Fundamental relationships between 3D pore topology, electrolyte conduction and flow properties: Towards knowledge-based design of ceramic diaphragms for sensor applications

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**Abstract**

Porous Diaphragms in pH-Sensors must meet apparently contradicting requirements such has high conductivity vs. low permeability and low outflow rate of the electrolyte vs. high flow velocity. In this study we intend to lay the foundations for knowledge-based materials design, so that the required materials properties can be achieved. This approach is based on a quantitative understanding of the relationships between 3D topological parameters with the corresponding effective transport properties (flow/permeability and conductivity). All transport relevant topological parameters (i.e. tortuosity, constrictivity, porosity and hydraulic radius) are determined by FIB-tomography and 3D image analysis. Effective properties (conduction and flow) are determined a) by 3D numerical simulation and b) with experimental characterization. The experimental work includes fabrication and characterization of porous YSZ sintered at 1250, 1300 and 1350 C. Fundamental relationships are established by comparison of topological data with results from simulation and from experiment. The following design guidelines are then postulated: a) flow properties are adjusted independently from the conduction via manipulation of the hydraulic radius, b) high local flow velocity and at the same time relatively low volume outflow can be achieved by adjusting the constrictivity via manipulation of sintering conditions and with addition of pore former.
1 Introduction

In this study we investigate microstructure-property relationships of ceramic diaphragms, which serve as liquid junctions for pH-probes [1,2]. Performance and reliability of pH-probes strongly depend on the diaphragm microstructure. Therefore, the aim is to develop criteria for knowledge based materials optimization. This optimization is challenging due to partly contradicting requirements of high conductivity and high flow velocity vs. low permeability and low flow rate.

![Fig. 1](image)

**Fig. 1**: Schematic illustration of the pH-probe (1a) and of the liquid junction inside the pH-probe (1b). L = thickness of diaphragm (1 mm), \( r_{\text{dia}} \) = radius of diaphragm window, \( \sigma \) = conductivity \([S/m]\), \( \kappa \) = permeability \([m^2]\), \( Q \) = volume flow rate \([m^3/s]\), \( v \) = average flow velocity \([m/s]\).

The pH-measurement is based on a series of electrochemical potential steps [2]. In the set-up of most commercial probes the reference and working electrodes are hosted in glass tubes filled with stable solutions (buffer, electrolyte). As illustrated in Fig. 1, the active contacts of the pH-probe with the surrounding measurement solution consist of a pH sensitive glass membrane (Fig. 1a bottom) and a porous diaphragm (i.e. the liquid junction, shown in Fig. 1b). More details about the principles of pH-probes and electrochemical processes at the electrodes can be obtained from literature [1–5].

The most basic requirement for a porous diaphragm in a pH-probe is to enable exchange of charge carriers between the electrode compartment (Fig. 1b, left) and the measurement solution (Fig. 1b, right). Hence, an open pore structure filled with electrolyte can provide a suitable junction with relatively high effective conductivity (\( \sigma_{\text{eff}} \)). For a reliable pH-measurement it is also crucial that the chemical environment of the electrode remains stable and therefore the inward diffusion and migration of foreign ions must be prevented (see e.g. [6,7]). In our set-up the electrolyte in the electrode compartment is thus pressurized with inert gas at 2 bars, in order to induce a convective flow through the membrane. A high outward flow velocity (\( v \)) is needed to counteract the inward diffusion of foreign cations (\( A^+ \)) and anions (\( X^- \)) (path of foreign ions is shown by red arrows in Fig. 1b). High flow velocities also help to reduce measurement errors at high and low pH, which are caused by the build-up of local potentials due to the accumulation of charges at the interface between membrane and measurement solution [3,4].

So far the requirements of high flow velocities (\( v \)) and high conductivities (\( \sigma_{\text{eff}} \)) are not in conflict with each other. However, the open pore structure also results in a relatively high volume flow rate (\( Q \)), which leads to a decrease of the pressure in the electrode compartment (and a drop of velocity). The
lifetime of the pressurized compartment is thus inversely proportional to the volume flow rate (Q) and to permeability (κ), respectively. Hence, the partly contradicting requirements for an optimized liquid junction are high conductivity (σ) and high flow velocity (v) vs low permeability (κ) and low volume flow rate (Q).

There are different 'knobs' that can be turned in order to approach these requirements (see e.g. [8]). We distinguish between a) microstructure optimization, b) adjustment of diaphragm dimensions (i.e. cross-section A and length L) and c) adjustment of 'external parameters', which include pressure in the electrode compartment (P_e) as well as intrinsic conductivity (σ_0) and viscosity (η) of the electrolyte. In the present study we keep diaphragm dimensions (b) and external parameters (c) fixed, since we want to understand how the required performance can be achieved only by optimizing the microstructure.

The basis for such materials optimizations is a fundamental understanding of the quantitative relationships between microstructure and transport properties (conduction and flow). In the next section a short summary of the underlying theory is presented. In our experimental work we then analyze four different diaphragms consisting of porous Zr-oxide (3YSZ). The microstructure is varied by changing the sintering temperatures from 1250 to 1350 °C and by varying the paste recipe. The pore structure is characterized by FIB-tomography and image analysis. From the 3D data we extract topological parameters that are relevant for transport (i.e. effective pore volume fraction ε_{eff}, tortuosity τ, constrictivity β and hydraulic radius r_h). Laboratory experiments provide information about the macroscopic transport properties, which include conductivity/resistivity, permeability, flow rate and flow velocity. The same information is also obtained from numerical simulation (finite element modeling, FEM) using 3D-data from tomography as structural input. Hence for the four samples we collect 3 complementary sets of data: a) Topological parameters describing microstructure characteristics, b) effective properties from numerical simulations and c) effective properties from physical experiments. The comparison of the 3 data sets provides a quantitative insight to the complex microstructure-property relationships, which is the basis for a controlled optimization of conduction and flow properties.

2 Theory

In this section the basic theory regarding transport in porous materials is summarized with a special focus on microstructure effects. Conduction and flow are treated in separate sub-sections. Historically, there has always been a big debate about the correct definition of the relevant microstructure characteristics. In particular for tortuosity many different definitions are still under debate. An excellent overview and 'a guide through the maze' is given by Clennell [9]. Basically, we distinguish two different approaches: the geometric and the physics-based definitions of microstructure characteristics. In our study we apply the geometric definitions for microstructure characteristics since their measurement from tomography data by image analysis is straightforward. The physics-based approach distinguishes between the different transport mechanisms and accordingly it describes the microstructure characteristics as a function of those mechanisms (e.g. hydraulic, electric and diffusional tortuosities). Hence, this approach is theoretically more sound, but the numerical implementation and it’s application to tomography data is more difficult. Confusion also arises due to the missing consensus in literature for physics-based definitions. However, recently a profound theory for the physics-based approach was presented by Berg including separate descriptions for conduction (electrical resistance) [10] as well as for flow (permeability) [11]. In the subsequent sections we mainly focus on these recent publications when dealing with the physics-based approach.

2.1 Microstructure influence on effective conductivity and electrical resistance

a) Geometric approach

According to Ohm's law the electric current (J) is proportional to the applied potential (Φ):
In porous media filled with liquid electrolyte the effective electrical conductivity ($\sigma_{\text{eff}}$) depends on both, intrinsic conductivity of the electrolyte ($\sigma_0$) and on the microstructure-factor (M):

\[ J = \sigma_{\text{eff}} \nabla \phi \]

Eq. 1:

The so-called M-factor (0≤M≤1) describes transport limitations due to geometric obstacles. In our approach, the M-factor includes three microstructure characteristics: effective pore volume fraction ($\varepsilon_{\text{eff}}$), geodesic tortuosity ($\tau_{\text{geod}}$) and constrictivity ($\beta$). The effective pore volume fraction (0 ≤ $\varepsilon_{\text{eff}}$ ≤ 1) represents the pore volume that contributes to transport (i.e. trapped pores are excluded). The geodesic tortuosity ($\tau_{\text{geod}} \geq 1$; $l_{\text{geod}}/\Delta s$) is based on a statistical analysis of the shortest pathways ($l_{\text{geod}}$) within the entire voxel space of the transporting phase, relative to the sample size in transport direction ($\Delta s$) [12]. Constrictivity (0 ≤ $\beta$ ≤ 1) finally is a parameter that accounts for the so-called bottleneck effects. According to Petersen [13], the influence of bottlenecks on flow through straight pipes with hyperbolic constrictions scales with the ratio of the cross-sectional area at the constriction (with radius $r_{\text{min}}$) over the cross-sectional area of the open pipe ($r_{\text{max}}$). Constrictivity of such a pipe can then be defined as follows:

\[ \beta = \frac{\Delta_{\text{min}}}{\Delta_{\text{max}}} = \frac{\pi r_{\text{min}}^2}{\pi r_{\text{max}}^2} = \left( \frac{r_{\text{min}}}{r_{\text{max}}} \right)^2 \]

Eq. 3:

For porous media with disordered microstructure we have introduced a method to determine constrictivity based on tomographic data [14]. Thereby $r_{\text{max}}$ and $r_{\text{min}}$ are defined as the mean values (i.e. $r_{50}$) from two different pore size distribution (PSD) curves. These two PSD methods, which are described in Münch and Holzer [15], provide statistical measures of the pore bulges (from continuous PSD, $r_{\text{max}}$) and of the bottlenecks (from MIP-PSD, $r_{\text{min}}$). Hence, all three characteristics ($\varepsilon_{\text{eff}}, \tau_{\text{geod}}$ and $\beta$) that contribute to the M-factor can be obtained by image analysis applied to tomographic data. More details about the definition of these geometric characteristics are given in the methods section below.

