity and degree of compression was investigated in part I. According to these results, a porosity of 73% corresponds to a compression level of 23 % (see part I, Fig. 4). It must be noted that the binder also contains pores on the sub- μm scale, which are not captured with X-ray tomography. Hence, the total porosity is even higher than 73%. However, due to the hydrophobicity it is assumed that the small pores in the binder do not contribute to liquid water transport (in contrast to gas transport).

The microstructure of the dry GDL is illustrated in Fig. 1. It is strongly anisotropic due to the predominantly horizontal orientation of the carbon fibers. In addition, the dimensions of the sample have a high aspect ratio, which also contributes to the anisotropy of the material properties (as discussed later). The thickness (size of image window in z direction, through-plane) of the GDL in the tomography image is only 70.4 μm . It must be emphasized, that the image only

represents a central domain of the GDL. Domains at the top and bottom of the GDL partially interfere with hydrophobic and hydrophilic membranes that are used as barrier layers in the setup for water injection. These heterogeneous boundary domains are removed from the imaging data, which is used for quantitative analysis.

2.2 In-situ X-ray tomography: pressure induced water injection

The experimental procedure for pressure induced water injection is described in detail by Lamibrac et al [30]. It can be summarized as follows: a GDL is fixed between two barrier membranes. The hydrophilic membrane at the bottom generates a homogeneous water inlet pressure distribution. The water is fed with a pressure controlled syringe pump. The hydrophobic membrane on top is open for gas diffusion and therefore the gas pressure in the GDL is constant at ambient conditions. The hydrophobic membrane also prevents a breakdown of liquid pressure upon breakthrough of the water phase. For water injection the pressure is increased in 10 steps (0, 5, 10, 20, 25, 30, 35, 40, 60 and 100 mbar). Each step includes an equilibration time of 20 min before the image acquisition is performed.

The entire setup is mounted on the rotation stage of the X-ray Computed Tomography (CT) scanner (GE Nanotom m). The images are acquired with an acceleration voltage of 60 kV and a current of 100 μ A. 2200 projections are collected over 360°. Each projection is an average of 3 images with an exposure time of 500 ms per image and one image is skipped before each projection acquisition (i.e. a scantime of 73 min is required for each tomographic structure). The voxel size is 2.2 μ m.

2.3 Quantitative image analysis

In part I the methods for quantitative 3D analysis have been adapted specifically for fibrous microstructures of the dry GDL. In the present study (part II) the methods are further adapted and tested for the specific case of injected water and its relationship with liquid permeability. In this context, inhomogeneous distribution and gradients in water saturation represent particular challenges for a characterization with volume-averaged microstructure characteristics. This problem is addressed in the following sections with particular attention.

2.3.1 3D reconstruction and segmentation of pore, liquid and solid phases

3D images are reconstructed from the raw data using GE datos|x 2 reconstruction software. Subsequently, the grayscale images are converted into a phase-segmented format, where each voxel is labeled either for solid, pore or liquid phase. First the solid and void phases are labeled by applying a suitable grayscale threshold to the tomographic image of the dry GDL. For the different capillary pressure steps, the water phase is then obtained as follows. The dry grayscale image is subtracted from the wet image. Then a threshold is applied to the resulting image so that the water phase can be segmented and labeled. More details about the segmentation procedure are described in a recent publication by Lamibrac et al [30]. For quantitative analysis rectangular domains are cropped in x- and y-directions (in-plane) with a size of 1000 x 1000 pixels, which corresponds to 2.2 x 2.2 mm. It was shown in a previous study that this area provides a representative RoI [35]. In z-direction (through-plane) the heterogeneous boundary regions are removed and the remaining thickness is only 70.4 μm .

2.3.2 Connectivity and effective volume fractions of empty pores (ϵ_{eff}) and liquid water (ϕ_{eff})

Only water clusters that are connected at the same time with inlet and outlet can contribute to the liquid permeability. Therefore, connectivity of the water clusters with inlet and outlet is determined in order to characterize the effective volume fractions. Upon liquid injection the connectivity evolves differently in through-plane and in-plane directions. Hence, for each pressure step we distinguish total and connected volume fractions of pores and water for in-plane and for through-plane directions (i.e. ϵ_{tot} , $\epsilon_{\text{eff_ip}}$, $\epsilon_{\text{eff_tp}}$ for the pores, and ϕ_{tot} , $\phi_{\text{eff_ip}}$, $\phi_{\text{eff_tp}}$ for the liquid water). All microstructure characteristics that are subsequently used for prediction of liquid permeability are deduced from the connected, effective volume fractions of the water phase (i.e. $\phi_{\text{eff_ip}}$, $\phi_{\text{eff_tp}}$).

2.3.3 Geodesic tortuosity (τ_{geod})

Tortuosity is defined as a statistical average for the ratios of path lengths (l) over sample thickness (Δs). Thereby, the shortest connections between inlet and outlet are identified as the transport pathways (Dijkstra algorithm [36]). For the analysis of geodesic tortuosity (τ_{geod}) each voxel attributed to the effective

volume of the liquid phase ($\phi_{\text{eff_ip}}$, $\phi_{\text{eff_tp}}$) represents a potential node in a graph and the connectivity of these nodes is determined using 26-neighbourhood criteria. For statistical accuracy any pixel in the so-called inlet plane representing the liquid phase is treated as starting point for the shortest path analysis (for further details see Stenzel et al [17]).

At low pressures the water saturation is much higher in the bottom regions close to the water inlet. Fig. 2 represents a zoom-in (compare with the overview in Fig. 4, bottom), which illustrates the heterogeneous water distribution across the GDL at an injection pressure of 10 mbar. Due to the gradients in saturation it makes a big difference whether tp-tortuosity is measured from top to bottom or vice versa. When measuring $\tau_{\text{geod_tp}}$ from top to bottom, the analysis of shortest path-lengths results mainly in vertical pathways (marked as white lines) with an average tortuosity close to 1. In contrast, when measuring $\tau_{\text{geod_tp}}$ from bottom to top, this procedure gives a large spectrum of paths lengths with different angles (marked as red lines in Fig. 2) and the associated tortuosity is significantly higher than 1. For liquid permeability we consider the vertical lines (white) as the relevant pathways, because these are the pathways with the least resistance. Therefore liquid tortuosity in tp direction is always measured from top to bottom (i.e. the outlet of water transport is defined as starting points for path lengths / tortuosity analysis). The ip tortuosity does not depend on the direction in the same way, since there are no gradients of saturation in ip direction. (Note: the volume contributing to transport is restricted to the area with white dashed lines. Therefore the effective volume has to be corrected accordingly, which is done with the constrictivity parameter described below in section 2.3.5).

2.3.4 Continuous pore size distribution (cPSD) and mercury intrusion porosimetry (MIP-PSD)

Continuous pore size distributions (cPSD) and mercury intrusion porosimetry (MIP-PSD) were introduced and described in detail by Münch and Holzer [34]. The two methods can be applied to any segmented phase (i.e. pore, solid or liquid) and they characterize fundamentally different size characteristics:

The cPSD is sensitive to the largest bodies in a networked microstructure and thus it describes the size distribution of bulges. The mean value (i.e. r_{50}) of the cPSD curve is thus interpreted as the typical size of

bulges, which is also called $r_{\max}$. For the dry GDL (SGL 25BA) at 25 % compression, the mean size of pore bulges ($r_{\max}$) is 20.2 μm .

The MIP-PSD is determined by simulating the intrusion of a non-wetting phase into a networked microstructure, in analogy to the experimental mercury intrusion porosimetry (MIP). The MIP analysis differs from the cPSD analysis due to an additional constraint describing connectivity with the pore entry. This constraint makes the MIP-method sensitive to transport limitations by narrow bottlenecks. Hence, the mean value (i.e. r_{50}) of the MIP-PSD curve is interpreted as the typical size of bottlenecks, which is called $r_{\min}$. It captures bottleneck sizes as a function of the transport direction. For the dry GDL (SGL 25BA) at 25 % compression, the mean size for the pore bottlenecks ($r_{\min}$) is 16.7 μm for tp direction and 11.0 μm for ip directions.

It must be emphasized that the measurement of the MIP-PSD for the liquid phase may be also strongly affected by the presence of gradients in saturation. Similar to the measurement of tp-tortuosity in the liquid phase (see Fig. 2), also the results from MIP-PSD analysis in tp-direction differ when measuring from bottom to top or from top to bottom. Our investigations show, that the limiting bottleneck size for tp-transport is captured correctly with MIP-PSD when the mercury intrusion is simulated in the direction of liquid injection (i.e. from bottom to top).

Important characteristic features of cPSD and MIP-PSD are illustrated in part I (Fig. 2). The MIP-PSD is based on the simulation of an intrusion process. It was shown that the intrusion behavior of a non-wetting phase and associated MIP-PSD are strongly dependent on the lengths of the transport pathways. This is an important finding that must be kept in mind for the investigation of different ip/tp breakthrough in the present study. At long transport pathways ($> 500 \mu\text{m}$) the intrusion is controlled by a characteristic bottleneck size (called breakthrough-radius) and the resulting MIP-PSD has a distinct discontinuous shape. This behavior is characteristic for the breakthrough in ip direction. However, if the transport pathways are shorter than a certain critical intrusion depth (CID, ca. 500 μm), then the intrusion behavior is controlled by local bottleneck sizes, meaning that the different transport pathways are limited by different bottleneck sizes. This behavior is also called short-range effect (SRE) and it is typical for tp breakthrough in thin GDL.