Van Brakel and Heertjes [16] combined all relevant microstructure effects including effective volume, tortuosity and constrictivity in the following expression:

\[ \sigma_{\text{eff}} = \sigma_0 \frac{\varepsilon_{\text{eff}} \beta}{\tau^2} \]

Eq. 4:

$\varepsilon_{\text{eff}}, \beta$ and $\tau_{\text{geod}}$ measured from tomography can be substituted in eq. 4, in order to estimate the effective conductivity. However, it must be realized that with this geometric approach the values measured for $\beta$ and $\tau$ greatly depend on some arbitrary definitions underlying the applied procedures of image analysis. For example the definition of $r_{\text{min}}$ and $r_{\text{max}}$ as being the $r_{50}$ (and not e.g. $r_{60}$) from MIP-PSD and c-PSD, respectively, is an arbitrary choice. Similarly, the choice of a shortest path algorithm for $\tau_{\text{geod}}$ is not based on physical theory. Alternative techniques exist to measure geometry-based tortuosity (e.g. $\tau_{\text{geom}}$ is obtained from path lengths along the median-axes skeleton). The fact that in the geometric approach $\varepsilon, \beta$ and $\tau$ depend on the chosen image analysis procedures implies that the prediction of effective conductivity with eq. 4 is not precise and not a-priory physics based. Taking into account these considerations, we have proposed a virtual materials testing approach in order to determine the relationship between conductivity and geometric characteristics on a statistical basis (see Gaiselmann et al. [12] and Stenzel [17]). For this purpose more than 100 different 3D microstructures were created using a stochastic model. The virtual structures cover a wide range of values for $\varepsilon_{\text{eff}}, \beta$ and $\tau_{\text{geod}}$. For all involved 3D structures the effective conductivities were determined with numerical simulation (FEM). The statistical analysis of these results using error minimization leads to the following equation:
Eq. 5: \[
\frac{\sigma_{\text{eff}}}{\sigma_0} = M_{\alpha} = \frac{e^{1.15 \phi^{0.37}}}{\tau_{\text{geod}}^{4.39}}
\]
This empirical equation was recently used in an experimental study about microstructure degradation in fuel cell (SOFC) electrodes [18]. The results confirm that the empirical equation is well capable to predict effective conductivities based on microstructure characteristics measured with the geometric approach. It must be emphasized that eq. 5 is only valid for our particular definition of geometric characteristics.

b) Physics-based approach

In literature, the relationship between porosity $$\varepsilon$$ and the effective conductivity of porous media filled with liquid electrolyte is often described by Archie’s law [19]:

Eq. 6:

\[
F = \frac{R_{\text{eff}}}{R_0} = \frac{1}{\varepsilon m} = \frac{\sigma_0}{\sigma_{\text{eff}}} = \frac{1}{M}
\]

Thereby, the formation factor F is the inverse of our M-factor (see eq. 2) and it describes the ratio of the effective electric resistance ($$R_{\text{eff}}$$) of a porous material over the intrinsic resistance $$R_0$$ of the liquid electrolyte. The exponent $$m$$ is called cementation factor. It has no strict physical meaning and is usually derived by fitting with experimental data.

In the physics based approach of Berg [10] this cementation factor is replaced by a more meaningful conductance reduction factor ($$i$$). The latter is derived from a consideration of the lengths of electric field lines ($$ds$$), which are longer than the direct length from inlet to outlet points ($$\Delta s$$). As a consequence the local (microscopic) potential gradients deviate from the macroscopic potential gradient. The ratio of the potential gradient at location $$x$$ (i.e. $$d\Phi/ds$$) over the macroscopic potential gradient ($$\Delta\Phi/\Delta s$$) is taken as the local conduction reduction factor $$i$$:

Eq. 7:

\[
i = \frac{d\Phi}{ds} \frac{\Delta s}{\Delta \Phi}, \text{ for } \lim ds \to 0 \text{ it follows that } i = \|\nabla \Phi\| \frac{\Delta s}{\Delta \Phi}
\]

The volume-weighted average of $$i$$ is then defined as the global conductance reduction factor $$i_g$$:

Eq. 8:

\[
i_g^2 = \frac{1}{\Omega} \int_{\Omega} i^2 \, d\Omega
\]

where $$\Omega$$ represents the pore volume (i.e. porosity $$\varepsilon$$ is $$\Omega/V$$). The formation factor is then expressed in terms of the global conductance reduction factor as follows:

Eq. 9:

\[
F = \frac{1}{i_g^2 \varepsilon}
\]

Furthermore, in the work of Berg [10] the global conductance reduction factor $$i_g$$ is divided into two separate microstructure characteristics. These components are tortuosity $$\tau_c$$ (i.e. length variation of electric field lines) and constriction factor $$C_c$$ (i.e. variation of cross section area and pore radius).

Tortuosity $$\tau_c$$ ($$\Delta s/l; \leq 1$$) is invers to our geodesic tortuosity ($$\tau_{\text{geod}} = l_{\text{geod}}/\Delta s; \geq 1$$). In the physics based approach the overall tortuosity $$\tau_c$$ is obtained by integrating the tortuosity $$\tau(\Gamma)$$ of electric field lines ($$\Gamma$$):

Eq. 10:

\[
\tau_c^2 = \frac{1}{\Omega_c} \int_{P} \tau(\Gamma)^2 \, d\Gamma = \frac{1}{\Omega_c} \int_{P} \left(\frac{\Delta s}{l_{\Gamma}}\right)^2 \, d\Gamma
\]

$$\tau(\Gamma)$$ is defined as the sample length $$\Delta s$$ over the length of a field line $$l_{\Gamma}$$. The set of all electric field lines $$P$$ constitutes the volume of the conducting porosity $$\Omega_c$$. 

The second morphological factor contributing to the conductance reduction factor \( i \) is the constricting factor \( C \), which describes the influence of variable cross-sections \( A(x) \) (i.e. the so-called bottleneck effect). It is obtained from two conductances \( G_{\text{const}} \) and \( G_{\text{var}} \), respectively, of tubes with the same volume, but one tube has constant \( \bar{A} \) and the other has variable \( A(x) \) cross-sections:

\[
G_{\text{const}} = \sigma \frac{\bar{A}}{l} = \sigma \int_0^l A(x) \, dx / l^2
\]

\[
G_{\text{var}} = \sigma \left( \int_0^l \frac{1}{A(x)} \, dx \right)^{-1}
\]

\( \sigma \) is the electrolyte conductivity and \( l \) is the tube length. The constricting factor \( C \) is then defined as the ratio of these two conductances:

\[
C = \frac{G_{\text{const}}}{G_{\text{var}}} = \frac{1}{l^2} \int_0^l A(x) \, dx \int_0^l \frac{1}{A(x)} \, dx
\]

Berg's constriction factor \( (C \leq 1) \) is in principle the inverse to our geometry based constrictivity \( (0 \leq \beta \leq 1) \). \( C \) can be expressed in a more general way, by taking into account that \( A(x) \) can be substituted with velocity \( v(x) \), which is proportional to \( I / A(x) \), and current \( I \) is constant in the pore channel. Furthermore, velocity is also proportional to the potential gradient \( d\phi / dx \), which leads to:

\[
C = \frac{1}{l^2} \int_0^l v(x) \, dx \int_0^l \frac{1}{v(x)} \, dx = \frac{1}{l^2} \int_0^l \|\nabla \phi(x)\| \, dx \int_0^l \frac{1}{\|\nabla \phi(x)\|} \, dx
\]

The constriction factor thus describes local changes in drift velocity and potential gradients, which are both proportional to variations of the pore dimensions. The above definition for \( C \) is based on the consideration of single straight tubes. For porous media with non-idealized microstructures the constriction factor is again derived from the specific properties of electric field lines \( (\Gamma) \):

\[
C(\Gamma) = \frac{1}{l^2} \int_{\Gamma_0} \|\nabla \phi(s)\| \, ds \int_\Gamma \frac{1}{\|\nabla \phi(s)\|} \, ds = \frac{1}{l^2} \int_0^l \Delta \phi \int_{\Gamma} \frac{1}{\|\nabla \phi(s)\|} \, ds
\]

The bulk constriction factor \( C_c \) for disordered porous materials is then defined as the current-weighted average of the electric field lines constriction factors \( C(\Gamma) \):

\[
C_c = \frac{1}{l_c} \int_\Gamma C(\Gamma)^2 \, dI_\Gamma
\]

where \( l_c \) is the total current through the porous medium and \( dI_\Gamma \) is the infinitesimal current of a field line. The subscript \( c \) for \( \tau_c \) and \( C_c \) thus indicates that these characteristics are weighted by the corresponding current \( l_c \).

The combined effects of tortuosity (due to variation of field line lengths) and constriction factor (due to variation of cross-section areas and associated drift velocities, respectively) can be related to the global conductance reduction factor as follows:

\[
i_g^2 = \frac{C_c}{\tau_c}
\]

Thus Archie's formation factor \( F \) can be rewritten as follows:

\[
F = \frac{1}{i_g^2 \varepsilon} = \frac{\tau_g^2}{C_c \varepsilon}
\]
It is important to note that the formation factor $F$ is the inverse of our microstructure factor $(M)$. Thus, comparison of eq. 18 and 5 illustrates the analogies and differences between the physics-based and geometric approaches. Both approaches describe the limiting influence of microstructure on effective conductivity by the same effects: pore volume fraction, variation of path lengths (tortuosity) and variation of cross-sections (constrictions/bottlenecks). But in the two approaches the same characteristics (e.g. tortuosity) are defined and determined in different ways and therefore for the same 3D-structure the analogous characteristics have different values. This explains why eq. 18 and 5 have different exponents. The advantage of integers as exponents to $\varepsilon$, $\tau$ and $C$ in the physics-based approach (eq. 18) is paid with the drawback of a more difficult numerical implementation, when applying it to 3D data from tomography. In contrast, the application of the geometric approach (eq. 5) is straightforward.

2.2 Microstructure influence on flow and permeability

a) Geometric approach

The following summary about flow in porous materials is based on a few selected articles [10,11,20–25]. From a mechanistic point of view wall friction forces and viscous phenomena are the main differences between flow and conductive transport. Wall friction typically leads to parabolic velocity profiles for flow in cylindrical tubes, which is not the case for conductive fluxes. Steady state laminar flow $(Q)$ of an incompressible liquid in a single pipe is described by the Hagen-Poiseuille equation:

\[
Q = v_{\text{average}} \ A = \frac{\pi \ r^4 \ \Delta P}{8 \ \mu} \ \frac{\Delta s}{\delta s} = \frac{r^2 \ A \ \Delta P}{8 \ \mu} \ \frac{\Delta s}{\delta s}
\]

with average velocity $(v_{\text{average}})$, tube cross-section $(A)$, tube radius $(r)$ and viscosity $(\mu)$. Eq. 19 can easily be adapted for flow in an idealized porous material consisting of a bundle of straight tubes. For a material with a more complex, disordered pore structure additional effects such as connected (effective) pore volume, tortuous pathways and bottlenecks must be considered. These microstructure effects are usually lumped in one single parameter, which is permeability $(\kappa)$. The flow properties of a disordered porous material can then be expressed with Darcy’s law:

\[
Q = v_{\text{average}} \ A = \frac{\kappa \ A \ \Delta P}{\mu \ \delta s}
\]

The comparison of Darcy’s law with the Hagen-Poiseuille equation reveals that, for a pipe (and for a material with straight tubes), permeability can be defined as:

\[
\kappa = \frac{r^2}{8}
\]

The main limiting effect in straight tubes is thus related to friction at the tube wall, which scales with the tube radius $(r)$. In order to account for wall friction effects in complex porous media the tube radius $(r)$ has to be replaced with the hydraulic radius $(r_h)$, which is described by the ratio of ‘volume open to flow’ over ‘wetted surface area’ [24]:

\[
r_h = \frac{\varepsilon}{S_S (1-\varepsilon)} = \frac{\varepsilon}{S_V} = \frac{\varepsilon \ V_{\text{tot}}}{S_{\text{tot}}}
\]

$S_s$ is the specific surface area per solid volume and $S_v$ is the specific surface area per total volume [m²/m³]. $V_{\text{tot}}$ and $S_{\text{tot}}$ are volume [m³] and internal surface area [m²] of the sample.
For complex disordered microstructures the permeability term must be extended to include those microstructure effects, which were previously also described for conductivity (i.e. $\varepsilon$, $\beta$, $\tau_{\text{geo}}$). Thus, in analogy to eq. 5 for conductivity, we introduce an $M$-factor for permeability ($M_K$):

Eq. 23: $\kappa = \frac{(c \tau_h)^2}{8} M_K = \frac{(c \tau_h)^2}{8} \frac{\varepsilon^a \beta^b}{\tau_{\text{geo}}^c}$

At this stage, we have not yet performed a comparable statistical analysis as we have done for conductivity [12,17] in order to establish a quantitative relationship with microstructure characteristics (see eq.5). Therefore, it is unknown whether the $M$-factor for permeability ($M_K$) is the same as for conductivity ($M_\sigma$). As a working hypothesis we assume that $M_K$ is equal to $M_\sigma$. Consequently the exponents $a$, $b$ and $c$ are set equal for conduction (eq. 5) and for flow (eq. 23). With the present study this hypothesis shall be tested. Furthermore it is also discussed in literature (see e.g. [23]) that the hydraulic radius must be corrected by a shape factor ($c$) in order to account for the complex geometry of porous media. In the present study it is intended to determine the shape factor ($c$) empirically, by comparing microstructure characteristics ($r_h$, $\varepsilon$, $\beta$, $\tau_{\text{geo}}$) from 3D analysis with measured permeability ($\kappa$).

b) Physics-based approach

In a similar way as for conductivity, Berg also presented a thorough description of the physics-based approach for permeability and flow [11]. This work is summarized in the following section.

The (macroscopic) permeability $k$ is divided into two factors:

Eq. 24: $k = k_s \varepsilon_s$

the effective porosity $\varepsilon_s$ and the effective permeability $k_s$. The latter parameter describes the effectiveness of the pore space $\Omega_s$ to conduct fluid flow and it is derived from the microscopic permeability $\kappa$.

Eq. 25: $k_s = \frac{1}{\varepsilon_s} \int_{\Omega_s} \kappa \, dV$

At the microscopic scale flow is governed by Stokes equation:

Eq. 26: $\mu \nabla^2 \mathbf{u} = \rho g \nabla h$

where $h$ is the piezometric head and $\mathbf{u}$ is the microscopic fluid velocity. The microscopic permeability $\kappa$ is then given as:

Eq. 27: $\kappa = -\mu \rho g \nabla \cdot \mathbf{u} \left(\frac{\Delta \varepsilon}{\rho g \Delta h}\right)^2$

At the microscopic scale permeability $K(S)$ of a single streamline $(S)$ can be further decomposed into distinct microstructure characteristics, which are streamline tortuosity ($\tau(S)$), streamline constriction ($C(S)$) and streamline conductance ($B(S)$):

Eq. 28: $\kappa(S) = -\mu \Delta s^2 / \rho g \Delta h = \frac{B(S) \tau(S)^2}{C(S)}$
The so-called effective hydraulic characteristics \((B_s, \tau_s, C_s)\) are obtained as volume weighted average of the corresponding microscopic characteristics, as for example shown in eq. 29 for the effective conductance \(B_s\):

\[
B_s = \frac{1}{\Omega_s} \int_{\Omega_s} B \, dV = \frac{1}{\Omega_s} \int_S B(S) \, dQ_s
\]

The characteristic hydraulic length \((L_h)\) is then derived from the effective conductance:

\[
B_s = \frac{L_h^2}{8}
\]

Finally it is shown that the macroscopic permeability \(k\) depends on three effective hydraulic characteristics and porosity, which themselves can be obtained from streamline characteristics:

\[
k = k_s \varepsilon_s = \frac{B_s \tau_s^2 \varepsilon_s}{C_s} = \frac{L_h^2 \tau_s^2 \varepsilon_s}{8 C_s}
\]

Comparison of eqs. 31 and 23 shows that permeabilities in the physics-based and in the geometric approaches are related to the same microstructure effects: hydraulic pore radii, tortuosity, constrictivity and pore volume. The analogous microstructure characteristics are defined in different ways, which leads to quantitative relationships with different exponential factors. The geometric approach is much easier to understand and the measurement of the corresponding characteristics is well established nowadays. This is why the geometric approach is preferred here for the purpose of materials optimization.

3. Methods

3.1 Fabrication of porous diaphragms

Ceramic diaphragms with different pore structures are investigated in this study. The fabrication includes paste optimization, extrusion and sintering. Two different pastes recipes are used for production of diaphragms, denoted as ZY3_00X and ZY3_003. The water-based pastes consist of a commercial powder of 3YSZ (Tosoh, Japan), mixed with dispersant, plasticizer and lubricant (all from Zschimmer&Schwarz, Germany). The main difference between the two recipes lies in the water content, which is 3.5 % higher for ZY3_00X.

The pastes are processed further at room temperature by twin-screw extruder (Thermo-Fisher Process-11, Germany) apparatus into 60 mm long rods with diameter of 1.5 mm. For the recipe 'ZY3_00X' three different microstructures are obtained by using three different sintering temperatures of 1250 °C, 1300 °C and 1350 °C. For 'ZY3_003' only one sample sintered at 1300 °C is included in this study. Sintering was performed in a tube furnace (Nabertherm RHTH 120-300/18, Germany) in air atmosphere with constant flow of 100 L/h, with heating rate of 100° K/h.