2.3.5 Constrictivity (β)

Constrictivity describes the influence of varying cross-sections and bottlenecks on transport [15]. It is defined as the ratio of the cross-section area at bottlenecks ($A_{\min}$) over cross-section area at bulges ($A_{\max}$):

$$\text{Eq. 16: } \beta = A_{\min} / A_{\max} = (r_{\min} / r_{\max})^2$$

As discussed and documented in part I, the cross-sections of bottlenecks perpendicular to the ip transport direction in SGL 25BA have elliptical shapes, which is caused by the horizontal orientation of fibers and associated anisotropy. Since the $r_{\min}$ from MIP-PSD only captures the short axis of these elliptical ip bottlenecks, we have introduced the following correction to characterize the cross-sectional area of bottlenecks with elliptical shapes:

$$\text{Eq. 17: } r_{\min_ip}^* = \sqrt{(r_{\min} r_{\max})}$$

The corrected $r_{\min_ip}^*$ describes a circle with an area that is equivalent to an ellipse with short axis $r_{\min}$ and long axis $r_{\max}$. It was shown in part I that the effective transport properties of dry GDL (SGL 25BA) can be predicted reliably, when constrictivity for ip-direction is calculated with the corrected $r_{\min_ip}^*$. In tp-direction the bottlenecks are rather isometric (circular) and therefore no such correction is needed.

2.3.6 Hydraulic radius (R_h)

Viscous effects at the pore walls introduce a resistance to fluid flow, which limits the permeability. For flow in a tube the viscous resistance correlates with the pore surface (S_{tot}) normalized by the corresponding pore volume (V_{pore}). The inverse of this ratio is called hydraulic radius ($R_{hI} = V_{\text{pore}} / S_{\text{tot}}$). For flow in partially saturated GDL materials with fibrous microstructure, the surface area relevant for wall frictions cannot simply be related with the pore surface and therefore the application of R_{hI} is problematic for GDL.

However, in a previous study it was shown that the hydraulic radius is approximately identical with the average of bottleneck ($r_{\min}$) and bulge radii ($r_{\max}$) (see Eq. 14: $R_{hII} = (r_{\min} + r_{\max})/2$). With this definition we are also capable to capture microstructural anisotropy, since $r_{\min}$ depends on the transport direction. Hence, in the present study we use the definition of R_{hII} (Eq. 14) for measuring hydraulic radius.

3. Results and discussion

In the following sections, the spatial distribution of liquid water resulting from pressure injection is characterized and its influence on permeability is investigated. The first section of the results (3.1) includes characterization of bulk saturation ($S - P_c$ curves), gradients in the local saturation and connectivity of the liquid phase (in ip- and tp-directions). Furthermore, also the different ip- and tp-breakthrough behaviors are characterized. In the second section (3.2) the morphological characteristics of the liquid phase are quantified, which are used to predict liquid permeability. In the third section (3.3), micro-macro relationships are established and predicted permeability (κ_{rel_pred}) is compared with simulated permeability (κ_{rel_sim}). In addition, the relative permeability from 3D analysis is also compared with conventional expressions from literature (Eq. 10-12) and the differences are interpreted in the view of detailed microstructure information.

3.1 Capillary properties related to pressure induced water injection

3.1.1 Saturation - Pressure ($S-P_c$) curves: global versus local saturations

Fig. 3 (A) shows the global saturation of liquid water (S) as a function of the injection pressure (P_c). The measured $S-P_c$ curve for our material (SGL 25BA), is similar to the GDL characteristics reported in a previous experimental study for Toray and SGL materials [30], but is significantly different from the conventional description with Eq. 8 (Van Genuchten) and Eq. 9 (Brooks Corey) for Toray material. The large difference may (partly) be related to gradients in saturation, which are not captured with Eqs. 8 and 9.

Fig. 3 (B) shows the profiles of local saturations across the GDL. At low injection pressures (≤ 10 mbar), the water saturations in the bottom layers close to the inlet ($z = 0$) are relatively high (up to $S = 0.7$). At the same pressure, the local saturation close to the outlet ($z = 70 \mu\text{m}$) is negligible. Hence, at low pressures (≤ 10 mbar) there are strong gradients in the local saturation. Nevertheless, first tp pathways connecting inlet- with outlet-planes of the thin imaging window are established already at 5 to 10 mbar. However, the saturation in the outlet region only starts rising significantly at pressures larger than 15 mbar, which is typically considered as the tp breakthrough pressure. At pressures higher than 20 mbar the water also penetrates into the upper regions close to the outlet and therefore the gradients in local saturation become shallow at elevated pressures (>30 bar).

The inhomogeneous liquid distribution in the GDL is also illustrated as projections in cross-sectional slices (see Fig. 4). At low pressures (10 mbar) the liquid water is injected mainly into the bottom regions of the GDL. At intermediate pressures (20 mbar) the water also expands into middle and upper regions. But it requires higher pressures (up to 100 mbar) to press a large amount of the liquid also into the top regions close to the outlet.

As a consequence of the gradients in liquid distribution, the local S - P_c curves differ significantly from the global S - P_c curve, which is illustrated in Fig. 5:

- In the bottom layer (inlet, $z = 0 \mu\text{m}$) the local saturation increases already at pressures below 15 mbar (which is defined as injection phase A). At 27 mbar (end of injection phase B) the maximum saturation level ($S = \text{ca. } 0.9$) is reached in the bottom layer. It hardly changes when further increasing the pressure (injection phase C).
- In the middle regions of the GDL ($z = 35.2 \mu\text{m}$) the saturation remains relatively low ($S < 0.2$) up to 15 mbar (injection phase A). Between 15 and 27 mbar (injection phase B) the saturation of the middle layer increases strongly but it reaches the maximum saturation only during injection phase C.
- In the top layer (outlet, $z = 70.4 \mu\text{m}$) the saturation remains low to moderate ($S < 0.5$) up to 27 mbar (end of injection phase B). Close to the outlet, high saturation levels ($S > 0.8$) are only reached at high pressures (> 60 mbar, injection phase C). (Note: the limit between injection phases A and B is estimated by the tp-breakthrough pressure (ca. 15 mbar) and the limit between phases B and C by the ip-breakthrough pressure (27 mbar).

3.1.2 Connectivity of liquid water: in-plane (ip) versus through-plane (tp) breakthrough

Only the connected portion of the liquid phase (i.e. the effective volume fraction ϕ_{eff}) contributes to the liquid permeability (κ_{liq}). Per definition, a water cluster is connected in a specific direction, if it contains a percolating pathway that continues through the entire sample from inlet- to outlet-plane. The connectivity of the water clusters is evaluated separately for ip- (x and y) and tp-directions (z) in Figs 6 and 7.

The evolution of the tp-connectivity (z-direction) upon pressure-induced injection is visualized in Fig. 6 (based on X-ray tomography experiments). Only the water phase is shown, whereas pores and solids are transparent. The colors mark the difference between water clusters that are either isolated (bright blue) or connected (dark blue) in tp-direction. During the injection phase A (10 mbar) only a few tp-pathways connecting inlet- (bottom) with outlet-planes (top) are established (dark blue: $\phi_{\text{eff_tp}} = 0.03$ at 10 mbar). The tp-connectivity then increases significantly from 10 to 20 mbar (dark blue: $\phi_{\text{eff_tp}} = 0.22$ at 20 mbar). Therefore, an average tp-breakthrough pressure is estimated to 15 mbar. However, it must be emphasized that the tp-connectivity rather evolves gradually from 5 to 30 mbar. This continuous tp-breakthrough evolution can be explained with relatively short transport distances in z-direction (ca. 70-100 μm) combined with the fragmentation of the water phase into clusters that are not connected in horizontal direction. As discussed in the next section, the water clusters do not interconnect in ip-directions up to 27 mbar (end of phase B). Hence, below 27 mbar in each cluster a different tp-breakthrough pressure can establish. Because of this fragmentation different local bottleneck sizes can control the breakthrough in each tp-pathway (according to the Washburn equation, Eq. 7).

The evolution of ip connectivity upon pressure induced water injection is visualized in Fig. 7. Up to 25 mbar (end of injection phase B) the liquid water is fragmented into isolated clusters. Up to this pressure there are no connected ip-transport pathways, neither in x- nor in y-directions ($\phi_{\text{eff_ip}} = 0$ at 25 mbar). The situation changes drastically at 30 mbar, where a large fraction of the water clusters is suddenly connected in x- and y-directions (dark blue: $\phi_{\text{eff_ip}} = 0.42$). Hence, it requires a relatively high saturation ($S = 0.65$) in order to establish ip-connectivity. Overall, the ip-breakthrough occurs suddenly at ca. 27 mbar and it represents a significant discontinuity in the evolution of the ip-permeability (κ_{ip}). During injection phase C ($P > 30$ mbar) the ip- and tp-connectivities become more and more similar (i.e. $\phi_{\text{eff_ip}} \approx \phi_{\text{eff_tp}}$, see Fig. 8).