3.2 FIB-tomography

3D-microstructures of four different materials are investigated: 00X_1250 °C, 00X_1300 °C, 00X_1350 °C and 003_1300 °C. All four samples are impregnated with a low viscosity resin prior to imaging. FIB-tomography is performed using a Helios Nanolab 600i (FEI) machine with Gallium liquid metal ion source (Ga LMIS). Methodological details related to FIB-tomography are described in previous publications [26–28]. 3D imaging with FIB includes an alternating procedure of ion sectioning and SEM imaging. The serial sectioning is done with an ion beam current of 2.5 nA and an accelerating voltage of 20 kV. SEM imaging is performed using the so-called through-the-lens detector (TLD) at 2.0 kV accelerating voltage and 0.69 nA beam current.

3.3 3D image analysis
The procedure for image processing of the acquired image stacks from FIB-tomography includes alignment (3D reconstruction), cropping to a region of interest, filtering of image imperfections (e.g. noise), segmentation, and finally extraction of topological parameters (i.e. microstructure characteristics). For image analysis we use software packages from Avizo (http://www.fei.com/software/avizo3d/) and Fiji (http://fiji.sc/Fiji), with the addition of some homemade plug-ins (see e.g. appendix in [29]).

Fig. 2 illustrates the 3D reconstructions of all four samples. The corresponding resolutions and dimensions of the tomographic data are summarized in Table 1. The main topological parameters are porosity (\(\varepsilon\)), percolation factor (\(P\)), average radii of pore bulges (\(r_{\text{max}}\)) and of bottlenecks (\(r_{\text{min}}\)), constrictivity (\(\beta\)), tortuosity (\(\tau\)) and specific surface area (\(S_v\)).

- Pore size distributions are determined by a method called continuous phase size distribution (c-PSD), following descriptions of Münch and Holzer [29]. The radius corresponding to 50 vol% in the c-PSD curve (\(r_{50}\)) is considered as a statistical measure for the average size of the pore bulges, which is subsequently called \(r_{\text{max}}\).

- Mercury intrusion porosimetry (MIP) is an experimental method that characterizes pore size distributions by pressure infiltration of liquid mercury. According to the so-called Washburn equation, the capillary radius is inversely proportional to the applied pressure. A cumulative MIP-PSD is thus obtained by linking the infiltrated volume with the corresponding pressure and capillary radius, respectively. It is well-accepted nowadays that the MIP-PSD mainly captures the size of bottlenecks, which dominate the infiltration process [30]. Here we apply the method of Münch and Holzer [29], which performs MIP-simulation based on tomographic data instead of experimental MIP. The radius corresponding to 50 vol% in the MIP-PSD curve (\(r_{50}\)) is considered as a statistical measure for the average size of the bottlenecks, which is subsequently called \(r_{\text{min}}\).

- Constrictivity (\(\beta\)), which was introduced in an earlier publication [14], is then given by the ratio of the cross-sectional areas at bottlenecks and bulges (\(A_{\text{min}}/A_{\text{max}}\)), which leads to \(\beta = (r_{\text{min}}/r_{\text{max}})^2\).

- The MIP-simulation also includes a connectivity check of the pore volume with the inlet plane (i.e. connectivity depending on the transport direction). Hence, MIP analysis also provides the fraction of interconnected pores (i.e. the percolation factor \(P\)), which provides the effective porosity (\(\varepsilon_{\text{eff}} = \varepsilon \cdot P\)).

- Geodesic tortuosity (\(\tau_{\text{geod}}\)), which was described in a recent study [17], is defined as the ratio of geodesic distance (\(l_{\text{geod}}\)) over sample thickness (\(\Delta s\)). In general, the geodesic distance can be interpreted as the shortest path length through the pore space from one side of the material to the other side. For statistical accuracy, the mean value of numerous geodesic distances is considered. For this purpose, any pixel in the so-called in-plane representing the pore phase is considered as starting point for shortest path analysis using the Dijkstra algorithm [31]. For the analysis of geodesic tortuosity the tomographic data is interpreted as a graph in which each voxel of the transporting phase is a node and the connectivity of these nodes is determined using 26-neighbourhood criteria.

- The specific surface area (\(S_v\)) is determined using the Porodict module for Minkowski functionals, which is part of the commercial GeoDict Software. It represents the surface area in the analyzed FIB-cube normalized to the volume of the FIB-cube \([\text{m}^2/\text{m}^3]\).

### Table 1: Summary of voxel data after 3D reconstruction of FIB-tomographs.

<table>
<thead>
<tr>
<th>Material recipe</th>
<th>Sintering temperature [°C]</th>
<th>Voxel size [nm]</th>
<th>Voxel matrix 1 x y z [μm]</th>
<th>Cube size 1 x y z [μm]</th>
<th>Voxel matrix 2 x, y, z [μm]</th>
<th>Cube size 2 x, y, z [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZY3_00X</td>
<td>1250</td>
<td>8</td>
<td>1271 724 637</td>
<td>10.17 5.792 5.096</td>
<td>512</td>
<td>4.096</td>
</tr>
<tr>
<td>ZY3_00X</td>
<td>1300</td>
<td>10</td>
<td>984 512 818</td>
<td>9.84 5.12 8.18</td>
<td>512</td>
<td>5.12</td>
</tr>
<tr>
<td>ZY3_00X</td>
<td>1350</td>
<td>10</td>
<td>1359 744 727</td>
<td>13.59 7.44 7.27</td>
<td>512</td>
<td>5.12</td>
</tr>
<tr>
<td>ZY3_003</td>
<td>1300</td>
<td>10</td>
<td>1337 590 691</td>
<td>13.37 5.9 6.91</td>
<td>512</td>
<td>5.12</td>
</tr>
</tbody>
</table>
Fig. 2: 3D microstructures obtained with FIB-tomography from four investigated samples (porous 3YSZ membranes, sintered at 1250, 1300 (2x) and 1350°C). The cubes are cropped to 5.12 µm edge lengths. The voxel resolution is 10 nm (further details are given in Table 1). Top row: original gray scale data from FIB-tomography; Middle row: segmented tomographs, where YSZ is yellow and pores are blue; Bottom row: surface visualization of the pores.

3.4 Numerical simulation
Transport properties are assessed by numerical simulation using the software GeoDict (http://www.geodict.com/). The mathematics involved in the simulations is described by Wiegmann and Zemitis [32]. The simulations use voxel based 3D data from tomography as input. The cube dimensions are shown in Table 1 (i.e. cube 1 for conduction and cube 2 for flow). Conductivity simulations are performed in x, y and z directions. The conductivity results for all directions are very similar (i.e. isotropic behavior). Therefore the results are presented as an average of the three measurements. The effective conductivities (σ_{eff}) are computed with input from the experimentally determined intrinsic conductivity (σ_0) of 8.171 [S/m] for 3M KCl electrolyte. Flow simulations are performed always in y-direction (along the extrusion direction) with stokes solver, using density and dynamic viscosity of 3M KCl at 20°C (1130 kg/m³ and 0.001 Pa s) and applying a pressure gradient of 2 bar/mm (i.e. 200 MPa/m). These settings also correspond with the conditions applied for the experimental investigations. The Reynolds numbers are always close to 10^4, which justifies the assumption of creep flow (and use of stokes solver). Permeability (κ) is then obtained by substituting flow rate (Q) or flow velocity (v_{average}) obtained from the simulations into the Darcy equation (eq. 20).

3.5 Experimental characterization

3.5.1 Manufacturing of the of pressurized reference systems
Fig. 1a represents a schematic illustration of the pH-probes consisting of two separate glass shafts for working and reference electrodes. The porous diaphragm is situated in the outer glass shaft, providing a liquid junction between the compartment with the reference electrode and the surrounding measurement solution (see Fig. 1b). In order to build authentic electrode shafts, a thin core LBF glass tube (Ø = 5 mm), exhibiting on one side a widening of 11 mm, was placed concentrically inside a broader LBF glass tube (Ø = 12 mm), leaving an 10 mm overhang of the outer tube at the widening
side (= bottom side in Fig. 1a). Both glasses were then connected at the position of the widening by melting. Afterwards the overhang was shaped into a hemisphere also by melting. By this method, two electrolyte compartments were generated. The hemisphere was directly connected with the core tube, forming the inner buffer compartment ('working electrode'), while both the outer and the core tube formed the hollow cylindrical reference buffer compartment, which was downwards terminated by the melting connection of the outer tube and the widening of the core tube. Note that the hemisphere is normally built of a pH membrane glass and the overhang is removed. In order to examine the project related samples the inner buffer compartment was not in use.

To ensure the proper embedding of the diaphragm into the shaft glass of the reference buffer compartment, an initial vitrification step was required. Depending on the hardness of the respective diaphragm, two methods were used: a) The standard method for fragile diaphragms required a 10 mm piece of the diaphragm to whose center a small ring of melted LBF glass was applied. The overhanging diaphragm was then knocked-off on one side, leaving a proper cutting edge right after the ring. The residual overhang was then used as a holder during embedding and was knocked-off after the embedding, resulting in an embedded diaphragm fragment of about 1mm. b) In case of harder diaphragms a longer piece of the diaphragm was vitrified over the entire length by using a thin LBF glass tube. In this case, fragments exhibiting a length of 1 mm were generated using a diamond saw. Regardless of the used preparation method, a small hole was melted into the outer LBF glass tube, just above the connection site, in order toembed the diaphragm.