As shown in Fig. 8, the connected, effective volume fraction of liquid water (ϕ_{eff} , blue) does not increase linearly with saturation because of incomplete connectivity. The tp-connectivity of liquid water is generally higher than the ip-connectivity ($\phi_{\text{eff_tp}} \geq \phi_{\text{eff_ip}}$). A prominent feature is the anisotropy of the breakthrough, which occurs at lower pressures for tp- (ca. 15 mbar) than for ip-direction (ca. 27 mbar).

In contrast to the liquid water, the empty pores are fully connected ($\varepsilon_{\text{tot}} = \varepsilon_{\text{eff_tp}} = \varepsilon_{\text{eff_ip}}$) almost for the entire range of saturations. A partial loss of ip-connectivity in the empty pores ($\varepsilon_{\text{eff_ip}} < \varepsilon_{\text{tot}}$) is only observed at a high level of saturation (i.e. $S_{\text{liq}} \geq 0.8$). In summary, there is a strong anisotropy regarding the connectivity of the water phase, but not so much for the connectivity of the gas phase (for more details about relative gas diffusivity in empty pores see part III).

3.1.3 Influence of size distributions (cPSD, MIP-PSD) and layer thickness on capillary properties

In GDL the liquid water generally behaves as a non-wetting liquid. During injection the non-wetting liquid first enters the biggest pores. In order to press the non-wetting fluid into smaller pores the pressure needs to be increased. The relationship between the capillary pressure and the corresponding pore size is described by the Washburn equation (Eq. 7). By measuring the capillary radius and the corresponding breakthrough pressure, a bulk contact angle can theoretically be calculated. However, there are many different PSD methods and the question arises, which method is suitable to describe the capillary radius.

In part I (Fig. 2) we have described two fundamentally different methods to characterize pore sizes: a) the continuous pore size distribution (cPSD), which describes dimensions of pore bulges and b) the mercury intrusion porosimetry (MIP-PSD), which captures the size of the bottlenecks (see also original description of these PSD methods in Münch and Holzer [34]). cPSD and MIP-PSD curves of a dry GDL (SGL 25BA, uncompressed, data set from part I) are shown in Fig. 9. Thereby, the radii corresponding to 50 Vol% in the cumulated size distribution are called r_{max} (cPSD) and r_{min} (MIP-PSD). Typically the pore size characteristics in GDL exhibit a distinct sequence, where r_{max} (cPSD) $>$ $r_{\text{min_tp}}$ (MIP-PSD_{tp}) $>$ $r_{\text{min_ip}}$ (MIP-PSD_{ip}).

The size of bottlenecks (r_{min}) is identified as a morphological feature that limits water propagation and therefore it is considered as an equivalent to the capillary radius. We now substitute the average bottleneck radii ($r_{\text{min_ip}} = 8.5 \mu\text{m}$, $r_{\text{min_tp}} = 17 \mu\text{m}$) as well as the breakthrough pressures ($P_{\text{c_ip}} = 27 \text{ mbar}$, $P_{\text{c_tp}} = 15 \text{ mbar}$) from Fig. 8 and the water-air surface tension from literature ($\sigma = 0.0725 \text{ Nm}^{-1}$) into the Washburn equation. This substitution reveals a contact angle of 100° ($\theta_{\text{ip}} = 99.1^\circ$, $\theta_{\text{tp}} = 100.1^\circ$). Hence, the bulk contact angle of our GDL appears to be slightly hydrophobic.

It must be mentioned that such macroscopic bulk contact angles do not necessarily represent true contact angles on the pore scale. The latter may vary considerably inside the GDL pore structure due to a mixture of hydrophobic and hydrophilic surface properties of different solid phases (fibers, binder, PTFE) as well as due to the complex local topology and the associated variable curvatures of the solids surfaces.

Hence, bulk properties such as bulk contact angle and mean bottleneck size have a limited meaning in explaining the capillary properties on a pore scale. Therefore, in the following sections we investigate local properties, such as the spatial distribution of the pore bulges and their connections via bottlenecks. These features are visualized in the PSD maps of Figs. 10 and 11. In order to make comparisons easier the color codes of these PSD maps are all calibrated to the same size range. For example domains in red color always represent radii of $\geq 40 \mu\text{m}$ for cPSD as well as for MIP-PSD maps.

The cPSD map in Fig. 10 shows many large pores in red color, which are randomly distributed throughout the entire GDL microstructure. Even in the middle layer of the GDL there are numerous red colored pores with radii of at least $40 \mu\text{m}$. These large pore bulges have the potential to host large water clusters.

However, in order to fill a large pore in the center or at the outlet of the GDL, the water has to pass through narrow bottlenecks. This limiting influence of bottlenecks is not captured with the cPSD method, because it does not consider effects of transport and connectivity. Therefore the cPSD curves do not reveal the capillary radius, which is used in the Washburn equation (Eq. 7).

The MIP analysis (visualized in Fig. 11) differs from the cPSD analysis (Fig. 10) due to an additional constraint describing the connectivity with the pore inlet. This constraint makes the MIP-method sensitive to transport limitations by narrow bottlenecks. In other words, the MIP-method describes how far a sphere of a given radius can migrate from the inlet plane into the bulk of the material. Only small spheres can pass through narrow bottlenecks. Therefore the MIP-size always decreases along the percolation pathways, until a characteristic limiting bottleneck size is reached (as visualized in Fig. 2 of part I). There is a critical intrusion distance (CID), above which all transport pathways have passed through a characteristic bottleneck size (which is called breakthrough radius).

The ip-intrusion (in x-direction) is visualized in a sequence of MIP-PSD maps on the left side of Fig. 11. At the inlet (top left image) water can enter into large pore bulges (red, 40 μm) without passing through narrow bottlenecks. After a transport distance of 1 x the thickness of the GDL (i.e. 120 μm from the inlet, 3rd image from top) the different transport pathways are still limited by different local bottleneck sizes between 15 to 40 μm , which leads to yellow, green and blue colors in the y-z plane. It requires a critical intrusion depth (CID) of about 4 x to 7 x the GDL thickness (i.e. 500 - 800 μm) until all ip-pathways are limited by the characteristic ip-bottleneck size of ca. 14 μm . This characteristic bottleneck size is illustrated by a uniform bright blue color in the bottom-left image. This uniform breakthrough radius is also visible in the MIP-PSD curve for ip-direction, which shows a steep increase at 14 μm (Fig. 9). According to the Washburn equation this breakthrough radius can be related to the breakthrough pressure (which was observed to be 27 mbar for ip-direction in Figs. 7 and 8).

The MIP-intrusion in tp-direction is shown in the image sequence on the right side of Fig. 11. At the inlet in the basal plane, there are again abundant large pores in red (i.e. 40 μm , bottom right). The colors change rapidly to yellow, green and blue in the middle and top layers, which documents the limiting effect of narrow bottlenecks. However, at the outlet (image top right) the different tp-pathways still have different limiting bottleneck sizes, which is because the transport distance is shorter than the critical intrusion depth (CID). The colors in the outlet layer represent a range of local breakthrough radii between 5 to 30 μm . According to the Washburn equation, these different sizes of potential bubble points at the outlet correspond with the discontinuous breakthrough behavior that was previously described for tp-direction (Figs. 6 and 8). It can be assumed that if the GDL thickness was larger than the CID (i.e. 500 - 800 μm), also for tp-direction the limiting bottleneck size would become uniform (ca. 15-20 μm), which would then lead to a discontinuous breakthrough behavior (ca. 20-25 mbar.) Hence, it can be concluded that the small GDL thickness and associated short range effect (SRE) causes a continuous tp-breakthrough behavior, which amplifies the anisotropy of capillary GDL properties.

3.1.4 Three phases of pressure-induced water injection

Based on the observations presented above we define three different phases in the evolution of pressure induced water injection. These phases have the following characteristics:

Injection phase A (0 - ca. 15 mbar): Isolated water clusters at the bottom (near inlet)

Water enters from below and forms water clusters mainly in the large voids at the bottom of the GDL (see also Figs. 4 and 7). Upward migration of water is strongly suppressed due to hydrophobic components (PTFE) and limiting bottlenecks. The water clusters are not connected in horizontal directions, so that different local capillary pressures may evolve in the different, isolated tp pathways. First local bubble points (i.e. first tp-breakthrough points) can already form at 5 mbar.

Injection phase B (15 - 27 mbar): tp-breakthrough and vertical expansion of water clusters into middle and top regions

Water clusters migrate mainly upwards (tp-direction), but not much sideways (ip-directions). The saturation mainly increases in the middle regions of the GDL. The number of tp-pathways connecting inlet with outlet increases continuously over an extended pressure interval. This continuous breakthrough behavior is typically observed when the length of percolation pathways is shorter than the so-called critical intrusion depth (as explained for thin layers in part I, Fig. 2). The breakthrough behavior in these short tp-transport pathways is controlled by variations of the locally limiting bottlenecks between 5 to ca. 30 μm . According to Eq. 7 (Washburn equation) this leads to a variation of local breakthrough pressures (i.e. bubble points).

Injection phase C: ip breakthrough and flooding of top regions (> 27 mbar)

During phase C the liquid water is pressed into the top regions (tp) and it also expands horizontally (ip). Phase C starts with the ip-breakthrough, which is a discontinuous event within a narrow pressure interval (i.e. at 25 mbar $\phi_{\text{eff_ip}} = 0.0$, whereas at 30 mbar $\phi_{\text{eff_ip}} = 0.43$). Such discontinuous breakthrough behavior is typical for bulk materials where the length of percolation pathways is larger than the so-called 'critical

intrusion depth'. At high pressures, any further increase of pressure (e.g. from 40 to 100 mbar) induces only a relatively small increase of the global saturation (from 0.82 to 0.9).

During phase C, the gas phase is pushed into narrow empty pores, where the non-wetting water phase can still not intrude. The remaining gas phase in SGL 25BA retains a high connectivity even at high levels of liquid saturation.

Under operando conditions, evaporation and condensation usually take place in the GDL and some of the water molecules are then transported in the vapor phase. This phase change induced transport is not captured with our pressure injection experiment, but it may have significant influence on the water distribution and associated GDL properties. Nevertheless, the injection phases A and B may still represent fuel cell conditions, if the water distribution is controlled by capillary pressure and liquid phase transport. This may be the case at low temperatures and/or for fuel cell designs without a micro porous layer adjacent to the GDL. The local pressures in the GDL can then vary independently from the pressure in the neighboring pores as long as the water clusters are isolated in ip-direction. Above the ip-breakthrough (at 27 mbar) almost all water clusters become connected with each other, which leads to homogenization of the pressure. Because the GDL is usually open to the gas channel, the pressure cannot raise any further and it is improbable that phase C (>27 mbar) can be reached, even under conditions where liquid transport is the dominant mechanism.

3.2 Quantitative topological characteristics of water clusters (ϕ , β , τ , R_h)

Transport properties of the liquid phase (i.e. liquid permeability κ) can be correlated with four important microstructure characteristics, which are effective volume fraction (ϕ_{eff}), geodesic tortuosity (τ_{geod}), constrictivity (β) and the hydraulic radius (R_h). These characteristics are extracted from the 3D-data representing the ip- or tp-connected liquid water phase at each pressure-step of the injection experiment.

3.2.1 Effective volume fraction (ϕ_{eff})

The effective volume fractions of the evolving liquid phase are presented above in context with Fig. 8. Due to the different breakthrough behaviors the effective volume fractions during injection phases A and B are

significantly lower for ip- than for tp-directions ($\phi_{\text{eff_ip}} \leq \phi_{\text{eff_tp}}$). It is also important to note that all the other topological properties (τ , β , R_h) presented below are extracted from the voxels representing these connected, effective volume fractions ($\phi_{\text{eff_ip}}$, $\phi_{\text{eff_tp}}$). Furthermore it must be kept in mind that the microstructure characteristics for tp-direction are strongly influenced by gradients in the local saturation, which are dependent on the layer thicknesses themselves. Consequently, the values obtained for τ , β and R_h for tp-direction represent properties that are specific for a certain GDL thickness (i.e. 70 μm).

3.2.2 Geodesic tortuosity ($\tau_{\text{geod_liq}}$)

Figure 12 shows the geodesic tortuosity in the liquid phase ($\tau_{\text{geod_ip/tp}}$) as a function of water saturation. In general, tortuosity of the water phase varies only in a limited range ($1 < \tau_{\text{geod}} < 1.2$) and it puts no strong limitations to the permeability. However, tortuosity shoots up to infinity when lowering the volume fraction to the percolation threshold. This percolation threshold is at much higher saturations for ip- than for tp-direction.

For the ip-direction, when increasing the saturation from the percolation limit to higher levels ($S > 0.7$), then the tortuosity decreases steadily from 1.2 to 1.05. This is compatible with the illustration in Fig. 7, where it is shown that the ip-transport pathways (red lines) become straighter with increasing pressure and saturation.

For the tp-direction, there is a weak tendency of increasing tortuosity from 1.05 at 10 mbar to 1.15 at > 30 mbar. It can be assumed that the first connected tp-pathways go straight through the thin GDL layer ($S = 0.15$). With increasing pressure and saturation, the tp-pathways become slightly more complicated as the water is pressed through narrow bottlenecks, and therefore tortuosity is increasing.

3.2.3 Mean radii of bulges (r_{max}) and bottlenecks (r_{min}), and constrictivity (β)

The connectivities in tp- and ip-directions are very different as illustrated in Figs 6 and 7. This triggers very different results for the pore size distributions and associated constrictivities. For the tp-direction the evolution of $r_{\text{max_tp}}$ (mean size of bulges from cPSD) exhibits a maximum of 25.4 μm at 20 mbar (Fig. 13a). At low saturation levels the largest voids are filled and therefore the $r_{\text{max_tp}}$ is growing in a first phase of

pressure injection (phase A). Above 20 mbar the water is then pressed into smaller pores and therefore the average size of bulges ($r_{\max_tp}$) is decreasing during injection phases B and C. Above the ip-breakthrough pressure (i.e. $P > 27$ mbar, saturations > 0.65 , phase C) the sizes of the bulges for ip- and tp-directions are almost identical (i.e. decreasing with pressure).

The curve for the tp-bottleneck sizes ($r_{\min} = r_{50}$ from MIP-PSD) versus saturation also exhibits a maximum, which is at 18 μm and 30 mbar (see Fig. 13b). The negative slope during phases B and C is compatible with the Washburn equation (Eq. 7, i.e. higher pressure = smaller radius). In contrast, the positive slope during phase A contradicts the capillary behavior predicted by the Washburn equation. In fact, the data points at 5 and 10 mbar represent only a few bubble points at low saturation levels. In thicker layers with the same microstructure no breakthrough event would occur at these low pressures. Therefore, the data points at 5 and 10 mbar are interpreted as result of local bubble point phenomena (lack of representativeness) that are strongly influenced by the short-range effect (SRE). This may explain why morphological properties ($r_{\min}$, $r_{\max}$, β , τ , σ) of these early-connected clusters at low pressures do not fit well with the general trend lines at higher pressures and saturations.

The curve for ip-bottleneck sizes starts at pressures above 25 mbar (Fig. 13b). Thereby, one has to consider that the saturation gradients at each pressure step are the result from an injection experiment in tp-direction. Hence, there is an overlap of tp-injection (and associated gradients of the local saturation) and ip-analysis (direction of MIP simulation). The migration of the waterfront in tp-direction during the intrusion experiment leads to an improvement of the liquid water connectivity in ip-direction (see Fig. 7). This behavior results in larger ip-bottleneck sizes with increasing pressures (which contradicts the Washburn equation). At relatively high pressures (i.e. at $P_c > 40$ mbar) the gradients of the local saturation become shallow. This leads again to a 'normal behavior' as predicted by the Washburn equation (i.e. negative slope of $r_{\min}$ vs. P_c). Hence, also the curves of ip-bottlenecks exhibit a maximum bottleneck radius. A corrected ip-bottleneck size was introduced in part I (Fig. 3), which accounts for elliptical bottleneck shapes (Note: Corrected values are marked with '*'). The corrected bottleneck size ($r_{\min_ip}^*$) has a higher maximum value of 14 μm , compared to 9 μm for the maximum of the uncorrected bottleneck size ($r_{\min_ip}$).

Fig. 13c shows the evolution of constrictivity in the liquid phase (Eq. 17: $\beta = (r_{\min}/r_{\max})^2$). The tp-constrictivities steadily decrease with higher pressure, as predicted by the Washburn equation. In contrast, the ip-constrictivities increase with higher pressure, for reasons discussed above (i.e. overlapping phenomena from tp-injection and ip-MIP simulation). Overall, the ip-constrictivity puts stronger limitations to the liquid permeability ($\beta_{ip} < \beta_{tp}$), which is due to the smaller ip-bottlenecks. This difference also explains the higher ip-breakthrough pressures.

3.2.4 Hydraulic radius (R_{h_liq})

The hydraulic radius (Fig. 13d) is defined here as the average from bulge- and bottleneck-radii (Eq. 14: $R_h = (r_{\min} + r_{\max})/2$). It also captures anisotropy effects due to the difference in ip- and tp-bottleneck sizes. Both curves for R_{h_tp} and R_{h_ip} go through a maximum, which is at 24 μm / 20 mbar for tp- and at 16 μm / 40 mbar for ip-directions. Because the permeability depends on R_h^2 (see Eq. 13), it is expected that the convex shape of the R_h -curve (as a function of S) will also influence the shape of the corresponding curve for the liquid permeability (as a function of S , compare Fig. 17).