The reference buffer compartment was then filled with 3.5 ml of the respective electrolyte solution (e.g. 3M KCl or 3M KCl-glycerol mixture) by using a pipette. After the insertion of an Ag/AgCl half-cell into the electrolyte, the outer and the core tube were melted together at the upper end of the electrode. Here, the half-cell wire and a thin platinum capillary were embedded into the glass. The closed system finally was pressurized up to 2.5 bars by using the platinum capillary as an entry. The capillary was automatically sealed when the final pressure was reached.

### 3.5.2 Measurement of the electrical resistance (R) and diaphragm resistivity (ρ)

The electrical resistance (R) of the reference system was determined by using a current pulse method. For this purpose the reference system and a large Pt counter electrode (A = 27 cm²) were immersed into a liquid electrolyte (3M KCl). The temperature of the solution was kept at 25 °C. Both the counter electrode and the current collector of the reference system were connected to a pulse generator (Knick M700). Since the ohmic resistance of the immersed diaphragm was of interest, a correction of the obtained values had to be performed. For this purpose, the resistance of 10 samples with Ag/AgCl half-cells was measured under the described conditions without diaphragms. These results comprise the ohmic contributions of the platinum electrode, the liquid electrolyte and the Ag/AgCl half-cells. In order to extract the ohmic resistance of the diaphragm, the average of the 10 readings was then subtracted. To assess the resistivity (ρ) (with units Ωm) of the immersed diaphragm in the reference system, the respective diaphragm dimensions (A = cross section, L = length) had to be considered (i.e. ρ = R A / L). Effective conductivity of diaphragm with electrolyte is the inverse of resistivity (σ_{eff} = 1/ρ).

### 3.5.3 Measurement of electrolyte outflow rate (Q) and permeability (κ)

The electrolyte outflow rate (by mass) was determined gravimetrically by weighing the samples directly after pressurization and then 24 hours later. Volumetric flow was then calculated from mass flow using a density of 1130 (kg/m³) for 3M KCl electrolyte at 20 °C. The specific outflow rate (dV/dt resp. dm/dt) depends on cross sectional area (A), length (L) and permeability (κ) of the diaphragm, as well as on the viscosity of the electrolyte (µ) and on the pressure difference between the inner electrolyte chamber and the environment, which is described in Darcy’s law (see eq. 20).

### 4. Results and Discussion

#### 4.1 Pore topology and prediction of effective conductivity
Table 2: Results from quantitative 3D analysis. \( \varepsilon \) and \( \phi \) are volume fractions of pore and YSZ. \( r_{\text{max}} \) is the average radius of the pore bulges, derived from c-PSD. \( r_{\text{min}} \) is the average radius of the pore bottlenecks, derived from MIP-PSD.

<table>
<thead>
<tr>
<th>Material recipe</th>
<th>Sintering temp. (°C)</th>
<th>Vol. fractions YSZ (( \phi_{\text{YSZ}} ))</th>
<th>Porosity (( \varepsilon ))</th>
<th>Percolation factor (P)</th>
<th>Effective porosity (( \varepsilon_{\text{eff}} ))</th>
<th>Pore radii ( r_{\text{max}} ) (nm)</th>
<th>Constriction ( \beta )</th>
<th>Geodesic tortuosity ( \tau )</th>
<th>Specific surf. Area ( S_v ) ( \left[ \text{m}^2/\text{m}^3 \right] )</th>
<th>Hydraulic radius ( r_h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZY3_00X</td>
<td>1250</td>
<td>0.701</td>
<td>0.299</td>
<td>0.999</td>
<td>0.299</td>
<td>77</td>
<td>53</td>
<td>0.478</td>
<td>1.139</td>
<td>6.64E+06</td>
</tr>
<tr>
<td>ZY3_00X</td>
<td>1300</td>
<td>0.790</td>
<td>0.210</td>
<td>0.989</td>
<td>0.207</td>
<td>94</td>
<td>57</td>
<td>0.368</td>
<td>1.235</td>
<td>4.03E+06</td>
</tr>
<tr>
<td>ZY3_00X</td>
<td>1350</td>
<td>0.918</td>
<td>0.082</td>
<td>0.457</td>
<td>0.038</td>
<td>101</td>
<td>20</td>
<td>0.040</td>
<td>1.811</td>
<td>1.60E+06</td>
</tr>
<tr>
<td>ZY3_003</td>
<td>1300</td>
<td>0.862</td>
<td>0.138</td>
<td>0.974</td>
<td>0.135</td>
<td>75</td>
<td>37</td>
<td>0.237</td>
<td>1.357</td>
<td>3.54E+06</td>
</tr>
</tbody>
</table>

The results from topological analysis of porous YSZ samples are summarized in Table 2. The pore volume fractions for different sintering temperatures (1250, 1300 and 1350 °C) are shown in Fig. 3. The bar heights represent the total porosity. It decreases from 0.30 at 1250 °C to 0.08 at 1350 °C, which documents densification related to increasing sintering temperatures. Connected (blue) and trapped pores (red) are also distinguished. At 1250 °C and 1300 °C the pore networks are almost completely connected, i.e. the percolation factor (P) is > 97 %. At 1350 °C the advanced densification leads to a loss of percolation (P = 46 %), so that more than half of the pores are trapped (red). Therefore the volume fraction of connected pores (blue, \( \varepsilon_{\text{eff}} \)) drops to 0.038 at 1350 °C.

![Fig. 3: Porosities measured from four tomographs of YSZ samples. The total porosity decreases with sintering temperature from 0.3 at 1250 °C to 0.08 at 1350 °C. The percolation factor (P) describing the fraction of connected pores (blue, \( \varepsilon_{\text{eff}} \)) is > 97 % for all samples except for the one sintered at 1350 °C, where P is only 46 %. Trapped porosity is shown in red.](image)

As shown in Fig. 4 the geodesic tortuosity (red) for materials produced with recipe 00X increases only slightly from 1.14 at 1250 °C to 1.24 at 1300 °C. However at 1350 °C tortuosity is significantly higher (i.e. 1.81). This step-like increase from 1300 to 1350 °C can be attributed to the strong densification and associated loss of percolation, which was documented in Fig. 3. Obviously at 1350 °C connectivity can only be maintained via relatively long deviations in the transport pathways, which results in higher tortuosity. The sample 003/1300 °C, which has lower porosity than 00X/1300 °C, exhibits a somewhat higher tortuosity. Hence, Fig. 4 also illustrates that tortuosity (red) inversely correlates with effective porosity (blue).
Fig. 4: Geodesic Tortuosity ($\tau$, red rhombus) and effective pore volume fractions ($\varepsilon_{\text{eff}}$, blue squares) plotted against sintering temperatures. Values from recipe 00X are connected with dashed lines as a guide for the eye. The changes in $\tau$ and $\varepsilon_{\text{eff}}$ are stronger in the temperature interval 1300 - 1350 °C than in the interval 1250 - 1300 °C, which is attributed to loss of connectivity above 1300°C.

The skeletonized pore networks for 3YSZ samples sintered at 1250, 1300 and 1350 °C are visualized in Fig. 5. The pore network is much finer at 1250 °C. It consists of numerous fine branches. In contrast the pore network at 1350 °C consists of fewer and coarser branches, which are partly disconnected.

Fig. 5: Skeletonized pore networks based on data from FIB-tomography (Voxel resolution: 10 nm, cube edge length 5.12 µm). Top row: The pore skeletons (red) are overlain on segmented microstructures in the lower part of the cube (black=YSZ, white=pores). Bottom row: The local thickness of pores is represented by color code and thickness variations of the tube-like skeleton. Red represents local pore radii of $>100$ nm. Blue is less than 20 nm. Green is $>20$ and $<100$ nm. Note that the network at 1350°C (right) is fragmented into isolated branches (loss of connectivity).

Average size of pore bulges ($r_{\text{max}}$), bottleneck dimensions ($r_{\text{min}}$) and constrictivities ($\beta$) are plotted in Fig. 6. Upon sintering the average radius of the pore bulges ($r_{\text{max}}$) increases slightly from 77 nm at 1250 °C to 101 nm at 1350 °C (for recipe 00X). In the same samples the average radius of the
bottlenecks \((r_{\text{min}})\) decreases from 54 to 20 nm. This drop of bottleneck size mainly occurs in the temperature interval from 1300 to 1350 °C, and it correlates with the observed increase of density and loss of percolation at 1350 °C. The constrictivity \((\beta)\) is calculated from the squared ratio \((r_{\text{min}}/r_{\text{max}})^2\). A slight increase of \(r_{\text{max}}\) and a significant drop of \(r_{\text{min}}\) at higher sintering temperatures leads to a drastic reduction of constrictivity from 0.37 at 1300 °C to 0.04 at 1350 °C.