3.3 Prediction of liquid permeability (κ) based on microstructure characteristics

In previous studies we have established quantitative relationships between microstructure characteristics and effective transport properties [14,16,17]. According to these relationships the permeability can be predicted from an M-factor and from the hydraulic radius (see Eq. 13: $\kappa = (R_h^2/8) M$).

3.3.1 Relationships between M-factor and microstructure characteristics (ϕ_{eff} , β , τ_{geod})

Fig. 14 shows the in-plane and through-plane M-factors and associated microstructure components ($\phi_{\text{eff}}^{1.15}$, $\beta^{0.37}$ and $\tau_{\text{geod}}^{-4.39}$). As a rough approximation, the evolution of the M-factors with increasing saturation can be described with linear trends. The positive slopes of these M-trends are the result of combined limiting effects from three microstructure components (see Eq. 15, $M = \phi_{\text{eff}}^{1.15} \beta^{0.37} / \tau_{\text{geod}}^{4.39}$), which can be summarized as follows:

For the tp-direction (Fig. 14a) the M_{tp} -factor is mainly limited by the low liquid volume fraction (i.e. $\phi_{\text{eff_tp}}^{1.15}$). In contrast, the constrictivity and tortuosity components in tp-direction are relatively high and

therefore they do not limit transport significantly. The positive slope of M_{tp} is clearly related to the increasing liquid volume fraction.

For the ip-direction (Fig. 14b), water transport only occurs in phase C above the discontinuous ip-breakthrough event ($S > 0.65$). For the ip-direction all three microstructure components have positive slopes and thus their influence on the evolution of the M_{ip} -factor is similar. At a closer view it becomes evident that also for the ip-direction the effective liquid volume fraction ($\phi_{eff_ip}^{1.15}$) represents the component with the most limiting influence.

The shapes of the M-factor trends are explored in more detail in Fig. 15a. It becomes apparent that the tp-trend is not perfectly linear. In particular, close to the lower intercept the M_{tp} -trend has a concave shape, which is explained by the fact, that the breakthrough in tp-direction is a continuous process that takes place over an extended range of pressures (5-20 mbar) and saturations (0.05 - 0.3). In contrast the ip-breakthrough is a discontinuous event at 27 mbar and therefore M_{ip} exhibits a relatively sharp lower intercept at $S = 0.65$.

In order to validate our results, the M-factor can also be defined as the normalized effective diffusivity ($M = D_{eff}/D_0$), which can be obtained by numerical simulation. For this purpose the same 3D-domains of the liquid water phase (as used for image analysis and prediction) are used as structural input for transport simulations with GeoDict.

In Fig. 15a the predictions based on microstructure characteristics (M_{pred} , blue lines) are compared with the results from numerical simulations (M_{sim} , black dotted lines). Considering the small layer thickness and the existing gradients of saturation it is expected that that tp-analyses of $\phi_{eff_tp}^{1.15}$ may suffer from a lack of representativeness. Nevertheless, quite similar evolution curves are obtained for predicted and simulated M-factors. However, at a closer look, some differences become apparent between predicted and simulated M-factors for the through-plane direction. During the intrusion phase B the predicted M-factors are somewhat higher than the simulated M-factors, whereas during intrusion phase C the predicted M-factors are lower. These differences are attributed to the mentioned limitations regarding

representativeness of tp-analyses, which are caused by small layer thickness and strong gradients of local saturation.

Nevertheless, the correlation plots in Fig. 15b document reasonable matches for tp-direction and very good correlation for ip-direction between predicted and simulated M-factors. These good correlations confirm the prediction capability of the proposed methods (using Eq. 15 in combination with the methods described in part I), which help to understand the influence of dimensionless characteristics (i.e. ϕ , β , τ) on the liquid permeability.

3.3.2 Relationships between permeability (κ) and hydraulic radius (R_h)

In Fig. 16a the predicted permeability ($\kappa_{\text{pred}} = (R_h^2/8) M$) is compared with permeability obtained from the simulation of viscous flow (κ_{sim}) with GeoDict software (www.geodict.com). The simulated values are considered as a reliable benchmark. For the ip-direction, predicted and simulated curves are very similar. For tp-direction, during injection phase B, κ_{pred} is higher than κ_{sim} (see Fig. 16a) and this difference is very similar as previously observed for M_{pred} and M_{sim} (see Fig. 15a). This indicates that the hydraulic radius for intrusion phase B is correct and does not introduce an additional uncertainty or error. For intrusion phase C the difference in tp direction between κ_{pred} and κ_{sim} is larger than between M_{pred} and M_{sim} . This points to an additional underestimation, which is introduced by the hydraulic radius (R_h) measured for tp-direction in phase C.

Overall, the basic shape of the curves for κ_{pred} and κ_{sim} in Fig. 16a are quite similar, for ip- as well as for tp-directions. At elevated saturations during injection phase C the trends for κ have convex shapes, which can be associated with the observed convex shapes for the hydraulic radii (Fig. 13d). The fact that this convex behavior is also obtained with transport simulations indicates that the trends of the hydraulic radii are principally captured in a correct way, apart from the mentioned underestimation (for tp-direction in phase C).

3.3.3 Relative liquid permeability (κ_{rel})

The relative permeability (κ_{rel}) is defined by the ratio of the liquid permeability as a function of saturation normalized by the intrinsic permeability at saturation $S = 1$. Fig. 17a shows the relative permeability obtained from prediction (blue, κ_{rel_pred}) and from simulation (black, κ_{rel_sim}). The trend lines for κ_{rel_pred} and κ_{rel_sim} are almost identical for ip-direction, which confirms the high prediction capability of the proposed methods. For tp-direction the predictions seem to overestimate κ_{rel} during intrusion phase B, and underestimate κ_{rel} during intrusion phase C. This difference is attributed to problems that arise with volume-averaged characteristics, when they are determined from thin layers containing strong saturation gradients (i.e. limited representativeness). Therefore, for tp-direction the simulated results (κ_{rel_sim}) are interpreted as being more reliable than the predicted results (κ_{rel_pred}).

Overall, all predicted and simulated curves for κ_{rel} exhibit similar but complex shapes consisting of concave, linear and convex segments. These segments are schematically illustrated in Fig. 17b. The central segment of the tp curve for κ_{rel_sim} can be approximated with a linear trend of $y = 1.4x - 0.29$, where y is κ_{rel} and x is S (see black dashed line, labeled with tp**). Similarly the central segment of the ip curve can be approximated with a linear trend of $y = 0.41x - 2.65$ (black dashed line, labeled with ip**). At low saturations ($S < 0.4$) the tp-curve deviates clearly from the linear trend. It shows a concave curvature (labeled with tp*, marked in red), which is attributed to the continuous breakthrough evolution between 5 to 20 mbar (see Figs. 6, 8). In contrast, the lower intercept of the ip-curve at $S = 0.65$ (labeled with ip*) has a corner-like shape. This sharp intercept corresponds with the discontinuous ip-breakthrough event at 27 mbar (see Figs. 7, 8). At high saturations the curves for κ_{rel_ip} and κ_{rel_tp} have both convex shapes (labeled with tp*** and ip***). These convex shapes are attributed to the influence of the hydraulic radius, which also follows convex evolution curves with increasing saturations during phase C (see Fig. 13d). The endpoints of both curves (labeled with ****) are approximately at $S = 0.9$ and $\kappa_{rel} = 0.85$. Higher saturations could not be reached in the experiment.

In summary, the complex shapes of the evolution curves for κ_{rel} with changing saturations can be explained as the superposition of three distinct microstructure effects, which are described by the M-factor (linear

trend at intermediate saturations), by the hydraulic radius (convex shape at high saturations) and the breakthrough behavior (concave shape at low saturations for tp-direction).

In literature (see e.g. [7]), semi-empirical relationships (Eq. 10: Mualem-Van Genuchten, Eq. 11: Burdine-Brooks Corey or Eq. 12: power law) are frequently used to describe the relative permeability in GDL. As shown in Fig. 17a all semi-empirical relationships from literature are characterized with concave shapes. None of them captures the complex shape of κ_{rel} as deduced from 3D-analysis. The semi-empirical functions can be fitted so that they match reasonably well for the central segments of the curves. In any case, the fitting approach with the conventional relationships does not provide any in-depth understanding of the true microstructure limitations for liquid transport, which is the main benefit from the methodology proposed in the present investigation.

4. Conclusions

In this study we investigate the influence of GDL microstructure on the water distribution as it evolves during pressure-induced liquid injection. Quantitative micro-macro relationships are established in order to improve our understanding of the liquid permeability and the underlying microstructure limitations. All investigations are based on tomography injection-experiments with a commercial GDL (SGL 25BA) in combination with 3D-analysis and 3D-transport simulations.