![Graph showing the relationship between average radii of pore bulges \((r_{\text{max}})\), bottleneck sizes \((r_{\text{min}})\) and the corresponding constrictivity \((\beta)\) plotted versus sintering temperatures. Major changes occur when increasing the sintering temperatures from 1300 to 1350 °C. The results for recipe 00X are connected with colored lines. Data points for recipe 003 are shown in gray.](image)

Fig. 6: Average radii of pore bulges \((r_{\text{max}})\), of bottlenecks \((r_{\text{min}})\) and the corresponding constrictivity \((\beta)\) plotted versus sintering temperatures. Major changes occur when increasing the sintering temperatures from 1300 to 1350 °C. The results for recipe 00X are connected with colored lines. Data points for recipe 003 are shown in gray.

The limiting influence of the microstructure on effective conductivity can be expressed as M-factor, which is obtained from measured microstructure characteristics according to eq. 5 \((M = \varepsilon_{\text{eff}}^{1.15} \beta^{0.37}/\tau^{4.39})\) [12,17]. Hence microstructure effects can be described quantitatively as a function of connected volume fraction \((\varepsilon_{\text{eff}}^{1.15})\), constrictivity \((\beta^{0.37})\) and tortuosity \((\tau^{4.39})\). These three topology effects and the corresponding predicted M-factors are plotted in Fig. 7. The figure illustrates that for all four investigated samples the most severe limitation comes from a relatively low amount of connected porosity \((\varepsilon_{\text{eff}}^{1.15})\), i.e. the blue bar has the lowest height). This pore volume effect decreases from 0.25 at 1250 °C to 0.02 at 1350 °C. The limiting effect from pore volume is followed by the limiting effect of tortuosity \((\tau^{4.39})\), green), which drops from 0.57 at 1250 °C to 0.07 at 1350 °C, and then by the constrictivity effect \((\beta^{0.37})\), dropping from 0.76 to 0.30 (red).

The product of these three topology components is called M-predicted. It decreases from 0.11 at 1250 °C to 0.0005 at 1350 °C. According to eq. 2, an M-factor of 0.11 means that the effective conductivity in the porous membrane saturated with liquid electrolyte is only 11% from the intrinsic conductivity in the pure liquid electrolyte \((\sigma_0 = 8.171 \text{ S/m}, \sigma_{\text{eff},1250°C} = 0.9 \text{ S/m})\). Increasing the sintering temperature from 1250 °C to 1350 °C leads to a reduction of the connected pore volume, increase of tortuosity and decrease of bottleneck dimensions, which all contribute to a drop of the M-factor and associated effective conductivity by a factor of ca. 1/200 \((\sigma_{\text{eff},1350°C} = 0.004 \text{ S/m})\).
Fig. 7: The pore structure of YSZ provides three limitations to conductive transport, which are related to pore volume (blue, $\epsilon_{\text{eff}}^{1.15}$), tortuosity (green, $\tau^{-4.39}$) and constrictivity (red, $\beta^{0.37}$). The three topological parameters are corrected with the corresponding exponents, which allows to calculate the M-factors (violet) according to eq. 5 ($M_x = \epsilon_{\text{eff}}^{1.15} \beta^{0.37} / \tau^{-4.39}$) [12,17]. The effective conductivity ($\sigma_{\text{eff, pred}}$) can be estimated by multiplying the M-factor with the intrinsic conductivity ($\sigma_0 = 8.171$ S/m) of the pure 3M KCl electrolyte.

4.2 Effective conductivities: Comparison of experiments, simulations and predictions

The predicted effective conductivities ($\sigma_{\text{eff, pred}}$) can be compared with measurements using two other techniques: a) experimental measurement of electrical conductivity ($\sigma_{\text{eff, exp}}$) and b) numerical transport simulation using tomographs as structural input ($\sigma_{\text{eff, sim}}$). The three data sets are summarized in Table 3 and plotted in Fig. 8. The bar plot (Fig. 8A) illustrates that the three methods give consistent results. With increasing sintering temperatures the conductivities are decreasing. In particular the predicted and simulated conductivities match very well with each other, so that they define a linear trend in Fig. 8b with a high correlation ($R^2 = 0.99$). Hence, the consistency of the different data sets confirms that the prediction of effective conductivity using M-factors derived with the geometric approach is a reliable method. It also confirms that the changes in effective conductivity can be quantitatively attributed by the geometric approach (eq. 5) to pore volume, tortuosity and constrictivity effects, as discussed above for Fig. 7.

At a closer view, the scatter and uncertainty of experimental data appears to be higher than in the simulated and predicted data sets. Overall, the experimental error for conductivity measurements is relatively high (see Tab. 3: standard deviations range from 18 to 77 %). It is well understood that such experimental errors are often introduced when the sealing around the porous rod is defect. An alternative source of error is the possible existence of microstructure heterogeneities at larger scales, which may arise upon extrusion of dense and viscous pastes. Such heterogeneities at larger scales are usually not captured by FIB-tomography, which is the reason why these problems do not appear in the simulated and predicted data sets. Due to these experimental problems, the interpretations of the present work are mainly based on the data sets of prediction and simulation, which are more reliable.
Fig. 8: Effective conductivities determined by three complementary methods: by experimental measurements (blue), by predictions based on topological parameters (red) and by numerical simulations (green). Fig. 8A: The bar plot shows that all three sets of data give similar results with decreasing conductivities at higher sintering temperatures. Fig. 8B: Simulated conductivities (y-axis) plotted versus predicted conductivities (x-axis) results in a high correlation ($R^2 =$ 0.99). Linear trend is forced through 0 intercept.

Table 3: Summary of effective conductivities from three different data sets: a) measured experimentally (subscript: exp), b) predicted based on topological analysis (subscript: pred) and c) from numerical simulation (subscript: sim). Experimental data: Each value of specific resistance ($R_{\text{spec,exp}}$) represents an average from 3 (or more) independent measurements. (¹ For 00X_1250°C the measured resistance was close to the base line value). Simulation data: $\sigma_{\text{eff, sim}}$ and $M_{\text{sim}}$ represent averaged values from 3 simulations in x-, y- and z-directions, except for 1350 °C, where simulation in x-direction failed (no connected pathway in x-direction). Predicted data: $\sigma_{\text{eff, pred}} = \sigma_0 M_{\text{pred}}$. 

<table>
<thead>
<tr>
<th>Material recipe</th>
<th>Sintering temperature [°C]</th>
<th>Spec. Resistance $R_{\text{spec,exp}}$ [Ω m]</th>
<th>Effective Conductivity $\sigma_{\text{eff,exp}}$ [S/m]</th>
<th>$\sigma_{\text{eff,pred}}$</th>
<th>$\sigma_{\text{eff,sim}}$</th>
<th>$M_{\text{exp}}$</th>
<th>$M_{\text{pred}}$</th>
<th>$M_{\text{sim}}$</th>
<th>std deviation</th>
<th>$\sigma_{\text{eff,exp}}$ std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZY3_00X</td>
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<td>1.000 ¹</td>
<td>0.874</td>
<td>0.792</td>
<td>0.122 ¹</td>
<td>0.107</td>
<td>0.097</td>
<td>0.378</td>
<td>38</td>
<td>0.072</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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<td>0.085</td>
<td>0.064</td>
<td>0.015</td>
<td>0.103</td>
<td>20</td>
<td>0.012</td>
</tr>
<tr>
<td>Electrolyte (3M KCl)</td>
<td></td>
<td>0.122</td>
<td>8.171 ¹(=σ0)</td>
<td>¹qualified estimation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 9: Hydraulic radii of porous YSZ samples, calculated from the quotient of pore volume \( (\varepsilon) \) over specific surface area \( (S_v) \) (see eq. 22). A) In the four YSZ-samples the changes of surface area \( (S_v) \) and porosity \( (\varepsilon) \) correlate with each other. B) Hydraulic radii \( (r_h) \) vary in a narrow range \( (45 \pm 7 \text{ nm}) \). The values are obviously too low since they are similar to the bottleneck dimensions \( (r_{\text{min}}) \). With a correction factor \( (c = \sqrt{2}) \) a more realistic value of the characteristic hydraulic radius \( (r_{h,\text{corr}}) \) is obtained, which is similar to \( (r_{\text{min}} + r_{\text{min}})/2 \).

4.3 Pore Topology, hydraulic radius and prediction of permeability

In contrast to the effective conductivity \( (\sigma_{\text{eff}}) \), permeability \( (\kappa) \) is not only dependent on dimensionless microstructure characteristics \( (\varepsilon, \beta, \tau) \) but it is also dependent on the so-called hydraulic radius \( (r_h) \), which is calculated from the quotient \( \varepsilon / S_v \) (see eq. 22). As shown in Fig. 9a, specific surface area \( (S_v) \) in the investigated samples strongly correlates with porosity \( (\varepsilon) \), i.e. \( S_v \) decreases with increasing sintering temperatures in a similar way as \( \varepsilon \). Consequently the hydraulic radii are all very similar \( (45 \pm 7 \text{ nm}) \), despite the fact that the microstructures in these samples have very different topological characteristics. As discussed in the context with eq. 23, \( r_h \) has to be corrected by a shape factor \( c \). In Fig. 9b the hydraulic radii are thus compared with the average sizes of pore bulges, which are slightly higher \( (r_{\text{max}}: 77 - 101 \text{ nm}) \), and with the average size of bottlenecks, which are in general similar or smaller than \( r_h \) \( (r_{\text{min}}: 20 - 57 \text{ nm}) \). When introducing a shape factor of \( c = \sqrt{2} \), the corrected hydraulic radius becomes very close to \( r_{h,\text{corr}} \approx (r_{\text{max}} + r_{\text{min}})/2 \), which is considered as a realistic value of the characteristic length.