The evolving water distribution upon pressure-induced injection is basically described by the Washburn equation (Eq. 7), which relates capillary pressure with the capillary radius. The MIP-PSD method captures the size of bottlenecks (r_{min}), which is interpreted as a measure for the capillary radius. The 3D simulation of mercury intrusion porosimetry (MIP) reveals fundamental differences in the breakthrough behavior for ip- and tp-directions, which are also observed with tomography experiments. The MIP simulations show, that the breakthrough anisotropy is mainly related to the high aspect ratio of the GDL dimensions (i.e. small layer thickness) and of the associated transport distances. In ip-direction, the transport distances are relatively long, which leads to a discontinuous breakthrough event at 27 mbar. The discontinuous behavior is characteristic for porous bulk materials. In tp-direction the short transport distances in the thin layer lead to a continuous breakthrough behavior. Thereby local bubble points at the outlet evolve over an extended

pressure range (5 - >20 mbar). This continuous breakthrough behavior is typical for thin layers. It is therefore attributed to the so-called short-range effect (SRE). Hence, the anisotropy of spatial water distribution and of the associated transport properties in GDL is interpreted as a result from structural anisotropy combined with the short-range effect in tp-direction. In particular, the strong gradients of liquid saturation that are observed at low injection pressures (< 25 mbar) can only be explained under the view of a short-range effect.

Quantitative micro-macro relationships are established in order to predict the liquid permeability based on microstructure characteristics of the water clusters for each step of the pressure injection. The methods to describe these characteristics must be adapted to specific features of the fibrous GDL microstructure and to the inhomogeneous water distribution. The most important methodic adaptations are the following:

For the tp-direction tortuosity (τ) has to be measured in top-to-bottom direction in order to capture correctly the microstructure effects on permeability including also the influence of gradients in saturation. In contrast, MIP-PSD and constrictivity (β) have to be measured in bottom-to-top direction, in order to capture the bottleneck effect correctly (i.e. following the direction of water injection).

For the ip-direction the bottleneck radius ($r_{\min}^*$) and associated constrictivity (β^*) have to be corrected for elliptical shapes of the bottlenecks (see part I). With these corrections the proposed micro-macro relationships are well capable to predict the trends for liquid permeability upon pressure injection. For ip-direction the predictions match well with the simulations. For tp-direction the limited representativeness (due to small layer thickness combined with gradients in saturation) introduces some uncertainty in the predictions.

The evolution curves obtained with 3D analysis for κ_{rel} (predicted and simulated) have complex shapes that consist of concave, linear and convex segments. These complex shapes for the relative permeability curves can be explained as superposition of three distinct microstructure effects: a) The M-factor dominates the general trend including the linear segment at intermediate saturations) b) The hydraulic radius dominates mainly the convex segment at high saturations and c) the breakthrough behaviors dominate the concave curve shapes at low saturations, which is continuous for tp-direction and discontinuous for ip-direction.

The evolution curves of the relative permeability obtained in this study deviate significantly from semi-empirical relationships that are frequently used in literature (Eqs. 10-12: Mualem-Van Genuchten, Burdine-Brooks Corey or power law). This difference indicates that the conventional, macroscopic descriptions are not capable to capture all relevant microstructure effects. However, it must be emphasized that our microscopic investigations of κ_{rel} are specific for one commercial GDL (SGL 25BA) and for the experimental conditions of pressure induced water injection. In future, the same methods for 3D image analysis and property-prediction shall be applied to other GDL materials and for other water transport conditions (e.g. evaporation - condensation instead of pressure induced injection). These investigations will be used to answer the question, whether the observed differences to the conventional relationships are of systematic character or if they are specific to pressure injection in SGL 25BA.

Acknowledgements

The research presented in this paper was funded by SNSF (Swiss National Science Foundation NFP 70, Grant No 407040_153790) and from Swiss Federal Office for Energy (SFOE / BFE Grant No. SI/501129-01). The financial support by these organizations is gratefully acknowledged.

References

- [1] L. Holzer, O. Pecho, J. Schumacher, Ph. Marmet, O. Stenzel, F. N. Büchi, A. Lamibrac and B. Münch, Microstructure-property relationships in a gas diffusion layer (GDL) for Polymer Electrolyte Fuel Cells, Part I: effect of compression and anisotropy of dry GDL, *Electrochim. Acta.*, (submitted).
- [2] K. Jiao, X. Li, Water transport in polymer electrolyte membrane fuel cells, *Prog. Energy Combust. Sci.* 37 (2011) 221–291. doi:10.1016/j.pecs.2010.06.002.
- [3] A.R. Kalidindi, R. Taspinar, S. Litster, E.C. Kumbur, A two-phase model for studying the role of microporous layer and catalyst layer interface on polymer electrolyte fuel cell performance, *Int. J. Hydrogen Energy*. 38 (2013) 9297–9309. doi:10.1016/j.ijhydene.2013.05.079.
- [4] X. Liu, F. Peng, G. Lou, Z. Wen, Liquid water transport characteristics of porous diffusion media

in polymer electrolyte membrane fuel cells: A review, *J. Power Sources*. 299 (2015) 85–96.
doi:10.1016/j.jpowsour.2015.08.092.

- [5] J.H. Nam, K.-J. Lee, G.-S. Hwang, C.-J. Kim, M. Kaviani, Microporous layer for water morphology control in PEMFC, *Int. J. Heat Mass Transf.* 52 (2009) 2779–2791.
doi:10.1016/j.ijheatmasstransfer.2009.01.002.
- [6] N. Zamel, X. Li, J. Becker, A. Wiegmann, Effect of liquid water on transport properties of the gas diffusion layer of polymer electrolyte membrane fuel cells, *Int. J. Hydrogen Energy*. 36 (2011) 5466–5478. doi:10.1016/j.ijhydene.2011.01.146.
- [7] N. Zamel, X. Li, Effective transport properties for polymer electrolyte membrane fuel cells – With a focus on the gas diffusion layer, *Prog. Energy Combust. Sci.* 39 (2013) 111–146.
doi:10.1016/j.pecs.2012.07.002.
- [8] H. Wu, X. Li, P. Berg, On the modeling of water transport in polymer electrolyte membrane fuel cells, *Electrochim. Acta*. 54 (2009) 6913–6927.
- [9] X. Wang, T.V. Nguyen, Modelling the effects of capillary property of porous media on the performance of the cathode of a PEMFC, *J. Electrochem. Soc.* 155 (2008) B1085-92.
- [10] K. Steinkamp, J.O. Schumacher, F. Goldsmith, M. Ohlberger, C. Ziegler, A Nonisothermal PEM Fuel Cell Model Including Two Water Transport Mechanisms in the Membrane, *J. Fuel Cell Sci. Technol.* 5 (2008) 11007. doi:10.1115/1.2822884.
- [11] J. Dujc, P. Marmet, J.O. Schumacher, Modelling the effects of using Gas Diffusion Layers with patterned wettability for advanced water management in proton exchange membrane fuel cells, *J. Electrochem. Energy Convers. Storage*. submitted (2016).
- [12] I. V. Zenyuk, E. Medici, J. Allen, A.Z. Weber, Coupling continuum and pore-network models for polymer-electrolyte fuel cells, *Int. J. Hydrogen Energy*. 40 (2015) 16831–16845.
doi:10.1016/j.ijhydene.2015.08.009.
- [13] L. Holzer, B. Iwanschitz, T. Hocker, L. Keller, O. Pecho, G. Sartoris, et al., Redox cycling of Ni–YSZ

anodes for solid oxide fuel cells: Influence of tortuosity, constriction and percolation factors on the effective transport properties, *J. Power Sources*. 242 (2013) 179–194.

doi:10.1016/j.jpowsour.2013.05.047.

- [14] L. Holzer, O. Stenzel, O. Pecho, T. Ott, G. Boiger, M. Gorbar, et al., Fundamental relationships between 3D pore topology, electrolyte conduction and flow properties: Towards knowledge-based design of ceramic diaphragms for sensor applications, *Mater. Des.* 99 (2016) 314–327. doi:10.1016/j.matdes.2016.03.034.
- [15] L. Holzer, D. Wiedenmann, B. Münch, L. Keller, M. Prestat, P. Gasser, et al., The influence of constrictivity on the effective transport properties of porous layers in electrolysis and fuel cells, *J. Mater. Sci.* 48 (2013) 2934–2952. doi:10.1007/s10853-012-6968-z.
- [16] G. Gaiselmann, M. Neumann, V. Schmidt, O. Pecho, T. Hocker, L. Holzer, Quantitative relationships between microstructure and effective transport properties based on virtual materials testing, *AIChE J.* 60 (2014) 1983–1999. doi:10.1002/aic.14416.
- [17] O. Stenzel, O. Pecho, L. Holzer, M. Neumann, V. Schmidt, Predicting effective conductivities based on geometric microstructure characteristics, *AIChE J.* 62 (2016) 1834–1843. doi:10.1002/aic.15160.
- [18] P.C. Carman, Fluid flow through granular beds, *Chem. Eng. Res. Des.* 75 (1997) S32–S48. doi:10.1016/S0263-8762(97)80003-2.
- [19] Kozeny J., Über kapillare Leitung des Wassers im Boden, *Sitzungsbericht Der Akad. Der Wissenschaften Wien*. 136 (1927) 271–306.
- [20] M.M. Tomadakis, Viscous Permeability of Random Fiber Structures: Comparison of Electrical and Diffusional Estimates with Experimental and Analytical Results, *J. Compos. Mater.* 39 (2005) 163–188. doi:10.1177/0021998305046438.
- [21] M.M. Tomadakis, S. V. Sotirchos, Transport through random arrays of conductive cylinders dispersed in a conductive matrix, *J. Chem. Phys.* 104 (1996) 6893. doi:10.1063/1.471356.