Using the corrected hydraulic radii and topological parameters \( (\varepsilon, \beta, \tau) \), permeability \( (\kappa) \) can then be predicted according to eq. 23 \( (\kappa = M_{r_h,\text{corr}}^2/8) \). These predictions are based on the assumption that the \( M_k \)-factor for permeability depends on \( \varepsilon, \beta \) and \( \tau \) in the same way as the \( M_\sigma \)-factor for conductivity (see eq. 5). The thus predicted permeabilities range from \( 3.4 \times 10^{-19} \) to \( 5.4 \times 10^{-17} \) \([\text{m}^2]\). All data needed for these predictions, including \( M \)-factors, hydraulic radii, specific surface areas and porosities are summarized in Table 4.
Table 4: Summary of microstructure data relevant for the prediction of permeability ($\kappa_{\text{pred}}$) according to eqs. 22 and 23 (see also Fig. 9). The hydraulic radius ($r_h$) is calculated from the quotient of porosity ($\varepsilon$) over specific surface area ($S_v$). Note: Permeabilities are predicted under the assumption that $M_k = M_\sigma$. Corrected hydraulic radius ($r_{h,\text{corr}} = \sqrt{2} r_h$) is discussed in text.
factor. The trend line for $\kappa_{\text{pred}}$ is very similar to the ones of $\kappa_{\text{sim}}$ and $\kappa_{\text{exp}}$. C) Permeability (log scale) vs porosity.

4.4 Permeability and Flow: Comparison of experiments, simulations, and predictions

Permeability values are obtained from experimental measurements of flow ($\kappa_{\text{exp}}$, Table 5), from numerical simulations of flow ($\kappa_{\text{sim}}$, Table 6) and from predictions based on hydraulic radius and M-factor ($\kappa_{\text{pred}}$, Table 4). As shown in Fig. 10A, all three methods consistently document decreasing permeabilities with increasing sintering temperatures (for recipe 00X).

In general the slope ($\alpha$) for the trend line of predicted permeability ($\kappa_{\text{pred}}$) vs M-factor is very similar as the ones for the simulated ($\kappa_{\text{sim}}$) and the experimental permeabilities ($\kappa_{\text{exp}}$) (Fig. 10B). The linear regressions for $\kappa_{\text{pred}}$ and $\kappa_{\text{sim}}$ reveal high correlations ($R^2 = 0.97$ and 0.99, respectively), whereas the linear correlation for $\kappa_{\text{exp}}$ is lower ($R^2 = 0.91$). It must be emphasized that the measurements of permeability and flow have a relatively high uncertainty due to experimental problems (as discussed above), which also results in relatively high standard deviations (see Table 5: std dev. = 14 - 112%). Thus for further discussion we mainly focus on the comparison of $\kappa_{\text{pred}}$ and $\kappa_{\text{sim}}$.

The slope of the linear regression ($\alpha$) in Fig. 10B can be related to hydraulic radius as follows (compare eq. 23):

$$\text{Eq. 32: } \kappa = \alpha M = \frac{r^2}{8} M$$

However, a linear trend in plots of $\kappa$ vs M is only obtained if the hydraulic radius is the same (or similar) for all samples under consideration. In fact the hydraulic radii of the four samples vary in a limited range ($r_{h,\text{corr}} = 65 +/- 10$ nm, see Fig. 9). It follows that for such a series of samples with a constant ratio $\kappa/M$ an average hydraulic radius ($r_{h,\text{average}}$) can be estimated from the slope ($\alpha$):

$$\text{Eq. 33: } r_{h,\text{average}} = \sqrt{\frac{8}{\alpha}} = \frac{8}{\alpha} \frac{k}{M}$$

Substituting $\alpha$ from the three linear trends in Fig. 10B into eq. 32 reveals hydraulic radii of 65.1 nm ($r_{h,\text{average,pred}}$), 64.5 nm ($r_{h,\text{average,sim}}$) and 63.9 nm ($r_{h,\text{average,exp}}$). Hence for all three methods the averaged hydraulic radii are very similar. It must be emphasized that the predicted permeabilities include a correction factor of $c = \sqrt{2}$. The consistency of the three data sets supports the use of this correction factor. It also supports our hypothesis that the permeabilities can be predicted with the same M-factor as used for the prediction of the conductivities.

Finally in Fig. 10C permeability (on log scale) is plotted versus porosity. This results in similar correlation factors as for the M-factor in Fig. 10B (i.e. $R^2 = 0.98$ for $\kappa_{\text{pred}}$ and $\kappa_{\text{sim}}$, and 0.91 for $\kappa_{\text{exp}}$).

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Table 5: Results from experimental measurements of mass flow. Permeability and average velocity are calculated using Darcy’s law (eq. 20). Density, length and viscosity are only known by approximation. The results for 1250 °C and 1350 °C are based on three independent measurements. Those for 00X_1300 °C and 003_1300 °C include six independent measurements. Hydraulic radius ($r_{h,\text{exp}}$) are determined by substitution of $\kappa_{\text{exp}}$ and $M_{\text{pred}}$ into eq. 33. ($r_{h,\text{exp}} = \sqrt{8 \frac{\kappa_{\text{exp}}}{M_{\text{pred}}}}$). (Note: measured flow properties have relatively high std deviations)
In the following discussion we focus on a comparison of simulated and predicted results. The experimental data give similar trends (as documented in Figs 8 and 10). However, they have higher scatter and uncertainty. In Fig. 11 permeability is plotted versus effective conductivity. For the results from numerical simulation (green rhombs) a perfect linear trend is obtained with a correlation R² of 0.998. This linear correlation indicates that the influence of microstructure characteristics (i.e. of ε, β and γ) is the same for permeability and conductivity.

The results from microstructure-based predictions (red circles) are very similar to those from simulation. It must be emphasized that a linear relationship is only achieved because the hydraulic radii of all four samples are very similar. In fact the slight deviations from linearity visible for predicted values in Fig. 11 correspond with the slight variations of the hydraulic radii (see Fig. 9B). Our results from numerical simulations and microstructure-based predictions are compatible with the hypotheses postulated in chapter 2. Obviously, the microstructure effects on conductivity are all well captured with the M-factor according to eq. 5. For permeability the same M-factor can be used as for conductivity but one has additionally to consider the influence of the hydraulic radius. The relationship between permeability (κ) and conductivity (σ_eff) can then be described as follows:

Eq. 34a: \[ \kappa = \gamma \sigma_{\text{eff}} \]

Eq. 34b: \[ \frac{r_h^2}{8} M_\kappa = \gamma \sigma_0 M_\sigma \]

where γ is the slope in plots of κ versus σ_eff (such as Fig. 11). Since the two M-factors are identical this leads to:

Eq. 35: \[ \gamma = \frac{r_h^2}{8} \frac{1}{\sigma_0} \]

The slope in Fig. 11 for simulated data is 7.22 × 10⁻¹⁷. A similar value of 6.36 × 10⁻¹⁷ is obtained by substituting \( \sigma_0 \) (8.171 S/m) and \( r_h,\text{sim} \) (64.5 nm) into eq. 35. Hence, when the intrinsic conductivity and

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Table 6: Results from numerical simulation of flow (using GeoDict). The simulation was performed by applying a pressure gradient of 2 bar/mm, in analogy to the experiments. For all data sets the Reynolds-Nr is approximately 10⁴, which justifies to use stokes solver in flow simulation. Hydraulic radii are calculated according to eq. 33 (substituting \( k_{\text{sim}} \) and \( M_{\text{pred}} \)). For sample 00X_1350 °C simulation failed due to a lack of connected pore pathways in cubes with a size of 512³ voxels. \( k_{\text{sim},1350} \) was calculated from \( k_{\text{sim},1250} \) multiplied by the proportionality of \( M_{\text{sim},1350}/M_{\text{sim},1250} \) (where \( M_{\text{sim},1350} \) was obtained from simulation of conductivity using a larger data cube).

Also shown at the bottom of Table 6 are four simulations, which are all based on the same tomographic data set from 00X_1300 as structural input. However, the voxel size is increased in log steps from 10 nm (original resolution) to 10 μm.

4.5. Relationship between Permeability and Conductivity
If the hydraulic radius are known, then permeability ($\kappa$) can be estimated from the effective conductivity ($\sigma_{\text{eff}}$) and vice versa (using eqs. 34 and 35).

**Fig. 11:** Plotting permeability versus effective conductivity for four porous YSZ diaphragms reveals linear trend lines. High correlations between permeability and conductivity are obtained for numerical simulations (green, $R^2 = 0.998$) as well as for microstructure-based predictions (red, $R^2 = 0.97$).