- [22] Y. Mualem, A new model for predicting the hydraulic conductivity of unsaturated porous media, *Water Resour. Res.* 12 (1976) 513–522.
- [23] N.T. Burdine, Relative permeability calculations from pore size distributions data, *Pet. Trans. AIME.* 198 (1953) 71–77.
- [24] M.T. van Genuchten, Closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *J. Soil Sci.* 44 (1980) 892–898.
- [25] J. Bear, *Dynamics of fluid in porous media*, New York, 1972.
- [26] P.A. García-Salaberri, J.T. Gostick, G. Hwang, A.Z. Weber, M. Vera, Effective diffusivity in partially-saturated carbon-fiber gas diffusion layers: Effect of local saturation and application to macroscopic continuum models, *J. Power Sources.* 296 (2015) 440–453.
doi:10.1016/j.jpowsour.2015.07.034.
- [27] P.A. García-Salaberri, G. Hwang, M. Vera, A.Z. Weber, J.T. Gostick, Effective diffusivity in partially-saturated carbon-fiber gas diffusion layers: Effect of through-plane saturation distribution, *Int. J. Heat Mass Transf.* 86 (2015) 319–333.
doi:10.1016/j.ijheatmasstransfer.2015.02.073.
- [28] R. Flückiger, F. Marone, M. Stampanoni, A. Wokaun, F.N. Büchi, Investigation of liquid water in gas diffusion layers of polymer electrolyte fuel cells using X-ray tomographic microscopy, *Electrochim. Acta.* 56 (2011) 2254–2262. doi:10.1016/j.electacta.2010.12.016.
- [29] I. Mayrhuber, F. Marone, M. Stampanoni, T.J. Schmidt, F.N. Büchi, Fast X-ray Tomographic Microscopy: Investigating Mechanisms of Performance Drop during Freeze Starts of Polymer Electrolyte Fuel Cells, *ChemElectroChem.* 2 (2015) 1551–1559. doi:10.1002/celc.201500132.
- [30] A. Lamibrac, J. Roth, M. Toulec, F. Marone, M. Stampanoni, F.N. Büchi, Characterization of Liquid Water Saturation in Gas Diffusion Layers by X-Ray Tomographic Microscopy, *J. Electrochem. Soc.* 163 (2016) F202–F209. doi:10.1149/2.0401603jes.
- [31] J. Eller, F. Marone, F.N. Büchi, Operando Sub-Second Tomographic Imaging of Water in PEFC Gas

Diffusion Layers, ECS Trans. 69 (2015) 523–531. doi:10.1149/06917.0523ecst.

- [32] E.A. Wargo, V.P. Schulz, A. Cecen, S.R. Kalidindi, E.C. Kumbur, Resolving macro- and micro-porous layer interaction in polymer electrolyte fuel cells using focused ion beam and X-ray computed tomography, *Electrochim. Acta.* 87 (2013) 201–212. doi:DOI 10.1016/j.electacta.2012.09.008.
- [33] C. Tötzke, G. Gaiselmann, M. Osenberg, J. Bohner, T. Arlt, H. Markötter, et al., Three-dimensional study of compressed gas diffusion layers using synchrotron X-ray imaging, *J. Power Sources.* 253 (2014) 123–131. doi:10.1016/j.jpowsour.2013.12.062.
- [34] B. Münch, L. Holzer, Contradicting Geometrical Concepts in Pore Size Analysis Attained with Electron Microscopy and Mercury Intrusion, *J. Am. Ceram. Soc.* 91 (2008) 4059–4067. doi:10.1111/j.1551-2916.2008.02736.x.
- [35] J. Roth, J. Eller, F. Marone, F.N. Büchi, Investigation of the Representative Area of the Water Saturation in Gas Diffusion Layers of Polymer Electrolyte Fuel Cells, *J. Phys. Chem. C.* 117 (2013) 25991–25999. doi:10.1021/jp4057169.
- [36] K. Thulasiraman, M.N.S. Swamy, *Graphs, Theory and Algorithms*, John Wiley & Sons, New York, 1992.

Figure captions:

Fig. 1: 3D microstructure of dry GDL (SGL 25BA) with a compression level of 23%. The images are acquired with X-ray tomography. The voxel resolution is 2.2 μm . Note: The homogeneous part of the GDL (RoI) has a thickness of only 70 μm , which is cropped from the entire GDL (ca. 130 μm) for quantitative investigations.

Fig. 2: Visualization of hypothetical transport pathways in the liquid phase based on tomography. It shows a vertical slice through a GDL (depth of slice is ca. 50 μm) with the projection of water injected at 10 mbar from the bottom. (Note: fibers and pores are not shown). The dotted lines represent hypothetical traces of tp-pathways associated with tortuosity ($\tau_{\text{geod_tp}}$). Due to the

gradient in water saturation it makes a big difference whether tortuosity is measured from bottom to top (red dashed lines) or from top to bottom (white dashed lines). For liquid transport in tp-direction the white lines are considered as the relevant pathways. Therefore τ_{geod} is measured from top to bottom.

Fig. 3a: Global saturations of gas and liquid phases as a function of the capillary pressure (S - P_c curves), obtained from in-situ X-ray tomography experiments (pressure injection). For comparison S - P_c curves predicted with Eqs 8 (Van Genuchten) and 9 (Brook Corey) are also shown (using fit parameters for Toray material from literature, see table 1). The ip breakthrough (marked in green) is a discontinuous event at ca. 27 mbar. In contrast, the tp 'breakthrough' evolves continuously over an extended pressure-range from ca. 5 to 20 mbar (blue). Fig. 3b: Concentration profiles of the local saturation as a function of the distance from inlet (z). At low pressures (<20 mbar) the local saturations show strong gradients across the GDL. The dotted line represents the total porosity (including empty and filled pores).

Fig. 4: In-plane projections showing the liquid distributions at 10, 20 and 100 mbar in cross-sectional slices of the GDL (depth of slice in ip-direction is ca. 50 μm , data from tomography, fibers not shown). At low pressures (10mbar) liquid water is mainly enriched in the bottom region. With increasing pressure the liquid water is propagating to top regions ('flooding'). Bright blue color marks the water, which is truncated at the frontal boundary of the image window. The orange rectangle (*) represents a zoom-in region that is used in Fig. 2 for illustration of tortuosity in tp-direction.

Fig. 5: Local water saturations (S_{local} - P_c curves) as a function of the distance to the inlet, starting with $z = 0$ (bottom of GDL) and ending with $z=70.4 \mu\text{m}$ (outlet, top). The bold, dotted line represents the global S - P_c curve from Fig. 3. Three different phases (A, B, C) of the liquid water injection are distinguished based on the characteristics of the propagating water (as described in text).

Fig. 6: Visualization of tp connectivity in water clusters. 3D reconstruction of wet GDL (view under 45° angle) showing the evolution of liquid water, which is injected at 10, 20, 30 and 100 mbar from bottom.

Clusters without connectivity between bottom and top layers are shown in bright blue color whereas clusters that are connected in tp direction are shown in dark blue color. Note: connectivity in tp-direction evolves rather continuously over an extended pressure range from <5 to >30 mbar.

Fig. 7: Visualization of in-plane connectivity for liquid water injected at 5, 10, 20, 25, 30 and 100 mbar (GDL top view projections). The colors mark the difference between water clusters that are either isolated (bright blue) or connected (dark blue) in ip-directions. The ip-breakthrough occurs abruptly between 25 and 30 mbar. Hypothetical ip-transport pathways in x- and y-directions are marked with red lines at 30 and 100 mbar. Note that the tortuosity of these red lines decreases with saturation and pressure.

Fig. 8: Total and effective volume fractions of empty pores (ε_{tot} , ε_{eff} , black) and liquid phase (ϕ_{tot} , ϕ_{eff} , blue) as a function of water saturation (S_{liq}) and capillary pressure (P_c), respectively. Due to different ip- and tp-breakthrough behaviors there is a significant difference between ip- and tp-curves for connected water ($\phi_{\text{eff_ip}}$ and $\phi_{\text{eff_tp}}$) at pressures < 30 mbar.

Fig. 9: Pore size distributions of dry, uncompressed GDL (SGL 25BA). The cPSD method captures the size of bulges, whereas the MIP-PSD method describes the bottlenecks. The mean value of bulges is called ' r_{max} ' and the mean value of bottlenecks is called ' r_{min} '.

Fig. 10: cPSD maps of a dry GDL (25BA, uncompressed) based on 3D images from tomography. The cPSD method captures the size of pore bulges. The color map with the corresponding pore sizes is shown in the bottom image. The images show the local size of pore bulges in horizontal cross-sections at the inlet (bottom), in the central region of the GDL (middle) and at the outlet (top).

Fig. 11: MIP-PSD maps of an uncompressed GDL (SGL 25BA, dataset from part I) based on 3D reconstructions from X-ray tomography. The MIP method simulates the intrusion of a non-wetting liquid (e.g. mercury or water) and thereby captures the limiting influence of bottlenecks. Left side: in-plane direction. Right side: through-plane direction. (Note: $1/2 \times$, $1 \times$, $2 \times$ etc. describes the intrusion distance relative to the GDL thickness).

Fig. 12: Geodesic tortuosity (τ_{geod}) for ip- and tp-transport in liquid water. Note: Only connected portions of the liquid phase are considered. A, B and C represent phases of the injection process.

Fig. 13: Average size of (a) bulges (r_{max}) and (b) bottlenecks (r_{min}) in the connected portion of the liquid water phase as a function of saturation (S) and capillary pressure (P_c), respectively. (c) Constrictivity: $\beta = (r_{\text{min}} / r_{\text{max}})^2$ (see Eq. 16). (d) Hydraulic radius: $R_h = (r_{\text{min}} + r_{\text{max}}) / 2$, (see Eq. 14). Note that ip-connectivities are only established during injection phase C.

Fig. 14: Evolution of predicted M-factors as a function of liquid saturation for (a) through-plane and for (b) in-plane directions. The M-factors represent a limiting influence for liquid transport, which originates from three dimensionless microstructure components: $\phi_{\text{eff}}^{1/3}$, $\beta^{2/3} \tau_{\text{geod}}^{-2/3}$. In general, relatively low effective volume fractions (ϕ_{eff}) of the liquid phase put the strongest limitations to liquid permeability.

Fig. 15a: Evolution of M-factors as a function of saturation and pressure for through-plane (tp) and in-plane (ip) directions. M-factors obtained by prediction based on microstructure characteristics are shown in blue color. M-factors resulting from numerical simulation of diffusion are shown in black (dotted lines). Fig. 15b: Correlation-plot showing that predicted and simulated M-factors correlate well with each other, both for ip- and tp-directions.

Fig. 16a: Evolution of liquid permeability (κ) as a function of saturation for through-plane (tp) and in-plane (ip) directions. Permeabilities from predictions are shown in blue and from numerical simulations in black (dotted lines). Fig. 16b: Correlation plot of predicted vs. simulated permeabilities. The correlation between κ_{pred} and κ_{sim} is very good for in-plane direction. For through-plane direction κ_{pred} is underestimated during intrusion phase C.

Table captions:

Table 1: Summary of fit-parameters for Eqs. 8 to 12, which describe capillary properties and relative permeability of GDL. The fit-parameters were determined by Zamel et al [6] with the full morphology approach applied to a 3D reconstruction of a commercial GDL material (Toray TPGH-120 with 80% porosity).

Table 2: Summary of microstructure characteristics of the liquid water phase (ϕ). Results from in-situ X-ray tomography experiments (pressure induced water injection) and 3D-analysis. $r_{\min}$ - and β -values corrected for elliptical bottleneck shapes (according to Eq. 14) are labeled with '*'.

Table 3: Summary of M-factors, hydraulic radii and permeability for the liquid water phase from pressure induced injection experiments. Predictions based on microstructure characteristics are compared with results from numerical transport simulation. The microstructure characteristics for $S = 1$ (infinite pressure) are equivalent to those from empty pores at $S = 0$ (i.e. values for $S = 1$ are measured from empty pores at $P = 0$ mbar).

Fig. 17a: Relative liquid permeability. Blue = prediction of κ_{rel_pred} based on microstructure characteristics, black = κ_{rel_sim} from numerical simulations of viscous flow. For comparison, conventional relationships from literature are also plotted: green curve = Eq. 10, van Genuchten/Mualem-function with $n=2$, $m=0.8$ / red curve = Eq. 11, Brooks-Corey/Burdine-function with $\lambda=3$ / dotted curves = Eq. 12: power law S^x . Fig. 17b: Schematic illustration of trend lines for κ_{rel_sim} with concave, linear and convex segments. Labels *, **, *** and **** are explained in text.

Figr-1

**Continuous Pore Size Distribution
(cPSD)**

Fig-2

Figr-3

Figr-4

Figr-5

Figr-6

Figr-7

Fig-8

Figr-9

Figr-10

Figr-11

Figr-12

Figr-13

Figr-14

Table 1:

Eq. 8	$S - P_c$	Van Genuchten	P_{cb}	0.0856	m	0.8	n	5
Eq. 9	$S - P_c$	Brooks-Corey	P_{cb}	0.075	λ	3		
Eq. 10	$k_{rel} - S$	Mualem - Van Genuchten	m	0.8	n_{gas}	0.5	n_{liq}	2
Eq. 11	$k_{rel} - S$	Burdine - Brooks-Corey	λ	3				
Eq. 12	$k_{rel} - S$	Power law	n	3.5				

Table 2:

		Vol.	Eff. Vol.		Bulges		Bottleneck Size						Geodesic		Predicted	
Pressure	Sat.	Fract ion	Fraction		(cPSD)		(MIP-PSD)				Constrictivity		Tortuosity		M-factor	
P _c	S _{liq}	ϕ	ϕ _{eff}		r _{max}		r _{min}	r _{min} [*]	r _{min}	β [*]	β	τ _{geod}			M _{pred}	
mba					μm	μm	μm	μm	μm	-	-	-	-	-	-	
r	-	-	-	-	μm	μm	μm	μm	μm	-	-	-	-	-	-	
			ip	tp	ip	tp	ip	ip*	tp	ip*	tp	ip	tp	ip	tp	
0	0.0	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.0	0.0	0.00	0.00	
5	0.0	0.04	0.00	0.04	0.0	7.1	0.0	0.0	6.0	0.00	0.73	0.0	1.1	0.00	0.00	
10	0.1	0.11	0.00	0.03	0.0	20.3	0.0	0.0	20.1	0.00	0.99	0.0	1.0	0.00	0.01	
20	0.3	0.27	0.00	0.21	0.0	25.4	0.0	0.0	23.0	0.00	0.81	0.0	1.0	0.00	0.11	
25	0.5	0.39	0.00	0.36	0.0	24.4	0.0	0.0	22.0	0.00	0.81	0.0	1.0	0.00	0.20	
30	0.7	0.51	0.43	0.50	23.3	23.5	5.9	11.7	19.8	0.25	0.71	1.1	1.1	0.10	0.22	
35	0.7	0.55	0.51	0.55	22.8	22.9	7.3	12.9	18.9	0.32	0.68	1.1	1.1	0.16	0.24	
40	0.8	0.60	0.56	0.59	22.5	22.5	8.7	14.0	18.5	0.39	0.67	1.1	1.1	0.24	0.26	
60	0.8	0.63	0.63	0.63	21.8	21.8	8.9	13.9	17.6	0.41	0.65	1.0	1.1	0.31	0.26	
100	0.9	0.65	0.65	0.65	20.6	20.6	8.8	13.5	16.8	0.43	0.66	1.0	1.1	0.36	0.30	
infinite	1.0	0.73	0.73	0.73	20.2	20.2	8.7	13.2	16.4	0.43	0.66	1.0	1.0	0.44	0.43	

Table 3:

Press ure	M-factor					Hydraulic		Liquid Permeability				Relative Permeability			
	Sat.	Predicted		Simulated		Radius		Predicted		Simulated		Predicted		Simulated	
	P	M _{pred}		M _{sim}		R _h		k _{pred}		k _{sim}		k _{rel_pred}		k _{rel_sim}	
	mbar	-	-	-	-	-	μm	x 10 ⁻¹² m ²				-	-	-	-
	S	ip	tp	ip	tp	ip	tp	ip	tp	ip	tp	ip	tp	ip	tp
0	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.05	0.00	0.0001	0.00	0.0001	0.0	6.5	0.00	0.0003	0.00	0.00	0.00	0.00	0.00	0.00
10	0.15	0.00	0.012	0.00	0.003	0.0	20.2	0.00	0.64	0.00	0.12	0.00	0.04	0.00	0.01
20	0.38	0.00	0.11	0.00	0.06	0.0	24.2	0.00	8.35	0.00	5.34	0.00	0.47	0.00	0.25
25	0.54	0.00	0.20	0.00	0.14	0.0	23.2	0.00	13.13	0.00	10.78	0.00	0.74	0.00	0.50
30	0.70	0.10	0.22	0.09	0.22	14.6	21.7	2.77	12.67	3.52	16.17	0.24	0.71	0.26	0.76
35	0.76	0.16	0.24	0.15	0.26	15.0	20.9	4.61	12.99	4.53	17.16	0.41	0.73	0.33	0.80
40	0.82	0.24	0.26	0.22	0.29	15.6	20.5	7.26	13.80	8.04	18.58	0.64	0.77	0.59	0.87
60	0.86	0.31	0.26	0.30	0.31	15.3	19.7	9.08	12.67	10.31	18.23	0.80	0.71	0.76	0.85
100	0.90	0.36	0.30	0.35	0.34	14.7	18.7	9.58	13.06	10.69	18.40	0.85	0.73	0.79	0.86
infinite	1.00	0.44	0.43	0.48	0.43	14.4	18.3	11.32	17.81	13.58	21.37	1.00	1.00	1.00	1.00