### 4.6 Microstructure optimization: solving apparently contradicting requirements

In the introduction it was discussed that porous membranes optimized for use as liquid junctions in pH-sensors have to fulfill apparently contradicting requirements (i.e. high conductivity versus low permeability and high flow velocity versus low volume flow). In this context two questions can be raised, which we try to answer under consideration of the lessons learned from this study:

- **Question 1:** Is it possible to decouple the influence of microstructure on conductivity ($\sigma$) and on permeability ($\kappa$) (or flow, respectively)?

  The investigations indicate that the dimensionless topological parameters ($\varepsilon, \beta, \tau$) have the same influence on conductivity (eq. 5) as they have on permeability (eq. 23) (i.e. $M_\kappa = M_\sigma$, see also Fig. 11). However, in contrast to conductivity, flow is also influenced by viscous force. Consequently flow properties of porous membranes scale with hydraulic radius. This difference between conductivity and flow property is nicely documented with results from four numerical simulations presented in Table 6 (bottom). All four simulations are based on the same tomographic data set from 00X_1300 as structural input. Hence, they all have the same dimensionless topological parameters ($\varepsilon, \beta, \tau$), the same M-factor and consequently also the same effective conductivity. However, the four simulations are different in the sense that the voxel size is increased in log steps from 10 nm (original resolution) to 10 $\mu$m. The simulations show that permeability increases by a factor 100 if $r_h$ is raised by a factor of 10. Hence, these results fit perfectly with theory according to eq. 23 (i.e. $\kappa \propto r_h^2$).

  For microstructure optimization of porous membranes it can be concluded that $\sigma_{\text{eff}}$ and $\kappa$ can be tuned independently with a scaling approach, if for example $r_h$ is changed and the topological parameters are kept constant. Such optimization can be achieved e.g. with a material consisting of dense packed mono-sized spheres. In such materials the sphere radius can easily be changed while keeping $\varepsilon, \beta, \tau$ constant (see related discussions by [22] and [21]). In more complex materials (e.g. when sintering is part of the fabrication process) it will be challenging to change particle size and to keep all other parameters constant, since for example sinter activity and associated densification are dependent on particle size. Thus more sophisticated experimental methodologies are required for the realization of such optimization strategies.
Fig. 12: Flow velocities and constrictivity ($\beta$) plotted versus permeability for four porous ceramic diaphragms sintered at different temperatures. The average flow velocity ($v_{\text{average}}$) scales linearly with permeability, whereas the characteristic (local) velocity in the center of bottlenecks ($v_{\text{BNC}}$) goes through a minimum for $003_{1300}$ °C, which is related to the strong drop of constrictivity at high sintering temperatures (i.e. low permeability). Note: $v_{\text{BNC}} = v_{\text{average}} / (\varepsilon_{\text{eff}} \beta)$

- Question 2: Is it possible to decouple the influence of microstructure on flow velocity and on volume flow ($Q$), or permeability ($\kappa$), respectively?

According to Darcy’s law the average flow velocity ($v_{\text{average}}$) is directly linked with volume flow ($Q$) and with permeability ($\kappa$):

Eq. 36:

$$v_{\text{average}} = \frac{Q}{A} = \frac{\kappa}{\mu} \frac{\Delta P}{\Delta s} = \frac{r^2}{8} \frac{\varepsilon_{\text{eff}}^{1.15} \rho^{0.37} \Delta P}{\tau_{\text{geo}}^{4.39} \Delta s}$$

However, in order to prevent inward diffusion of contaminants it is not the average flow velocity that is critical. Instead, local variations in the velocity field may have a strong impact on the migration of ions and on the prevention of their migration, respectively. It is well known that flow velocities at constrictions (i.e. in the bottlenecks) are much higher than in the bulge-regions. Hence, velocity variations along the transport pathways scale indirectly with constrictivity ($\beta$). In addition one has to consider that flow velocity also varies perpendicular to the transport direction. Poiseuille flow is typically characterized by a parabolic velocity profile with maximum velocity in the tube center. Taking together both effects, a characteristic velocity 'maxima' can be estimated as follows:

Eq. 37:

$$v_{\text{BNC}} = \frac{v_{\text{average}}}{\varepsilon_{\text{eff}} \beta}$$

$v_{\text{BNC}}$ is the velocity at 'bottleneck center' (i.e. velocity on the median axis through a constriction). The factor $1/\varepsilon_{\text{eff}}$ is introduced because $v_{\text{average}}$ is calculated for the total sample volume, disregarding volume effects related to non-permeable domains such as solids and trapped pores.

Fig. 12 illustrates the difference between average 'intrinsic' velocity ($v_{\text{average}}$) and the local velocity at bottlenecks ($v_{\text{BNC}}$). The average velocities are rather low and they scale linearly with permeability. The local bottleneck velocities are much higher. In Fig. 12 $v_{\text{BNC}}$ plotted vs $\kappa$ goes through a minimum, since it depends on $1/\kappa$ and for the investigated samples $\beta$ does not correlate linearly with $\kappa$.

In summary, it must be emphasized that the local velocity at bottlenecks ($v_{\text{BNC}}$) may be more important for the prevention of inward diffusion of potentially contaminating ions than the average velocity ($v_{\text{average}}$). The local velocities are sensitive to variations in pore radius and thus they vary with local changes in constrictivity. Thus, for microstructure optimization one has to consider that the constrictivity is strongly affected by the sintering process, which affects the bottleneck dimensions. In
order to achieve high local velocities ($v_{BNC}$) and at the same time maintain permeability and conductivity in a required property window, fine tuning of the bottlenecks by varying sintering temperature (starting e.g. with 1300 °C) and sintering time appears to be a promising and feasible optimization strategy. Thereby the negative effects on conductivity related to smaller bottlenecks and associated densification could be compensated by the addition of pore former (i.e. influencing porosity and tortuosity in a different way than constrictivity).

5. Conclusions

- The knowledge-based design of porous diaphragms requires a fundamental understanding of the relationships between microstructure characteristics and effective properties. We distinguish between geometric and physics-based approaches.
- The physics-based approach is theoretically more sound. It describes microstructure characteristics as a function of the transport mechanism (see e.g. [10,11]). For example hydraulic tortuosity for flow and electric tortuosity for conduction are defined and measured in different ways. Unfortunately, numerical implementation and application to tomography data are challenging for the physics-based approach.
- In the geometric approach the microstructure characteristics are independent from transport mechanisms. For example the same geodesic tortuosity is used for conduction and permeability. The measurement of microstructure characteristics is straightforward and therefore, at this stage, it is more suitable for materials optimization and engineering.
- Using the geometric approach, a statistical analysis by Stenzel et al [17] led to the following predictive equation for effective conductivity: $\sigma_{eff} = \sigma_0 \varepsilon_{eff}^{-1.15} M^{0.37}/M^{4.39} = \sigma_0 M$ (eq. 5).
- One important hypothesis for the present study is that permeability is influenced in the same way by dimensionless microstructure characteristics ($\varepsilon$, $\beta$, $\tau$ and $M$-factor) as the effective conductivity.
- In addition, permeability also depends on hydraulic radius ($r_h$) and shape factor (c). This leads to the following predictive equation for permeability: $k = ((c r_h)^2/8) \varepsilon_{eff}^{1.15} M^{0.37}/M^{4.39} = ((c r_h)^2/8) M$ (eq. 23). For the shape factor (c) in sintered YSZ diaphragms we obtain a value of $\sqrt{2}$. Our results indicate that with the geometric approach permeability can be predicted reasonably well using the same dependency on $M$-factor and on dimensionless parameters ($\varepsilon_{eff}^{1.15} M^{0.37}/M^{4.39}$) as for conductivity (compare eq. 23 and 5).
- Using the geometric approach, effective conductivity and permeability are predicted based on 3D-analysis of four different diaphragms. The results of 3D-analysis (Fig. 7) document that the most limiting effect on conduction and flow upon increasing sintering temperature is the loss of effective pore volume fraction due to densification and loss of connectivity. The second important effect is the increase in tortuosity, followed by decrease of constrictivity. The hydraulic radius remains almost unchanged when increasing the sintering temperature (Fig. 9).

- For validation, the predicted conductivities and permeabilities are compared with results from simulation and from experimental measurements. The correlations between predicted and simulated properties (for conduction and permeability) are excellent ($R^2 = 0.99$, see Figs 8 and 10). This confirms a high reliability for predictions made with the geometric approach.
- The experimental data exhibit some relatively high standard deviations. These errors are attributed to experimental problems, such as large-scale heterogeneities in the microstructure or leakages in the set-up. However, the general trends in the experimental data are the same as the ones from prediction and simulation.
- Based on these results the following design guidelines are proposed for further optimization of the diaphragm properties: a) Permeability can be adjusted independently from the electric conduction via manipulation of the hydraulic radius (e.g. using a scaling approach by varying the primary particle sizes), b) A high local flow velocity and at the same time relatively low volume outflow can be achieved by adjusting the constrictivity via manipulation of sintering conditions and with addition of pore former. These design guidelines are currently under investigation.
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